Research News

The Elusive Replacements for CFCs

As CFCs are phased out to protect the ozone layer, chemical companies scramble to find substitutes for these vital compounds and to develop economical ways to make them in large quantities

THE BEGINNING OF THE END for chlorofluorocarbons (CFCs) came on 15 March, when a report by NASA's Ozone Trends Panel indicated that the man-made chemicals threaten Earth's ozone layer. To protect the ozone layer, the report implied, CFC use should be significantly curtailed or stopped altogether. Nine days later, Du Pont—the world's leading manufacturer of CFCs—announced it would phase out CFC production. Other suppliers followed suit with plans to curtail their own production.

Phasing out CFCs should relieve the danger to the ozone layer, but their disappearance will create another headache. These handy compounds have hundreds of uses in manufacturing processes and in consumer products, and they are exceptionally well suited for their jobs. "The CFCs are great compounds," said Du Pont research manager Leo Manzer. "They've been around for 50 years and they're everywhere."

Developing replacements for CFCs will not be easy. The currently known replacements are inferior to the originals in many ways, and commercial manufacturing processes for the CFC substitutes either do not exist or are more complicated and expensive than those for CFCs.

Several chemical companies are now attempting to develop CFC replacements. The search for substitutes is not so much a quest for new chemical compounds, since the few feasible replacements are mostly known. Instead, it is a hunt for the best way to make these new compounds in industrial quantities. At stake is the entire CFC market, which now has $600 million in annual domestic sales and $2 billion worldwide, most of which is expected to be superseded by the replacement market within 20 years. The chemical companies that find the best, most economical ways to manufacture these replacements in commercial quantities will capture the lion's share of the new market.

CFCs have four basic uses: refrigerants, blowing agents for making foam, cleaning fluids, and propellants. As refrigerants, they are used in most freezers and refrigerators, as well as in air-conditioning units in automobiles and buildings. As blowing agents, they are used in making both rigid foam, which appears in such items as foam ice chests and fast-food hamburger boxes, and flexible foam, as in furniture cushions and foam pillows. As cleaning agents, they wash hundreds of products, from computer chips to artificial hip joints. As propellants, they are used in aerosol sprays in much of the world, although their use is banned in the United States. CFCs also power fire extinguishers, sit in urethane shoe soles, and are used in making silly string.

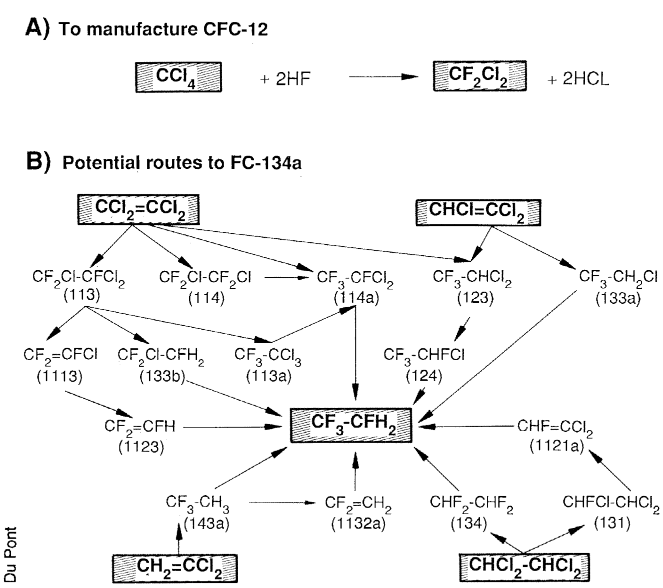
Why are CFCs good for so many different things? There are several reasons. Their low boiling points, specific heats, and heats of vaporization make them good refrigerants. Their insulating value makes them good for insulating foam, and a low permeation rate means they do not leak out of the foam. Low surface tension and low viscosity make them good cleaning agents because they can wet even tiny spaces easily. (Water, in contrast, cannot get into small spaces.) High vapor densities mean there is no significant loss of the cleaning agent through evaporation.

Because they are nontoxic and nonflammable, CFCs are safe to use in consumer applications, even for making boxes to hold food. (Thomas Midgley, the inventor of CFCs, introduced the gases at a meeting of the American Chemical Society in 1930 by inhaling them and then puffing out a candle.) CFCs can be produced with a simple chemical reaction and can be manufactured with high purity, so they are relatively easy to make cheaply in industrial quantities.

Unfortunately, one of their good points has disastrous consequences. CFCs are extremely stable. They will function for decades inside a commercial refrigerator, for example, and they can be used and reused as cleaning agents. But because CFCs are so stable, they do not decompose in the lower atmosphere as many industrial chemicals do, and they eventually rise to the stratosphere. There, ultraviolet radiation breaks the CFCs apart, and the released chlorine atoms destroy ozone molecules.

Although CFCs were invented in 1930, only recently have scientists agreed on the danger they pose. In 1972, the first evidence appeared that CFCs were not breaking apart in the atmosphere but were accumulating. A paper published in 1974 suggested CFCs might decompose in the stratosphere and damage the ozone layer, but evidence for the theory was slow to build. Pressure from environmental groups led the United States and a few other countries to ban CFCs in aerosol sprays in the late 1970s, but other uses continued to grow.

With the discovery 3 years ago of the "ozone hole"—a periodic decrease in the



Du Pont

The production of HFC-134a *is much more complex than that of CFC-12. Chemical researchers are trying to determine which of the many possible routes to HFC-134a offers the best chance for developing an efficient large-scale manufacturing process.*

amount of the ozone in certain layers of the atmosphere over Antarctica—CFCs were a natural suspect. A scientific consensus grew that CFCs were damaging the ozone layer, and in September 1987, 24 countries signed the Montreal Protocol, which called for cutting CFC use in half by 1998. Six months later, the findings of NASA's Ozone Trends Panel indicated that the protocol's limitations probably would not be enough to save the ozone layer. Cutting out most or all of CFC use would be the only safe bet.

That made finding replacements urgent.

In one sense, it is not hard to find substitutes. One simply goes to a table of related substances and looks for those with the desired properties: relatively stable, but no threat to the ozone layer; nontoxic and nonflammable; and with a reasonable boiling point, specific heat, insulating value, and so on. Many of the suggested substitutes are CFCs that have been modified to do less damage to the ozone layer. Adding hydrogen to the compounds make them decompose in the lower atmosphere, chopping ozone damage to a fraction of the original; removing chlorine from the materials eliminates the damage completely.

Chemical companies also are sifting through a wide range of other materials. Petroferm, a Florida chemical company, has developed a compound it says cleans printed circuit boards as well or better than CFCs. The compound is made from terpenes that are extracted from citrus fruit rinds.

Right now, the major chemical companies have their money on the modified CFCs, some of which are already commercially available. Their performance is generally inferior to the originals, but various hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) appear to be acceptable replacements for CFCs. Companies developing the alternatives must answer two questions about the replacement materials.

First, they must determine which are the best substitutes, depending on such factors as performance, safety, waste by-products, and cost. To date, HFC-134a (CF_3CFH_2) is the leading candidate to replace CFC-12 (CCl_2F_2) in most refrigeration uses. HCFC-22 ($CHClF_2$) is already being marketed as both a blowing agent and a coolant for commercial and residential air-conditioning systems. It has been approved by the Food and Drug Administration for use in fast-food containers. HCFC-141b (CCl_2FCH_3) and HCFC-123 (CF_3CHCl_2) are possible compounds for use in making urethane and other foams.

Early in 1987, Du Pont researchers believed they had found a near ideal replacement for CFC-113 as a cleaning agent. HFC-132b worked well as a solvent, was nonflammable, and would do only a tiny fraction of the damage to the ozone layer that CFC-113 causes. In May 1987, however, researchers found that male rats became sterile after exposure to HFC-132b, which killed any hopes for commercial use. The search continues for an acceptable cleaning agent substitute.

After a replacement compound is found, the chemical companies must find the best way to manufacture it. Since these chemicals are commodities—the CFC-11 made by Du Pont, for example, is the same as the CFC-11 made by its competitors—the "best" manufacturing process depends mostly on factors that affect its cost: the cost of raw materials, the amount of energy used, the yield, the cost of waste disposal, and so on.

Du Pont's Manzer said the basic problem in manufacturing the new compounds is that the processing technique is significantly more complicated. There are few commercial chemical manufacturing methods simpler than those for the current CFCs. When CCl_4 is reacted with HF, it produces CFC-11 (CCl_3F) and CFC-12 along with hydrochloric acid (HCl). By controlling the temperature and pressure, one can get high yields of the desired CFC. Various modifications of this technique produce CFC-113, -114, and -115.

But there are no such simple methods to produce the contemplated replacements. Take HFC-134a, for example. "There is no evidence to indicate the possibility of developing a single-step process to HFC-134a directly from a chlorocarbon, analogous to our existing CFC-12 processes," Du Pont's Manzer said. Instead, there are at least a couple of dozen potential routes, beginning with four different precursors. These potential manufacturing processes have from two

The Old and the New

CFC-12, or CCl_2F_2, is used in air-conditioning systems, refrigerators, and freezers. It is one of the most widely used chlorofluorocarbons, and it is one of the most damaging to the ozone layer.

HFC-134a, or CF_3CFH_2, is a leading candidate to replace CFC-12. It is a hydrofluorocarbon and contains no chlorine, so it offers no threat to the ozone layer.

The numbering system for CFCs and related compounds looks confusing, but it does have a method, called the "rule of 90." To get the chemical formula from the number, one adds 90 to it; the digits of the resulting number give the number of carbon, hydrogen, and fluorine atoms. For instance, adding 90 to 134 gives 224. Thus HFC-134a has two carbon atoms, two hydrogen atoms, and four fluorine atoms. The "a" refers to how the atoms are arranged; HFC-134b is a different substance.

The numbering system apparently was invented at Du Pont in the early 1930s. Du Pont scientists did much of the early work on CFCs, and their numbering system became standard. According to Du Pont lore, the system was deliberately made confusing to give Du Pont scientists a step up on the competition.

The two substances, CFC-12 and HFC-134a, are similar. Their boiling points are within a few degrees of each other, and their molecular weights differ by less than 20%. Neither is flammable. HFC-134a is close enough to CFC-12 that it should perform the same refrigeration functions with little loss of efficiency.

The differences between the two chemicals will cause some headaches, however. HFC-134a must be run through a refrigeration system at a higher pressure than CFC-12, so current refrigerators and air conditioners will have to be either refitted with stronger compressors or else replaced. In the case of commercial refrigerators, which are meant to last for 30 years or more, it will be smarter to refit them. It would not be economical, though, to refit home refrigerators and automotive air conditioners, so they will be allowed to wear out and then be replaced with new models designed for HFC-134a. The automobile industry expects to spend $100 million to retool its assembly lines to make the new air-conditioning compressors.

A second problem is that HFC-134a will not work with the existing lubricants used in refrigeration systems. Chlorine makes CFCs soluble in oils, but HFC-134a is not soluble in the oils used now. If HFC-134a is to replace CFC-12, a new lubricant must be found. Further, while CFC-12 is proven to be nontoxic, toxicology studies on HFC-134a remain incomplete.

The major drawback of HFC-134a at the moment, though, is that no good manufacturing process exists for it. CFC-12 is easy to make—basically, one takes carbon tetrachloride (CCl) and adds hydrofluoric acid at high temperature and pressure. No such simple process appears available for HFC-134a, and several companies are looking into different processing techniques. ■ **R.P.**

to four steps, and each step translates into an entire plant once commercial manufacturing begins—reactor, feed systems, distillation columns, decanters, driers, storage tanks, compressors, pumps, and all the other paraphernalia of a chemical plant.

Manzer's job and that of his counterparts at other companies is to determine the most promising process for making a given compound. Once that decision is made, the company must build a pilot plant to learn those things about the process that were not apparent in the laboratory, such as catalyst lifetimes, the effects of recycling intermediate compounds, how the system handles the small impurities present, and what the best materials are to stand up to the various hazardous materials that are being put under high temperature and pressure. Du Pont has started construction on pilot plants to produce HFC-134a, HCFC-123, and HCFC-141b and has announced plans to build commercial-scale plants for HFC-134a and HCFC-141b/142b. The company says it will spend $1 billion over the next 10 years on plants to make CFC replacements.

It seems certain that whichever substitutes are chosen, they likely will cost more and do the job less effectively than CFCs. For instance, the leading candidate to replace the blowing agent CFC-11 is flammable and could cost three times as much to manufacture. The most attractive substitute to replace CFC-12 as a refrigerant will not work in the refrigeration and air-conditioning systems now in use. They would have to be refitted or replaced.

HCFC-22, which is already being sold for use in air-conditioning systems and in making foam containers, causes less than 5% of the ozone layer damage that CFCs do. However, HCFC-22 has poor insulating qualities, which makes it a poor candidate for insulation sheeting, and it has a low boiling point that makes it incompatible with existing automobile air conditioners. An automobile that used HCFC-22 would need a higher pressure cooling system with stronger hoses, a larger compressor, and a heavy-duty battery for extra power. General Motors has estimated it would cost $600 million to modify its manufacturing process to accommodate HCFC-22.

The Alliance for Responsible CFC Use estimates it will cost more than $10 billion to wean the world from CFCs, including the costs of building new chemical plants and retooling industry to make products that will work with the substitute materials. Nonetheless, it is a small price to pay when one considers the alternative—the loss of the global ozone layer and the resulting havoc wreaked upon much of the life on Earth.

■ ROBERT POOL

Subtleties of Mating Competition

Male and female primates have a similar "aim" in life, which is to be reproductively successful, but their strategies for achieving that aim are different. For females, the principal constraint on reproductive success is access to sufficient food resources. While it is also true that males must eat to survive, it is also true that what limits their reproductive success is access to mature, mating females. As a result, males usually find themselves in various kinds of competition with each other for the chance to inseminate estrous females, a fact that leaves its biological mark. For instance, males often have to fight each other for the right to control a group of mature females, and as a result natural selection may have endowed the male of the species with weapons of conflict, such as large body size relative to the female, or long, dagger-sharp canine teeth. But there are more subtle forms of competition too: sperm competition.

Some years ago Roger Short of the Medical Research Council's Reproductive Biology Unit in Edinburgh showed that among great apes, gorillas and orangutans have small testes for their body size, whereas chimpanzees have relatively large—not to say enormous—testes. Short explained the difference as the outcome of different breeding systems. Gorilla and orangutan males, for instance, compete with other males for control of a group of females: the winners then have relatively unchallenged access to the females, a mating system known as unimale polygyny. Male gorillas and orangs are much larger than females, as is often seen in polygynous species.

In chimpanzee social organization, by contrast, several adult males have roughly equal access to all the females in the group, a promiscuous arrangement known as multimale polygyny. Physical competition among males is relatively constrained, as reflected in their modest body size. Where they do compete with each other, however, is in the female's fallopian tube: they copulate frequently, and (via the exigencies of natural selection) try to outdo their competitors by leaving more sperm, hence the large testes. This pattern of multimale polygyny being associated with relatively large testes holds up not just among apes but, as Short later demonstrated in collaboration with Alexander Harcourt, Paul Harvey, and S.G. Larson, in many primates.

This equation has now been extended by Anders Pape Moller of Uppsala University, Sweden. Reasoning that quality as well as quantity might be the target of natural selection, he examined not only the volume of ejaculate across 25 primates species, but also the total sperm number, degree of sperm motility, and number of motile sperm. Taking into account effects of absolute body size, Moller found that those species that had relatively large testes also excelled in quality of ejaculate: more sperm, highly motile sperm, and a high percentage of motile sperm. Competition, honed by natural selection, clearly reaches the subtlest of levels. ■ ROGER LEWIN

ADDITIONAL READING

A. P. Moller, "Ejaculate quality, testes size and sperm competition in primates," *J. Hum. Evol.* 17, 479 (1988).