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Earth-Friendly Cool Cars In 2011

Fluorine-based-refrigerant makers jockey to save auto-air-conditioning market from CO_2 threat

Marc S. Reisch

Big changes are under way in automotive air-conditioning that could add anywhere from $40 to more than $1,000 to the price of a new car with air-conditioning. Leading the way is the European Community, whose Parliament voted in June to phase out HFC-134a, the workhorse hydrofluorocarbon refrigerant used in virtually all automotive air conditioners today.

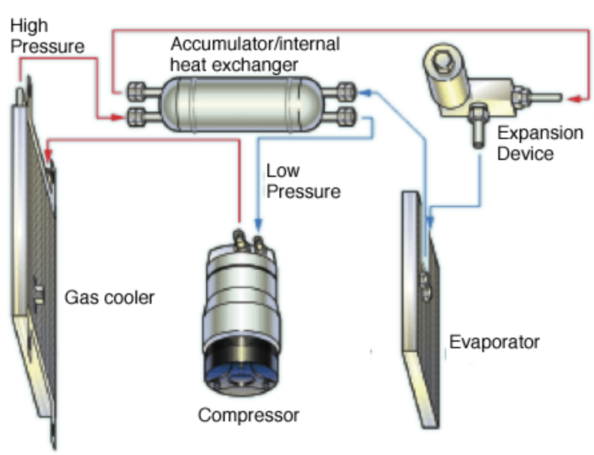
The trouble with HFC-134a is that when it leaks from air conditioners during use and servicing, the refrigerant becomes a gas that scientists believe contributes to global warming and climate change. In fact, it has a global warming potential 1,300 times more powerful than an equivalent amount of CO_2, the standard measure of global warming gases.

As part of a long-term commitment to reduce emissions of global warming gases under the Kyoto Protocol to the United Nations Framework Convention on Climate Change, the 25 European Union countries have now agreed to ban HFC-134a in new cars beginning in 2011. In addition, the EU will ban use of HFC-134a as well as any other fluorinated gas with a global warming potential greater than 150 in all vehicles in 2017.

Because the U.S. has not ratified the Kyoto protocol, carmakers aren't under immediate pressure to switch to alternative refrigerants for cars sold in the U.S. market. However, the European requirements are forcing all automakers to consider a switch to avoid the inventory and servicing headaches associated with supplying and maintaining a variety of air-conditioning systems.

Automakers, component suppliers, and refrigerant manufacturers, including DuPont, Honeywell, Arkema, and Ineos, are now searching for alternatives to HFC-134a. Ironically, the most likely replacement candidate for HFC-134a at this time appears to be CO_2. Component suppliers such as Visteon, Behr, Obrist, and Valeo have already developed air-conditioning systems that use CO_2.

Suppliers of fluorochemical refrigerants will have to rush to catch up if they intend to qualify replacement candidates for use in car air-conditioning systems in Europe by 2011. In February, Honeywell and DuPont identified fluorine-based replacements with low global warming potential that could work in systems designed for HFC-134a with some tweaking. Visteon has also demonstrated an air-conditioning system using Honeywell's candidate, dubbed Fluid H. Arkema and Ineos say they are working on replacement candidates, too.



THE COMPETITION Auto air conditioners could soon depend on CO_2, as does this newly designed system from component supplier Visteon.

This is not the first time that environmental regulations have forced automobile makers to switch refrigerants. In the mid-1990s, the industry switched from CFC-12, a chlorofluorocarbon that depleted upper atmospheric ozone, to HFC-134a, a gas that does not deplete ozone. Governments worldwide endorsed the switch under the 1987 Montreal Protocol on Substances That Deplete the Ozone Layer.

According to DuPont, the switch also brought with it an important secondary benefit. The transition from CFC-12 to HFC-134a brought with it an approximately 85% reduction in contribution to global warming from car refrigerants. But that is still not enough for EU countries, which have committed to achieving an 8% reduction in emissions of greenhouse gases in the period from 2008 to 2012 compared with 1990 levels.

A report from the United Nations Intergovernmental Panel on Climate Change says the potential damage from fluorinated gases−including emissions from refrigerators, air conditioners, fire extinguishers, and insulating foam−has declined significantly since 1990 (C&EN, May 2, 2005, page 28). Back in 1990, worldwide fluorocarbon emissions had the same global warming potential as 7.5 billion metric tons of CO_2. Those emissions were equivalent to about 33% of the CO_2 produced by fossil-fuel burning. By 2000, global fluorocarbon emissions had declined to the equivalent of 2.5 billion metric tons of CO_2, equivalent to about 10% of CO_2 produced from fossil fuel.

Despite the improvement, the European Community is adamant about the need to reduce emissions of fluorinated gases. It argues that, although fluorinated gases account for just 2% by volume of EU greenhouse gas emissions, the global warming potential of the many variants now in use is still too high. So in addition to the limits placed on automotive air conditioners, the community has also placed restrictions on sulfur hexafluoride used in electrical transmission systems and perfluorocarbons used in fire extinguishers.

Because of their use in moving vehicles, auto air conditioners pose special challenges in their design, says Fred Sciance, environment and energy manager at the public policy center of General Motors. The systems must be small enough to be crammed under car hoods, and they must also be light enough to minimize the energy needed−and the CO_2 produced to make the energy−just to haul them around. They must also endure road vibrations, corrosion from road salt, and other environmental insults.

HFC-134a is especially valuable as an auto refrigerant, Sciance points out, because it is nontoxic and nonflammable, attributes that are important in case an air-conditioning system leaks after a crash. Any substitute for HFC-134a must have those two important characteristics, he says.

For Sciance, the EU ban poses a real dilemma. For safety reasons, a number of standby substitutes now available are not really suitable, he says. HFC-152a, with a global warming potential of 140, is compatible with HFC-134a systems, but it is slightly flammable. In litigious societies, such as the U.S., it is not a good choice. Propane, referred to as R-290 in the industry, has a global warming potential of 11. However, it is a flammable gas and so is unacceptable.

Sciance argues that “there is no compelling reason to move away from HFC-134a on environmental grounds.” Any leaks that do occur from HFC-134a are offset, he says, by the environmental benefits obtained from the low energy use of such systems. He concedes that CO_2 systems might be slightly more beneficial to the environment in the cooler climates of Northern Europe, but they bring other complications.

For one, Sciance says, CO_2 systems work at much higher pressure than do systems that use HFC-134a. They require more energy to operate. In addition, high-pressure systems are likely to leak more readily than would low-pressure HFC-134a systems. He worries that leakage and the need for frequent recharging of the system would lead to customer dissatisfaction.

“CO_2 systems may be the answer for Europe, but they may not be right elsewhere,” Sciance says. If CO_2 systems turn out to be more costly or more troublesome, the automobile manufacturer might end up providing a CO_2 refrigerant system to European customers and an HFC-134a system to customers in other parts of the world.

Even before the EU decided to go with a ban on HFC-134a, the Environmental Protection Agency's Mobile Air Conditioning Climate Protection Partnership, involving government, industry, and environment groups, began to work on ways to reduce environmental damage from auto air conditioners. Sciance says the group is well on its way to identifying ways to reduce HFC-134a refrigerant emissions by at least 50% and indirect greenhouse gas emissions from the fuel used to power vehicle air conditioners by at least 30%. System changes might increase the cost of a car by about $40.

However, advances identified by the partnership may have only short-term benefits for HFC-134a systems because of the impetus created by the EU ban. Outside the EU, other forces are lining up against HFC-134a. In September 2004, California's Air Resources Board approved new regulations to reduce greenhouse gas emissions from new motor vehicles effective with the 2009 model year. However, automakers have sued the state in an effort to toss out the new regulation, which has been suspended pending the outcome of a trial in January 2007 at the U.S. District Court for the Eastern District of California.

The California regulations, which other states could adopt, apply to emissions of CO_2, methane, and nitrous oxide from car tail pipes, as well as CO_2 and HFC emissions from air conditioners. The complex regulations leave the method for reducing greenhouse gas emissions up to vehicle makers but are likely to force carmakers to consider substitutes for HFC-134a. When fully implemented in 2016, if they go into effect, the regulations will cost consumers an additional $1,064 for their air-conditioned cars.

Sciance says what he would like most of all from refrigerant makers is an alternative refrigerant as close as possible to HFC-134a with a global warming potential under 150. To this end, a group of automakers, refrigerant makers, and systems suppliers was formed at the end of June to evaluate new refrigerants with low global warming potential.

General Motors will support the research program, set up under the auspices of the Society of Automotive Engineers International, Sciance says. “I encourage chemical companies to move as promptly as they can to allow us to evaluate new products that meet EU regulations,” he says. “They need to comply with our development lead times and get involved now to meet the 2011 deadlines.”

Honeywell's Fluid H might fit the bill. It is a two-ingredient azeotrope that blends 1,1,1,2-tetrafluoropropene with trifluoromethyl iodide. Honeywell says its early tests indicate that Fluid H is nontoxic, does not deplete upper atmospheric ozone, and has a global warming potential under 10, which would allow it to easily meet new EU regulations. Its performance is also very close to that of HFC-134a, so systems using the new fluid would require only minor change.

Richard Preziotti, vice president and general manager of Honeywell fluorine products, says Honeywell can meet the EU's 2011 deadlines. The firm plans to have pilot-plant quantities of Fluid H available next year and commercial quantities available by 2011.

DuPont identified its best replacement candidate, dubbed DP-1, at the end of June. It has a global warming potential of 40. Early testing shows that, like Honeywell's refrigerant, DP-1 is nontoxic, does not deplete upper atmospheric ozone, and will work in HFC-134a systems with only minor modifications.

Mark S. Baunchalk, global business manager for fluoroproducts, declines to characterize DP-1's chemistry other than to say it is fluorine-based. He says he is confident that the new refrigerant could replace HFC-134a at lower cost than would a switch to CO_2.

Arkema plans to offer its candidate in the first quarter of 2007. Toxicity and flammability testing are still under way, the company says.

So changes are on the way, and HFC-134a is likely heading for a phaseout. But fluorine-based refrigerant makers will have to work fast if they expect to hold on to the auto refrigerants market.

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Keeping His Cool

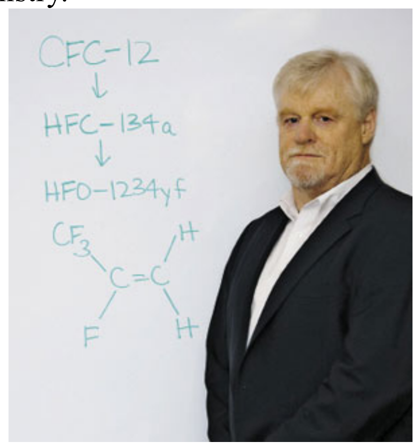
Honeywell's Ian Shankland is awarded Perkin Medal for game-changing refrigerants

Marc S. Reisch

FIRST AS A BENCH CHEMIST at Honeywell International and later as a leader of research teams at the firm, Ian R. Shankland has devoted most of his 27-year career to the practical implications of the Montreal Protocol on Substances That Deplete the Ozone Layer. The international treaty, which entered into force in 1989 and has been amended several times since, required the phaseout of several groups of halogenated hydrocarbons that were damaging Earth's protective upper atmospheric ozone layer.

For his devotion to preserving the environment, Shankland, a physical chemist and director of technology at Honeywell, will receive the Perkin Medal on Wednesday of this week at a dinner in his honor in Philadelphia. The award, from the American Section of the London-based Society of Chemical Industry (SCI), recognizes outstanding work in applied chemistry.

Shankland will receive the medal for his efforts to develop commercial alternatives to ozone-depleting fluorochemicals commonly used as refrigerants, aerosols, foam-blowing agents, and sterilants. SCI executives say the medal also serves as a positive example to chemists who will increasingly find that they must respond to government-mandated regulations with novel and cost-effective chemistry solutions.



Honeywell

FOLLOW THE LEADER Shankland charts auto air-conditioning refrigerants from earliest to current to latest—HFO-1234yf, whose development he is leading.

Shankland and his colleagues developed seven commercial substitutes for ozone-depleting substances. They are hydrochlorofluorocarbon (HCFC)-141b, a low-ozone-depleting blowing agent for closed-cell polyurethane insulating foam; HCFC-141b-based solvents for precision electronics cleaning; hydrofluorocarbon (HFC)-245fa, a second-generation foam-blowing agent; R-410A, a refrigerant for residential air conditioners; R-507, a refrigerant for stationary and commercial refrigeration units; and two blends of fluorochemicals and ethylene oxide used by hospitals and medical device makers to sterilize heat-sensitive reusable apparatus.

More recently, scientists have learned that some of these substitutes are powerful global-warming gases. To meet new European regulations, Shankland and his team responded with blowing agents and refrigerants that combine low ozone-depleting potential with low global-warming potential. They include a refrigerant for automotive air conditioners, hydrofluoroolefin (HFO)-1234yf, which Honeywell is developing with DuPont, and a proprietary blowing agent code-named HBA-1 for insulating foam used in new construction.

SCI executive committee member David N. Weidman tells C&EN that in choosing a winner the group reviewed a strong slate of founders of major companies with a deep science background–people similar to last year's Perkin Medal winner, Herbert W. Boyer, cofounder of the biotechnology company Genentech. Weidman, who is also chief executive officer of Celanese, says the group also reviewed individuals who have made strong scientific contributions to the chemical industry–people like Dow Chemical scientist James C. Stevens, an inventor of catalysts and plastics who won the 2006 medal.

The selection of Shankland, he says, was made easier by the recognition that the chemical industry may once again need to focus on solutions to complex regulatory issues. The 18-year period following the Montreal protocol was a relatively quiet one without major new chemical regulatory initiatives, Weidman points out. But that has now changed, thanks to the launch of the European

Union's program for the Registration, Evaluation & Authorization of Chemicals, REACH, which went into effect last year, and to increased government concerns worldwide over the global-warming potential of industrial emissions, he says.

Shankland worked for Weidman between 1995 and 1997, when the latter headed the fluorine products business at Honeywell's predecessor, AlliedSignal. Weidman says he saw firsthand Shankland's success at developing substitutes for ozone-depleting chemicals. Challenges posed by REACH and the call for reductions in global-warming gases will affect a wide variety of chemicals. “Society will continue to have higher and higher expectations of the chemical industry,” Weidman notes. Those who follow the example set by Shankland and his company will prosper under such demanding circumstances, he says.

Shankland, who grew up in Australia, developed a keen appreciation for chemistry during his junior year in high school because of an enthusiastic teacher, Michael Kovaleff, with whom he still keeps in touch today. Top grades in a statewide exam helped further direct his focus on chemistry, although he was keen on mathematics, too. He settled on physical chemistry as his undergraduate major at the University of Adelaide as a way to combine his love of chemistry and math.

In graduate school he concentrated on the study of fluids, gases, and their transport properties. After receiving his Ph.D. at the University of Adelaide, he expected to pursue an academic career. In the late 1970s, the newly married Shankland and his wife, Erica, moved to Brown University, in Providence, R.I. There he completed a three-year postdoctoral stint with Joseph Kestin, head of the Center for Energy Studies, on a project to measure the heat transport properties of subterranean brine.

Shankland initially intended to go back to Australia, but he decided to interview for a research position at the Allied Chemical research installation in Buffalo, N.Y. In 1981, he seized the opportunity to get a bit of industrial experience as a way to enhance his academic credentials. He and his wife planned to stay in Buffalo for only a year, but they spent 17 years there. In Buffalo, they raised two daughters and saw snow storms the likes of which they had never seen in Australia. Shankland now works at Honeywell headquarters in Morristown, N.J.

Shankland recalls that his earliest projects for Allied focused on the use of fluorocarbons in gas-fired heat pumps for home heating and cooling and in solar hot-water systems. But his priorities shifted when the Montreal protocol was signed in 1989. The international agreement called for a 50% phaseout of chlorofluorocarbons (CFCs) by 2000; Allied, a major CFC maker, had to move quickly to come up with alternatives. “We had to develop environmentally safer products that retained the good attributes of CFCs such as low toxicity, low flammability, and good heat-transfer properties,” he recalls.

CFCs were also chemically inert, which means they did not decompose in an air conditioner or in foam. “But that was their Achilles' heel,” Shankland says. “They were so chemically stable that when they leaked into the atmosphere, they didn't decompose. Their atmospheric lifetimes were hundreds of years—sufficient time to be transported to the stratosphere, where they do decompose by exposure to ultraviolet radiation,” he explains. “As a consequence, they liberate chlorine atoms that catalytically destroy Earth's protective ozone layer.” Without that layer, UV radiation at ground level would rise, leading to increases in skin cancer, damage to crops, and harm to marine life.

Shankland met the crisis head on. “It was a good time for science and the environment and a great time to be a chemist,” he says. He immediately began working to find a new blowing agent to replace CFC-11 in refrigerator insulation foams. Soon after, he took on responsibility for finding a replacement for the CFC-12 used to make medical device sterilization gases.

Shankland and the team of scientists he led worked with academic colleagues, refrigeration equipment makers, and even competitors to develop and qualify a new generation of non-ozone-depleting chemicals. After the Montreal protocol came into force, says Kenneth N. Marsh, a thermodynamics expert and editor of the American Chemical Society's *Journal of Chemical & Engineering Data*, he and Shankland “had many discussions regarding the measurement of the properties of some new non-ozone-depleting refrigerants." Those talks ultimately led to the development of the refrigerant mixture R-410A for residential air-conditioning units.

John Winfield, a fluorine chemist at the University of Glasgow, in Scotland, says, "I regard the work that Ian has led in the production of the alternative foam-blowing agent HFC-245fa very highly." He says the research team and "world class" facilities assembled at Allied were "no doubt due to a great extent to Ian's leadership."

Another colleague, William F. Walter of United Technologies' Carrier heating and refrigeration equipment unit, recalls working closely with Shankland in the 1990s. Walter was a bench chemist, and Shankland chaired a committee of refrigerant suppliers and users established to set standards. "Ian had the insight to understand what industry needed," says Walter, who is now Carrier's manager of industry relations. Shankland spent a lot of time meeting with equipment makers, Walter adds.

THE DISCOVERY of the stratospheric ozone hole in the upper atmosphere of Antarctica led to amendments to the Montreal protocol in the mid-1990s. They called for the ultimate phaseout of all chlorine-containing fluorocarbons just when Honeywell had opened a new plant to make the chlorine-containing foam-blowing agent HCFC-141b.

Trying to get ahead of the curve, Shankland proposed a project to develop a replacement that ultimately became HFC-245fa. When HCFC-141b was phased out on Jan. 1, 2003, Honeywell was ready. The company had started up a "brand-new, $100 million 245fa plant about six months before that," he says. To complete the HFC-245fa development project, Shankland gathered a team of more than 50 people. The plant design and building phase, he points out, involved many more people.

"If you look at what's been done from an overall industry perspective, including end users like the automotive industry and stationary air conditioner makers, billions of dollars were spent moving away from CFCs," Shankland says.

Now another phaseout effort is under way. Many more dollars are being spent to find replacements for the now-standard automotive air-conditioning chemical, HFC-134a, which does not deplete atmospheric ozone but has a global-warming potential (GWP) 1,400 greater than an equivalent amount of carbon dioxide, the standard measure of global-warming gases.

Emissions of global-warming gases are regulated by the Kyoto Protocol to the United Nations Framework Convention on Climate Change, which the U.S. has not signed. The European Union did sign it, though, and has enacted a ban on the use of HFC-134a in new cars beginning in 2011. The EU has also directed that any replacement must have a GWP of less than 150. Shankland's team at Honeywell is now working together with DuPont to develop HFO-1234yf, a substitute with a GWP of about 4.

Shankland says he's not entirely convinced of the need to replace HFC-134a. "Even though HFCs are potent greenhouse gases," he says, "they make a small contribution overall because CO_2 emissions and other greenhouse gas emissions, such as nitrous oxide and methane, are very high by comparison."

However, he acknowledges the need to deal with the reality of the new EU regulations and greenhouse gas regulations under consideration in California, Australia, and Japan. Honeywell and DuPont should have HFO-1234yf in production in time for automotive customers to meet the new regulations. The hydrofluoroolefin's main competition, ironically enough, is from CO_2 itself, which some automakers and environmental groups are proposing as a substitute for HFC-134a.

Shankland contends that CO_2 is not nearly as energy efficient in the long run as HFO-1234yf. He argues that a climate-performance analysis over 10 to 20 years shows that air-conditioning's greatest contribution to global warming comes from the CO_2 emitted while burning fossil fuels to drive air-conditioning systems—and not from the refrigeration gas in those systems.

"To decrease the environmental footprint of your refrigerator or automotive air conditioner, it is important to increase its energy efficiency," he says. "I would propose that we use a technology with the lowest life-cycle climate performance. Choose a technology with low GWP, but also choose a technology that is energy efficient."

Having worked on replacements for ozone-depleting chemicals, Shankland is gratified that "recent measurements show that chlorine is decreasing in the atmosphere." He can look back on work with fellow chemists and find nine substitutes for ozone-depleting substances that he saw go from the bench to production and widespread adaptation.

"You don't have many opportunities to do that," Shankland says. "And to do it more than once, that's extraordinary. You have to be lucky in life as a chemist to have that opportunity."

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http://media.gm.com/content/media/us/en/news/news_detail.brand_gm.html/content/Pages/news/us/en/2010/July/0723_refrigerant

2010-07-23

GM First to Market Greenhouse Gas-Friendly Air Conditioning Refrigerant in U.S.

Breaks Down Faster in Atmosphere but Keeps Vehicles as Cool as Today

WARREN, Mich. – General Motors Co. will introduce a new greenhouse gas-friendly air-conditioning refrigerant in 2013 Chevrolet, Buick, GMC and Cadillac models in the U.S. that keeps vehicle interiors as cool as today while reducing heat-trapping gases in the atmosphere by more than 99 percent.

The biggest benefit of the new refrigerant, (HFO-1234yf) supplied by Honeywell, is that it breaks down faster in the atmosphere than the refrigerant currently used (R-134a), On average, R-134a refrigerant has an atmospheric life of more than 13 years, giving it a global warming potential (GWP) of over 1,400.

By comparison, the new refrigerant lingers in the atmosphere for just 11 days and has a GWP of only 4, a 99.7 percent improvement. GWP is a value used to compare different greenhouse gases that trap heat in the atmosphere. The base measurement for GWP is relative to that of carbon dioxide (CO_2).

The U.S. Environmental Protection Agency awards regulatory credit for the improved environmental performance of the new refrigerant, which helps GM meet the overall requirements of the EPA's new motor vehicle greenhouse gas regulations. The new regulation requires an overall 40 percent improvement in overall U.S. fleet average vehicle fuel economy by 2016. The use of HFO-1234yf will help GM vehicles significantly exceed its targets under the new regulations.

"GM's decision to adopt this new refrigerant is additional proof of our commitment to be on the forefront of green technologies that will keep our planet healthy for our children and grand-children," said Mike Robinson, GM vice president of Environment, Energy and Safety Policy. "It's not just about meeting regulatory requirements; it's about environmental leadership and GM plans to lead in developing new technologies that will take the vehicle out of the environmental debate."

Said Terrence Hahn, vice president and general manager for Honeywell Fluorine Products: "We're pleased that GM is taking the lead in choosing HFO-1234yf, a refrigerant that has a lower impact on global warming. This is another example of how Honeywell is developing innovative new environmental and energy-efficient solutions to meet our customers' current and future needs."

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Greenlight For New Automotive Refrigerant

Regulation: Compound has low global warming potential, EPA says

Cheryl Hogue

The Environmental Protection Agency on Feb. 28 gave a green light to an alternative automotive air conditioning refrigerant, hydrofluoroolefin-1234yf (HFO 1234yf). The compound in current widespread use, hydrofluorocarbon134a (HFC-134a), has a much higher global warming potential, the agency says.

Using a refrigerant with less global warming potential than HFC-134a is a cost-effective way for automakers to meet greenhouse gas emission standards for cars and light trucks that will take effect with model year 2012, EPA says.

With EPA's approval of HFO-1234yf, "the automobile industry now has the option to adopt a low global warming potential refrigerant that is also energy efficient, thus lowering the carbon footprint of every new automobile," says Terrence Hahn, a vice president for Honeywell, which produces the new compound in a joint venture with DuPont.

The chemical meets a European Union regulation that bans the use of HFC-134a starting this year and allows only refrigerants with a global warming potential of less than 150. HFO-1234yf has a global warming potential of four while HFC-134a is rated at 1,430.

HFO-1234yf was developed jointly by DuPont and Honeywell in response to the EU regulation, says a company spokeswoman. When DuPont commercializes the product later this year, the initial focus will be to supply automakers who are working to comply with the EU regulation, she tells C&EN. However, EPA's approval is another milestone in long-term commercialization, she says.

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Honeywell, DuPont Face European Probe

Antitrust: Arkema complaint leads to scrutiny of refrigerants market

Marc Reisch

Under prompting from French specialty chemical maker Arkema, the European Commission (EC), the administrative arm of the 27-nation European Union, has opened an antitrust proceeding to investigate whether an agreement between Honeywell and DuPont to develop and produce a next-generation auto refrigerant is anticompetitive.

The EC’s investigation escalates a dispute between Arkema and the U.S. partners over the patent rights to hydrofluoroolefin (HFO)-1234yf, a refrigerant recently introduced for the air-conditioning systems of cars that will be sold under new European environmental regulations. HFO-1234yf also has applications in fluorochemical markets such as refrigeration, home air-conditioning, and foam blowing. Those markets are worth as much as $5 billion globally in annual sales, according to Ray K. Will, principal consultant with business information publisher IHS Chemical.

An Arkema spokeswoman says that the firm has proprietary technology to make HFO-1234yf but that Honeywell owns application patents in Europe and the U.S. that keep Arkema from those markets. Although Arkema contests the patents, the spokeswoman says the company is also willing “to obtain a license under fair and reasonable conditions in order to supply HFO-1234yf to car makers as soon as possible.”

Both Honeywell and DuPont say they are confident the commission will rule that they have acted in compliance with European competition rules.

The two U.S. firms formed their agreement to jointly produce, but separately market, HFO-1234yf. Because HFO-1234yf has a low global-warming potential and is a drop-in replacement for the widely used refrigerant hydrofluorocarbon (HFC)-134a, it is the auto industry’s refrigerant of choice.

The EC says it will also investigate whether Honeywell “engaged in deceptive conduct” by not disclosing its patent position while HFO-1234yf was being evaluated to replace HFC-134a.

Court battles over the rights to HFO-1234yf have been going on since 2009, when Honeywell first sued Arkema in a European court for infringing its patents. Arkema sued Honeywell in June 2010 in U.S. District Court for the Eastern District of Pennsylvania seeking to invalidate Honeywell’s U.S. patents. Arkema says it has also filed an action in the European Patent Office to invalidate Honeywell’s patents.

NEW YORK TIMES, September 7, 2012

CHILLING EFFECT

As Coolant Is Phased Out, Smugglers Reap Large Profits

The Marcone company of St. Louis, which distributes appliance parts, was implicated in a coolant smuggling scheme.

By ELISABETH ROSENTHAL and ANDREW W. LEHREN

MIAMI — The chief executive of the century-old company from America's heartland shifted nervously on the witness stand here as he tried to explain how a trusted senior vice president had been caught on a wiretap buying half a million dollars in smuggled merchandise, much of it from China.

But the contraband purchased by Marcone, a St. Louis-based company that claims to be the nation's largest authorized source for appliance parts, was not counterfeit handbags or fake medicines. It was a colorless gas that provides the chill for air-conditioners from Miami to Mumbai, from Bogotá to Beijing.

Under an international treaty, the gas, HCFC-22, has been phased out of new equipment in the industrialized world because it damages the earth's ozone layer and contributes to global warming. There are strict limits on how much can be imported or sold in the United States by American manufacturers.

But the gas is still produced in enormous volumes and sold cheaply in China, India and Mexico, among other places in the developing world, making it a profitable if unlikely commodity for international smugglers.

So in 2009, Carlos Garcia, the Marcone vice president, generated big business for his company's growing air-conditioning operation by selling smuggled foreign gas to repairmen at rock bottom prices in a promotion called Freaky Freon Fridays, drawing on a brand name that many use as a synonym for coolants.

Although it has been illegal to sell new air-conditioners containing HCFC-22 in the United States since 2010, vast quantities of the gas are still needed to service old machines. Importing HCFC-22 without the needed approvals, as Marcone did, violates international treaties and United States law and regulations.

Yet for a long time, “Mr. Garcia was a hero to his company” for the profits his Freaky Freon Friday campaign generated, an assistant United States attorney, Thomas A. Watts-FitzGerald, told a rapt federal courtroom here in April.

On June 26, Mr. Garcia was sentenced to 13 months in federal prison.

A video of a company official charged in the case, Carlos Garcia, was used in evidence at his trial in federal court. He was convicted.

International efforts to curb the use of HCFC-22 are faltering for dozens of reasons, from loopholes in environmental treaties to the reluctance of manufacturers to step up development of more environmentally friendly machines.

But the underlying problem is that even as international treaties and United States law demand that companies renounce the use of the coolant, economics propels them to use ever more — sometimes even if it means breaking the law.

Although the Marcone case is the largest smuggling prosecution anywhere so far, investigators believe that smuggled gas is used by other companies in the United States, and European customs officials have intercepted shipments of contraband gas arriving in Finland, Slovenia and Poland in the last two years, said Halvart Koeppen, a United Nations official who tracks illegal trade of the gas. This is “the tip of the iceberg,” he said.

Much of the global air-conditioning industry relies on the gas the way the auto industry does on gasoline. But while oil is getting harder to find and more expensive, HCFC-22 is becoming more abundant and remaining cheap on the global market.

“There is no question that this is inhibiting phaseout,” said Rajendra Shende, a former head of the United Nations Ozone Action Program who runs the Terre Policy Center, an environmental research institute in Pune, India.

In the meantime, the price of legitimately obtained gas has been rising in the United States and throughout Europe. That is because governments of industrialized nations, to comply with the ozone treaty known as the Montreal Protocol, restrict the use of the environmentally damaging gas in various ways. In the United States, the Environmental Protection Agency requires that companies obtain a license to make, sell or buy specific amounts of HCFC-22, with such “allowances” decreasing year by year.

The dwindling supply has led to pronounced spikes in price. What once cost retailers like Marcone \$55 a canister was by 2009 going for \$140 in the United States. By reducing the supply of the coolant and encouraging prices to rise, the United States government hoped to force manufacturers and consumers to scrap old machines and invest in more environmentally friendly, if more expensive, alternatives. But it has not worked out that way, especially in recessionary times when people hang on to old appliances and search for cheap shortcuts.

Many air-conditioning manufacturers have even figured out how to sidestep the 2010 ban on selling new machines containing HCFC-22, by offering unfilled air-conditioning compressors that service workers swap into existing units and then fill with the gas, creating refurbished machines that are as good as new.

The chemical giant DuPont has estimated that the service demand for HCFC-22 could exceed the supply by 27.5 million pounds annually in the United States for the next three years.

A big chunk of that shortfall will be made up through smuggling, experts say. And smuggled gas is cheaper, going for $130 a canister in the Marcone case.

The smuggling is difficult to stop because gas canisters can be readily mislabeled to mask their content. Inspections are time-consuming, policing requires expensive testing equipment that is in short supply, and border agents have more pressing targets like guns and narcotics.

In the 1990s, when the world began a successful campaign to eliminate the use of an even more powerful ozone-depleting substance called CFC-12, smuggling was also a problem. But 20 years later, the challenges are far greater: the center of the cooling industry has moved to Asia, where gas production is more difficult to monitor. China now makes more than 70 percent of the world's room air-conditioners and more than half of the world's supply of HCFC-22.

It is also easier for smugglers to hide contraband in the dizzying flows of legitimate goods in an increasingly globalized world.

"This is a crime that has all the profits of drug trafficking and none of the risk," said Mr. Watts-FitzGerald, the prosecutor in the Miami case. In many ways, it was Mr. Garcia's bad luck that the only United States attorney's district office to have a special environmental crimes unit is in South Florida.

Its relentless two-year investigation — complete with wiretaps and informants — raised the curtain on a multimillion-dollar web of smugglers and trafficking routes stretching from factories in the developing world — mostly China — to the Dominican Republic, Wales, Mexico and other points before the coolant gas ended up in American homes.

The smuggled Marcone coolant entered the United States through a variety of ruses, evidence collected by prosecutors showed.

Some of the Chinese gas on offer traveled to Ireland and the Dominican Republic before arriving in Miami, hidden among legitimate goods in three cargo containers on a small freighter. Mr. Garcia helped falsify shipping documents, express-mailing faked invoices to middlemen in the Dominican Republic to ease passage into the United States.

Other canisters came in an illegal shipment from Harp International, a leading manufacturer of the gas in Wales, accompanied by false documentation that the gas had been recycled to comply with import restrictions.

One lot of smuggled gas traveled a particularly dizzying journey: made in the United States and exported to Mexico, only to be sent back to Miami.

DuPont exports gas to Mexico — the top foreign destination for American-made HCFC-22 — because it makes more of the coolant at its Louisville, Ky., factory than it is allowed to sell in the United States. But because Mexico does not yet restrict use of the gas, the market price in Mexico is far lower than in the United States.

The smugglers took advantage of the differential, buying cheaper DuPont gas in Mexico and routing it back through the Caribbean to Miami for sale at north-of-the-border prices. The shipment was stopped after federal agents noticed that the canisters' markings indicated that they had been packaged for the Mexican market.

As a result of the Miami investigation, Marcone pleaded guilty to violating federal laws, although on the witness stand its chief executive said he had not realized Mr. Garcia's imports were illegal. So did several smugglers, including a Florida couple and a now-jailed Irish national financed by a Peruvian businessman who was recently indicted as well.

Caught on a wiretap, Mr. Garcia once asked a supplier whether the product was from Honeywell or DuPont.

"From China," the man answered.

Over time, he apparently became comfortable with his booming business, bragging about how easy it was to smuggle coolants into the United States.

"Remember that there are a bunch of tricks," he said.

How a Contraband Coolant Entered the United States

On June 26, Carlos Garcia, vice president of the St. Louis-based appliance supplier Marcone, was sentenced to 13 months in prison for his role in the illegal importing of more than $11 million worth of a controlled refrigerant gas called HCFC-22 by Marcone's Miami branch. Federal laws strictly limit imports of this ozone-depleting gas while its use in this country is being phased out.

Some of the methods used to illegally import HCFC-22

FROM CHINA	**FROM WITHIN THE UNITED STATES**	**FROM BRITAIN**
At least three separate smuggling operations funneled Chinese-made HCFC-22 into the U.S. In one case, shipments were routed through the Dominican Republic, where Mr. Garcia told smugglers how to fake invoices to get the coolant past customs officials. Smugglers later paid him a kickback of $5,120.	Coolant was manufactured for legitimate export by DuPont at its Louisville, Ky. plant. From there, it was shipped to Texas for packaging and then exported to Mexico. There, smugglers bought it and illegally reimported it into the U.S. via the Dominican Republic.	The American subsidiary of Harp International, a major refrigerant supplier based near Cardiff, Wales, falsified documents to give the impression that a shipment of HCFC-22 destined for Marcone was recycled and therefore in compliance with EPA import restrictions.

A version of this article appeared in print on September 8, 2012, on page A1 of the New York edition with the headline: As a Coolant Is Phased Out, Smugglers Reap Big Profits.

http://www.terradaily.com/reports/UN_hails_25-year_ozone_treaty_for_preventing_disaster_999.html

UN hails 25-year ozone treaty for preventing disaster

Geneva (AFP) Sept 14, 2012

The United Nations treaty to protect the ozone layer signed nearly 25 years ago prevented an environmental disaster, a chief UN scientist said Friday, cautioning though that the Earth's radiation shield is still under threat.

"The Montreal Protocol has prevented a major environmental disaster," Gael Braathen, the World Meteorological Organization's senior scientific officer for atmospheric environment research, told reporters in Geneva.

The treaty was signed on September 16, 1987, amid growing concern over swelling holes in the ozone layer, which filters out ultraviolet rays that damage vegetation and can cause skin cancer and cataracts.

It banned ozone-depleting substances such as chlorofluorocarbon gases (CFCs), once present in things like refrigerators and spray cans.

Since then, ozone depletion has levelled off, Braathen said, adding though that it would still take a very long time for the ozone layer to recover.

"As we speak, ozone depletion is going on," he said, adding that "we haven't really seen any kind of unequivocal recovery yet".

In the Arctic, record ozone damage was reported in the stratosphere in 2011, but levels normalised in 2012, he said.

"Ozone-depleting gases have a long lifetime in the atmosphere so it will take some decades before the ozone is back to where it was in the past," he added.

According to the WMO's figures, the amount of ozone-depleting gases in the Antarctic reached a peak in the year 2000. The amount is now decreasing at a rate of about 1.0 percent a year.

The ozone layer outside the polar regions is projected to recover to its pre-1980 levels before the middle of this century, the WMO said.

In contrast, the ozone layer over the Antarctic is expected to recover much later.

Antarctic ozone hole said healing

Canterbury, New Zealand (UPI) Sep 14, 2012

International efforts to reduce emissions of ozone-depleting substances are slowly diminishing the hole of the ozone layer over the Antarctic, a scientist says.

However, Adrian McDonald at New Zealand's University of Canterbury said, it is difficult to determine when the ozone might return to natural levels, because of the complexity of interactions between greenhouse gases in the atmosphere.

"Ozone levels above Antarctica are projected to return to 1980 levels (previous to the ozone hole) after 2050," McDonald, from the university's astronomy and physics department, said. "The Montreal Protocol means that emissions of ozone depleting substances (CFCs) have largely been banned worldwide."

The use of CFCs, once widely found in common household items such as refrigerators and aerosol sprays, was curbed under the Montreal Protocol agreed by the international community in 1987.

The ozone layer, about 15 miles high in the stratosphere, acts as a filter protecting life on Earth from ultraviolet solar radiation. Its depletion over Antarctica has been a concern in Southern Hemisphere countries such as New Zealand.

http://www.nytimes.com/2012/11/23/science/earth/air-conditioner-repairs-undermine-coolant-restrictions.html
NEW YORK TIMES, November 22, 2012

CHILLING EFFECT

Effort to Curb Coolant Falters, Sometimes at Home

A repair technician in New Jersey removed an air-conditioning unit that uses HCFC-22, which is banned for use in new units, to install a new one that uses a different coolant, R-410A.

By ELISABETH ROSENTHAL and ANDREW W. LEHREN

When Mark Spector's central air-conditioning system stopped cooling his Trumbull, Conn., home this summer, he sent an S O S to his repairman. What happened next illustrates the myriad challenges the United States faces as it tries to phase out the popular but environmentally devastating cooling gas that was in Mr. Spector's unit.

The Environmental Protection Agency has tried to reduce use of this gas, HCFC-22, which depletes the ozone layer and contributes to global warming, by imposing strict quotas on its production. Since 2010, it has also banned the sale of new air-conditioning units containing the compound, and has promoted recycling of the gas from old machines so it will not be released.

But what followed at Mr. Spector's home circumvented all the agency's rules and good intentions: Instead of finding and repairing the hole in his aging unit, a complicated task, a serviceman pumped in more coolant, which leaked out by the next day. When Mr. Spector called around for another solution, a salesman offered to swap in a new condenser unit, but one that still used HCFC-22 — meaning one more American home would continue relying on an environmentally damaging coolant for years.

HCFC-22 is being phased out of air conditioners worldwide under an international treaty called the Montreal Protocol, and the United States has aggressively pressed poor countries to pick up the pace. But the United States has yet to put its own house in order. And, with 140 million central air units still running on HCFC-22 in this country, it is a major offender.

Leaks abound in working equipment. Coolant seeps out of discarded equipment in landfills. Regulatory loopholes allow manufacturers to sell parts that rely on HCFC-22, so systems using the old gas can be refurbished rather than replaced. There is almost no reclamation of the gas from old machines for recycling. The E.P.A. is behind schedule in imposing rules to ratchet down domestic production, and smuggling is rarely detected. Even where there are regulations — for example, repair technicians are legally bound to collect old gas rather than vent it — there is little enforcement.

And, as Mr. Spector discovered, many of the environmental crimes and misdeeds that keep the country dependent on HCFC-22 happen on your property, most likely without your knowledge.

"It's totally illegal to vent gas, but it's also totally inconspicuous," said Stephen O. Andersen, a former E.P.A. official who has campaigned for better controls on cooling gases. "I always watch like a hawk when they're in my yard," he said of technicians.

The concentration of HCFC-22 in the atmosphere is 218 parts per trillion, more than double the amount two decades ago, and it gets there in a number of ways. Low-quality or old equipment leaks, and detecting the colorless and odorless gas without pressure-testing devices is difficult. Sometimes the release is intentional, because it costs less. For example, installing a new part properly usually requires first siphoning a machine's coolant into a canister, for later replacement. But it is quicker, though illegal, just to cut the line. A technician saves half an hour on a job, and the customer gets a smaller bill.

Bobby Ring, who runs a servicing company in suburban New Jersey, said that makes it hard for him to compete. "There are contractors out there who refuse to make the investment in recovery equipment to reclaim or recover refrigerants, and no one is looking, so — *phsssst* — they let the refrigerant escape," he said.

Although large companies, which are required to report use of the gas, have been fined for large leaks, the E.P.A. has never prosecuted a residential service company for intentionally releasing HCFC-22.

Asked about the lack of backyard enforcement, David Bloomgren, a spokesman for the E.P.A., said it is "a challenge to locate or obtain evidence of illegal venting," so the agency focused on large polluters but encouraged homeowners to report possible backyard violations they observed to an E.P.A. tip site at epa.gov/tips/.

While it is hard to quantify exactly how much coolant is illegally released from America's residential air conditioners, the E.P.A. estimates that only 7 percent of used coolant is turned in for recycling.

"The vast majority of it hits the sky," illegally vented, said Kevin Zugibe, chief executive of Hudson Technologies Inc., a company set up to recycle HCFC-22. Under the Montreal Protocol, the United States has until 2015 to cut production and imports of newly made HCFC-22 to 10 percent of what it was a decade ago.

Without a much better supply of recycled HCFC-22, the United States will not be able to do that — or have enough to service all the older air conditioners, grocery store freezers and other refrigeration equipment.

In the European Union, only recycled or reclaimed HCFC-22 can be legally used to service equipment. In Australia and Japan, recovery of the gas from old appliances is mandatory, and technicians receive a fee for collection.

But the E.P.A. has no plans to enact requirements or incentives for recycling in the near future, preferring to rely on market pressures, Mr. Bloomgren said. In January, the E.P.A. proposed more specific limits on domestic production for the coolant, in the hope that curtailing supply would force "more recovery and reuse of HCFC-22 in large systems, as well as encourage transition to HCFC-22 alternatives." It said those rules would be in place by May, but they still are not.

But with weak incentives, repair technicians say, it seems a waste of time to collect the gas, and some distributors even charge extra to those who do the right thing and bring it back for recycling.

The E.P.A. has tried to address overuse of the gas by regulating air-conditioning equipment, forbidding the sale of new machines containing the gas starting in 2010.

Initially, when the rules were proposed months earlier, manufacturers responded by introducing systems that ran on more environmentally friendly — if costlier — gases; they struck old models from catalogs. But at the last minute and in the face of a recession, the E.P.A. publicized that it would allow owners of older systems to replace any and all parts so long as the new parts did not contain the coolant.

Unfortunately, as Mr. Spector discovered this summer, that created a loophole that subverted the mandate: Manufacturers could sell condenser units — the major component of every air-conditioning system — that were empty of coolant gas. Then, after installation, a worker could simply add new HCFC-22, complying with the letter if not the spirit of the law.

Advertisements and sales personnel even promoted the practice as a way to obtain what is essentially a new central air-conditioning system at a fraction of the cost. A replacement compressor for an old HCFC-22 system costs about $1,200 to $1,500, while a new system using a more environmentally friendly gas costs at least three times as much.

"It's probably legal since you could claim it's just servicing, but it's ethically disturbing and not fair to companies who've spent a lot to develop new products," said Dr. Andersen, who is the director of research at the Institute for Governance and Sustainable Development.

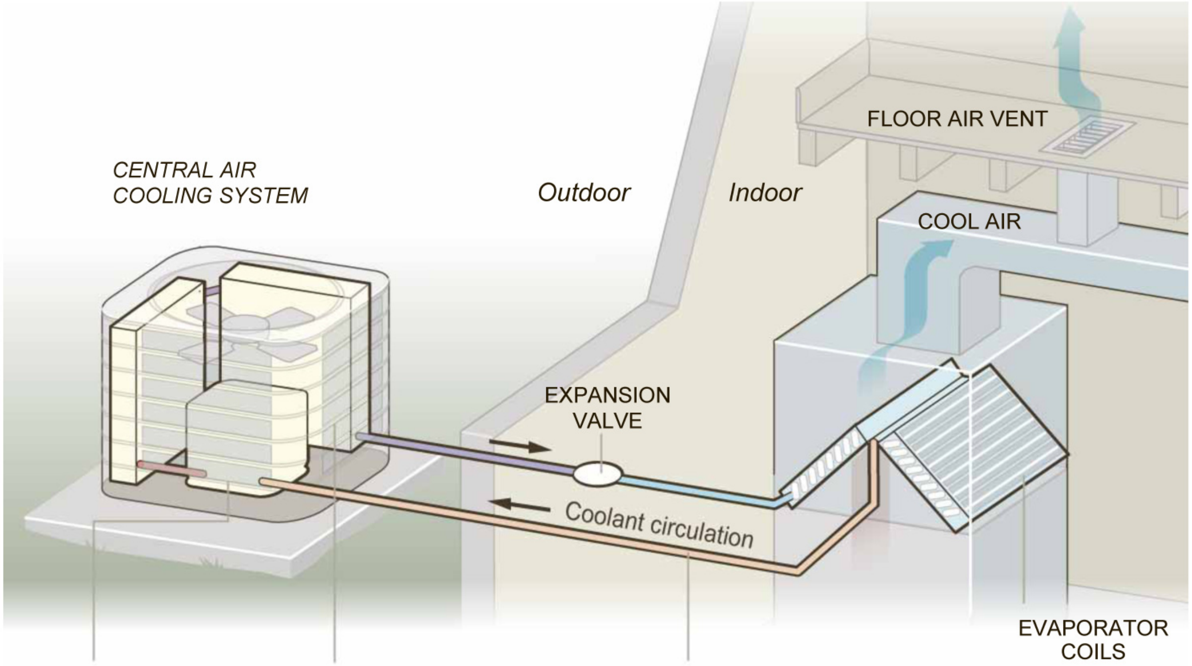
Though some manufacturers initially cried foul and resisted the practice, they realized they could not afford to do so, said John Mandyck, vice president of Carrier, the cooling and heating systems company. During the past year, an estimated 20 percent to 30 percent of all sales in the United States to replace failed units have been for HCFC-22 condensers.

In the end, Mr. Spector bought an entirely new system, running on R-410A, the gas that has been used in almost all new machines in the United States since 2010 and is far more energy-efficient and better for the ozone layer.

But it is still a potent agent of global warming and, therefore, in a class of chemicals that experts say must ultimately be phased out, too. The problem is that the next generation of cooling gases are all at least mildly flammable, and the E.P.A. is still reviewing their safety in home use, with a first approval possible as early as next year — not soon enough to help Mr. Spector.

What to Know About Your Air-Conditioning Unit

Most residential air-conditioning units, central or window, still rely on HCFC-22, a gas that the Environmental Protection Agency banned in new equipment in 2010 because of its ozone-depleting and global-warming potential. New systems are required to use a more environmentally friendly gas, typically R-410A. But the industry has found ways to keep using the older cooling gas.



COMPRESSOR AND CONDENSER COILS

This is the heart of every HVAC system, where a cooling gas is compressed to liquid form, initiating the cooling cycle. Service technicians can replace the compressor and condenser with new ones that still use the old gas. During servicing, they should also collect the gas and replace it once their work is done. But to save time, some simply release it into the air.

PIPES FILLED WITH COOLING GAS

Although air-conditioners should be closed systems, many are not. Cooling gas can leak from valves and joints, particularly in poorly maintained or aging systems. It is often easier to keep topping off leaky systems instead of servicing or replacing the broken components.

COOLING GAS ALTERNATIVES:	HCFC-22	R-410A	R-32	HYDROCARBONS
GLOBAL WARMING EFFECT	High	High	Moderate	Low
OZONE DEPLETION	Moderate	None	None	None
LEGAL STATUS	Older gas, being phased out by the E.P.A., and is available only for servicing old machines.	The gas in all new HVAC systems in the United States.	Being evaluated by the E.P.A. for use in residential systems, although it is mildly flammable.	Butane and isopropane are used in commercial refrigeration, but for home use these flammable gases require a system redesign.

Chemical & Engineering News JUNE 10, 2013

U.S., China To Cooperate On Reducing Potent Greenhouse Gases

Presidents Obama and Xi agree to curb manufacture of hydrofluorocarbons

By Cheryl Hogue

In a move signaling greater cooperation on climate change, President Barack Obama and Chinese President Xi Jinping announced on June 8 that they would work cooperatively to phase down production and use of hydrofluorocarbons (HFCs).

HFCs are a family of potent greenhouse gases whose use is growing rapidly worldwide. They are refrigerants developed as substitutes for two classes of compounds that deplete the stratospheric ozone layer: chlorofluorocarbons and hydrochlorofluorocarbons. HFCs do not harm stratospheric ozone, but they are highly efficient at trapping heat in the atmosphere. For instance, one molecule of HFC-134a, used in car air conditioners, has 1,300 times the global warming potential of a molecule of CO_2 over a century, according to the Intergovernmental Panel on Climate Change.

A year ago at the United Nations Conference on Sustainable Development, countries struck a nonbinding deal to phase down HFCs. The new agreement between Obama and Xi, announced at a retreat for the two superpower presidents in California, lays out a broad course for implementing that global goal. They pledged that the U.S. and China will work together and with other countries to address the growing challenge of human-caused climate change by phasing down manufacture and consumption of HFCs.

In the past, the U.S. and China, the world's two largest emitters of greenhouse gases, have often been at loggerheads in discussions on curbing greenhouse gas releases. The agreement appears to mark a change in direction.

"The U.S. and China are the two biggest players in the international climate arena, and the fact that they're talking about cooperation is a pretty big deal," says Fred Krupp, president of Environmental Defense Fund, an advocacy group.

Achim Steiner, executive director of the UN Environment Programme, says the agreement by Obama and Xi gives a confidence boost to those working to hammer out a new international climate-change treaty. Negotiators from around the globe hope to finish a new accord by 2015 that would include emissions limits for all nations that are major releasers of greenhouse gases.

The Washington Post JUNE 8, 2013

President Obama and Chinese President Xi Jinping agree to wind down production and use of hydrofluorocarbons, or HFCs

By Steven Mufson

The agreement between President Obama and Chinese President Xi Jinping on Saturday to wind down the production and consumption of a class of chemicals commonly used in refrigerators and air conditioners could mark a key step toward eliminating some of the most potent greenhouse gases.

The United States and roughly 100 other countries have already pledged to seek substitutes.

For the first time, the United States and China will work together to persuade other countries, most notably holdouts such as Brazil and India, to join the effort to slash or eliminate the use of hydrofluorocarbons, or HFCs.

The chemical group currently accounts for only 2 percent of greenhouse gases, but consumption is growing exponentially as people in developing countries grow wealthy enough to purchase air conditioners. A global push to get rid of HFCs could potentially reduce the greenhouse gases by the equivalent of 90 gigatons of carbon dioxide by 2050, equal to roughly two years' worth of current global greenhouse gas emissions, experts estimate.

March 2, 2015

EPA Approves New Climate-Friendly Refrigerants/Rule

Under the authority of the Clean Air Act, EPA's SNAP Program evaluates substitute chemicals and technologies that are safe for the ozone layer. This final rule expands the list of SNAP-approved substitutes to include more low-global warming potential (GWP) alternatives that can replace both the ozone-depleting substances and high-GWP hydrofluorocarbons (HFCs). The approved substitutes have GWPs that range from 3 to 675 and can replace older compounds with GWPs between 1400 to 4000.

After receiving input from industry, environmental groups, and others, EPA is approving low-GWP hydrocarbon refrigerants, subject to use conditions, in the following refrigeration and air conditioning applications:

- Ethane in very low temperature refrigeration and in non-mechanical heat transfer;
- Isobutane in retail food refrigeration (stand-alone commercial refrigerators and freezers) and in vending machines;
- Propane in household refrigerators, freezers, or combination refrigerators and freezers, in vending machines, and in room air conditioning units;
- The hydrocarbon blend R-441A in retail food refrigeration (stand-alone commercial refrigerators and freezers), in vending machines and in room air conditioning units; and
- HFC-32 (difluoromethane) in room air conditioning units. HFC-32 has one-third the GWP of the conventional refrigerants currently being used in room air conditioning units.

These refrigerants are already in use in many of these applications in Europe and Asia. In addition to adding these climate-friendly alternatives, EPA is also exempting all of these substances, except HFC-32, from the Clean Air Act venting prohibition, as current evidence suggests that their venting, release, or disposal does not pose a threat to the environment.

Learn more about EPA's SNAP Program and this rule: http://www.epa.gov/ozone/snap/index.html
Source: http://yosemite.epa.gov/opa/admpress.nsf/0/1691E88E1FBE79FE85257DFC0057AA19

Federal Register

Vol. 80, No. 69, Friday, April 10, 2015

Excerpts from Rules and Regulations (original document 49 pages)

40 CFR Part 82 [EPA–HQ–OAR–2013–0748; FRL–9922–26–OAR] RIN 2060–AS04

Protection of Stratospheric Ozone: Listing of Substitutes for Refrigeration and Air Conditioning and Revision of the Venting Prohibition for Certain Refrigerant Substitutes

AGENCY: Environmental Protection Agency (EPA).
ACTION: Final rule.

Hydrocarbon refrigerants have been in use for over 15 years in countries such as Germany, the United Kingdom, Australia, and Japan in household and commercial refrigerators and freezers. To a lesser extent, hydrocarbon refrigerants have also been used internationally in small air conditioning (AC) units such as portable room air conditioners. Because hydrocarbon refrigerants have zero ozone depletion potential (ODP) and very low global warming potentials (GWPs) compared to most other refrigerants, many companies recently have expressed interest in using hydrocarbons in the United States. Also, some companies have reported improved energy efficiency with hydrocarbon refrigerants…

This action lists the following refrigerants as acceptable, subject to use conditions, for use in specific end-uses within the refrigeration and AC sector: Ethane (R–170), HFC–32 (R–32), isobutane (R–600a), propane (R–290), and the hydrocarbon blend R–441A. Types of residential and light commercial AC equipment addressed in this action include window AC units; packaged terminal AC units and heat pumps; and portable room AC units. Types of refrigeration equipment include stand-alone retail food refrigeration equipment, very low temperature freezers, thermosiphons (non-mechanical heat transfer equipment), household refrigerators and freezers, and vending machines.

All of the end-uses in this final rule are for stationary refrigeration or AC. EPA previously issued several final rules addressing the use of flammable refrigerants in motor vehicle air conditioning (MVAC). On June 13, 1995, at 60 FR 31092, the Agency found all flammable substitutes to be unacceptable for use in MVAC unless specifically listed as acceptable, subject to use conditions, because of flammability risks and the lack of sufficient risk assessment and other relevant information to demonstrate safe use in that end-use at that time. Some of these risks are unique to motor vehicles. In recent years, EPA has listed three low-GWP refrigerants as acceptable, subject to use conditions, for MVAC systems (i.e., R–152a, R–1234yf, and R–744). Two of these refrigerants are flammable, although less flammable than hydrocarbons. Under 40 CFR part 82, subpart G, Appendix B, all other flammable substitutes remain unacceptable for use in MVAC because EPA has not taken action to specifically list them as acceptable, subject to use conditions…

HFCs are accumulating rapidly in the atmosphere. For example, the atmospheric concentration of HFC–134a, the most abundant HFC, has increased by about 10% per year from 2006 to 2012, and concentrations of HFC–143a and HFC–125 have risen over 13% and 16% per year from 2007–2011, respectively (Montzka, 2012; NOAA, 2013). The alternatives addressed in this action have GWPs significantly lower than both the ozone-depleting substances (ODS) and HFC substitute refrigerants in the end-uses in which they are being listed. ODS in the end uses in this final rule include chlorofluorocarbon (CFC)-12 (ODP 3 of 1 and GWP of 10,900), R–13B1 (also known as bromotrifluoromethane or halon 1301, with ODP of 10 and GWP of 7,140), CFC–113 (ODP of 0.8 and GWP of 6,130), R–502 (a blend of CFC– 115 and HCFC–22, with ODP of 0.334 and GWP of 4,660), and HCFC–22 (ODP of 0.055 and GWP of 1,810). The GWPs 4 of the hydrocarbon refrigerants we are adding to the SNAP lists in this rule are less than 10, while HFCs listed as acceptable in the end-uses in this rule have GWPs ranging from 1,430 to 3,920. Thus, the listed refrigerants provide industry additional options with lower atmospheric impacts.

In this action, EPA is listing the following refrigerants as acceptable, subject to use conditions, in the identified end-uses.

Retail food refrigeration. EPA finds isobutane (also referred to as R–600a) and the hydrocarbon blend R–441A acceptable, subject to use conditions, as substitutes in retail food refrigeration (new stand-alone retail food refrigeration equipment only). The use conditions require the following:

i. The quantity of the substitute refrigerant (i.e., ‘‘charge size’’) must not exceed 150 g (5.29 oz);
ii. These refrigerants may be used only in new equipment designed specifically and clearly identified for the refrigerant—i.e., none of these substitutes may be used as a conversion or ‘‘retrofit’’ refrigerant for existing equipment;
iii. These refrigerants may be used only in stand-alone retail food refrigeration equipment that meets all requirements listed in Supplement SB to the 10th edition of UL Standard 471, dated November 24, 2010. In cases where this final rule includes requirements more stringent than those of the 10th edition of UL Standard 471, the appliance would need to meet the requirements of the final rule in place of the requirements in the UL Standard;
iv. The refrigerator or freezer must have red Pantone Matching System (PMS) #185 marked pipes, hoses, or other devices through which the refrigerant passes, to indicate the use of a flammable refrigerant. This color must be present at all service ports and other parts of the system where service puncturing or other actions creating an opening from the refrigerant circuit to the atmosphere might be expected and must extend a minimum of one (1) inch in both directions from such locations.
v. The following markings, or the equivalent, must be provided and must be permanent:
   (a) ‘‘DANGER—Risk of Fire or Explosion. Flammable Refrigerant Used. Do Not Use Mechanical Devices To Defrost Refrigerator. Do Not Puncture Refrigerant Tubing.’’ This marking must be provided on or near any evaporators that can be contacted by the consumer.

(b) ‘‘DANGER—Risk of Fire or Explosion. Flammable Refrigerant Used. To Be Repaired Only By Trained Service Personnel. Do Not Puncture Refrigerant Tubing.’’ This marking must be located near the machine compartment.
(c) ‘‘CAUTION—Risk of Fire or Explosion. Flammable Refrigerant Used. Consult Repair Manual/Owner’s Guide Before Attempting To Service This Product. All Safety Precautions Must be Followed.’’ This marking must be located near the machine compartment.
(d) ‘‘CAUTION—Risk of Fire or Explosion. Dispose of Properly In Accordance With Federal Or Local Regulations. Flammable Refrigerant Used.’’ This marking must be provided on the exterior of the refrigeration equipment.
(e) ‘‘CAUTION—Risk of Fire or Explosion Due To Puncture Of Refrigerant Tubing; Follow Handling Instructions Carefully. Flammable Refrigerant Used.’’

This marking must be provided near all exposed refrigerant tubing. All of these markings must be in letters no less than 6.4 mm (1⁄4 inch) high…

Household refrigerators and freezers. EPA finds propane (also referred to as R–290) acceptable, subject to use conditions, as a substitute in household refrigerators and freezers and combination refrigerator/freezers. The use conditions require the following:

i. The charge size for any household refrigerator, freezer, or combination refrigerator and freezer for each circuit using R–290 must not exceed 57 g (2.01 oz);
ii. This refrigerant may be used only in new equipment specifically designed and clearly identified for the refrigerant—i.e., none of these substitutes may be used as a conversion or ‘‘retrofit’’ refrigerant for existing equipment;
iii. This substitute may be used only in equipment that meets all requirements in Supplement SA to the 10th edition of UL Standard 250, dated August 25, 2000. In cases where this final rule includes requirements more stringent than those of the 10th edition of UL Standard 250, the appliance would need to meet the requirements of the final rule in place of the requirements in the UL Standard;
iv. The refrigerator or freezer must have red PMS #185 marked pipes, hoses, and other devices through which the refrigerant passes to indicate the use of a flammable refrigerant;
v. Permanent markings must be provided on the equipment, as described above for stand-alone commercial refrigerators and freezers. All of these markings must be in letters no less than 6.4 mm (1⁄4 inch) high.

Household refrigerators, freezers, and combination refrigerator/freezers are intended primarily for residential use, although they may be used outside the home. Household freezers only offer storage space at freezing temperatures, unlike household refrigerators. Products with both a refrigerator and freezer in a single unit are most common. Wine coolers used in residential settings are considered part of this end-use. EPA previously found the flammable hydrocarbon refrigerants isobutane and R–441A acceptable, subject to use conditions, in this end-use (December 20, 2011, at 76 FR 78832, codified at Appendix R of Subpart G of 40 CFR part 82).

Vending machines. EPA finds R– 441A, isobutane, and propane as acceptable substitutes in vending machines, subject to the same use conditions described above for standalone retail food refrigeration equipment, except that paragraph iii. reads as follows:

Equipment must meet all requirements of Supplement SA to the 7th edition of UL Standard 541, ‘‘Refrigerated Vending Machines,’’ dated December 30, 2011 (instead of Supplement SB to the 10th edition of UL 471). Supplement SA specifically addressing flammable refrigerants is very similar to the Supplement SB in the UL 471 Standard for commercial refrigerators and freezers, and thus, similar requirements apply to these types of refrigeration equipment. In UL 541, the relevant references on equipment markings for flammable refrigerants in Supplement A are Sections SA 6.1.2–SA 6.1.5.

Vending machines are self-contained units for refrigerating beverages or food which dispense goods that must be kept cold or frozen. This end-use differs from other retail food refrigeration because goods are dispensed, rather than allowing the consumer to reach in to grab a beverage or food product. The design of the refrigeration system of a vending machine is similar to that of a self-contained commercial refrigerator or freezer. Typically the difference lies in how payment for goods is made and in the selection mechanisms found in vending machines but not in self contained commercial refrigerator freezers, and possibly the outer casing (e.g., glass doors and open, reach-in designs are generally used in self contained commercial refrigerator freezers whereas glass wall and other types of casings are used for vending machines). We are aware that for vending machines, it is possible to detach easily and replace the refrigeration circuit from the outer casing of the equipment. In such a situation, replacing the old refrigeration circuit with a new one within the old casing would be considered ''new'' equipment and not a retrofit of the old, existing equipment.

Residential and light commercial AC and heat pumps. EPA finds propane (also known as R–290), difluoromethane (also known as HFC–32 or R–32), and R–441A acceptable, subject to use conditions, as substitutes in residential and light commercial AC for self contained room air conditioners, including PTAC units and PTHPs, window AC units, and portable AC units designed for use in a single room. The use conditions require the following:

i. These refrigerants may be used only in new equipment designed specifically, and clearly identified, for the refrigerant—i.e., none of these substitutes may be used as a conversion or ''retrofit'' refrigerant for existing equipment;
ii. These refrigerants may be used only in air conditioners that meet all requirements listed in Supplement SA to the 8th edition, dated August 2, 2012, of UL Standard 484, ''Room Air Conditioners.'' In cases where this final rule includes requirements more stringent than those of the 8th edition of UL Standard 484, the appliance would need to meet the requirements of the final rule in place of the requirements in the UL Standard;
iii. UL 484 includes charge limits for room air conditioners and adherence to those charge limits would normally be confirmed by the installer. In addition to requiring the charge limits in the UL 484 Standard, EPA is requiring the following charge size limits, adherence to which must be confirmed by the original equipment manufacturer (OEM). In cases where the charge size limit listed is different from those determined by UL 484, the smaller of the two charge sizes would apply. For a review of how these charge size limits were derived, see ''Derivation of Charge Limits for Room Air Conditioners,'' (EPA, 2015) in the docket. The charge size limit must be determined based on the type of equipment, the alternative refrigerant used, and the normal rated capacity of the unit. The limits are presented in Tables 2 through 6 below in Section III.C.3, ''Charge size,'' and in Tables A, B, C, D and E of the regulatory text at the end of this preamble.
iv. The air conditioner must have red PMS #185 marked pipes, hoses, or other devices through which the refrigerant passes to indicate the use of a flammable refrigerant. This color must be present at all service ports and other parts of the system where service puncturing or other actions creating an opening from the refrigerant circuit to the atmosphere might be expected and must extend a minimum of one (1) inch in both directions from such locations;
v. The following markings, or the equivalent, must be provided and must be permanent:
   (a) On the outside of the air conditioner: ''DANGER—Risk of Fire or Explosion. Flammable Refrigerant Used. To Be Repaired Only By Trained Service Personnel. Do Not Puncture Refrigerant Tubing.''
   (b) On the outside of the air conditioner: ''CAUTION—Risk of Fire or Explosion. Dispose of Properly In Accordance With Federal Or Local Regulations. Flammable Refrigerant Used.''
   (c) On the inside of the air conditioner near the compressor: ''CAUTION—Risk of Fire or

Explosion. Flammable Refrigerant Used. Consult Repair Manual/Owner's Guide Before Attempting To Service This Product. All Safety Precautions Must be Followed.''

(d) For portable air conditioners, PTAC and PTHP, on the outside of the product: ''WARNING: Appliance shall be installed, operated and stored in a room with a floor area larger than ''X'' m2 (Y ft2).'' The value ''X'' must be determined using the minimum room size in m2 calculated using Appendix F of UL 484. The evaporator must remain no higher than 0.6 m above the floor.

(e) For window air conditioners, on the outside of the product: ''WARNING: Appliance shall be installed, operated and stored in a room with a floor area larger than ''X'' m2 (Y ft2).'' The value ''X'' must be determined using the minimum room size in m2 calculated using Appendix F of UL 484. The evaporator must remain no higher than 1.06 m above the floor.

All of these markings must be in letters no less than 6.4 mm (1⁄4 inch) high.

Due to their flammable nature, ethane, isobutane, propane, HFC–32, and R– 441A could pose a significant safety concern for workers and consumers in the end-uses addressed in this rule if they are not handled correctly. In the presence of an ignition source (e.g., static electricity spark resulting from closing a door, using a torch during service, or a short circuit in wiring that controls the motor of a compressor), an explosion or a fire could occur when the concentration of refrigerant exceeds its LFL. The LFLs of the substitutes are: ethane—30,000 ppm; HFC–32—139,000 ppm; isobutane—18,000 ppm; propane—21,000 ppm; and R–441A— 20,500 ppm. Therefore, to use these substitutes safely, it is important to minimize the presence of potential ignition sources and to reduce the likelihood that the levels of ethane, HFC–32, isobutane, propane, or R–441A will exceed the LFL.

EPA is requiring a varying charge size for room AC units. The maximum charge must be no greater than the amount calculated for a given sized space according to Appendix F to Supplement SA of UL Standard 484. This section of the UL standard uses a formula for the charge of a fixed room air conditioner based upon the size of the space where the refrigerant may escape and the LFL of the refrigerant. Height of the mounting of the unit is also a variable, because empirical studies have found that leaked refrigerant is more likely to mix thoroughly with the surrounding air, rather than pooling, when the AC unit is mounted higher. The formula is as follows:

$$m_{max} = 2.5\ (LFL)^{\frac{5}{4}}\ h_o\sqrt{A}$$

Where,

M_{max} is the maximum charge size allowed for the space, in kg,

LFL is the lower flammability limit of the refrigerant in kg/m^3,

h_0 is the installation height of the indoor unit in m (0.6 m for an AC unit on the floor, 1.0 m for an AC unit in a window, 1.8 m for a wall-mounted AC unit, and 2.2 m for a ceiling-mounted AC unit), and

A is the floor area of the room, in m^2.

The equipment manufacturer would then design AC units to be used in rooms with a minimum size and would label the minimum room size on the equipment.

Although using a formula to determine the maximum charge size and minimum room size is appropriate from an engineering perspective, it does not ensure that a consumer will select an appropriate AC unit for the size of their room. It is likely that some consumers may be unaware of the exact size of the room to be cooled and thus may select an inappropriately sized AC unit that increases the flammability risk. Or, a consumer may believe that a larger, more powerful AC unit will provide better, faster cooling and therefore may select an inappropriately sized AC unit that increases the flammability risk. To address these concerns, EPA is supplementing the charge size guidelines in Appendix F of UL 484 with a use condition that restricts the maximum refrigerant charge of equipment based upon the cooling capacity needed, in BTU/hour. Equipment manufacturers are responsible for designing equipment below a maximum charge size consistent with the intended cooling capacity. This will allow the manufacturer, who is better positioned than the consumer, to address these challenges. Placing the responsibility on the manufacturer to design equipment that restricts the maximum refrigerant charge based upon the cooling capacity needed also provides a better means for EPA to ensure compliance with the use conditions, and thus to ensure that the risk to human health will not be greater than that posed by other available substitutes. We believe that these requirements, in combination with the other use conditions and commonly found informational materials, provide sufficient safeguards against instances of consumers selecting inappropriately sized equipment.

EPA recommends that only technicians specifically trained in handling flammable refrigerant substitutes dispose of or service refrigeration and AC equipment containing these substances. Technicians should know how to minimize the risk of fire and the procedures for using flammable refrigerant substitutes safely. Releases of large quantities of flammable refrigerants during servicing and manufacturing, especially in enclosed, poorly ventilated spaces or in areas where large amounts of refrigerant are stored, could cause an explosion if an ignition source exists nearby. For these reasons, it is important that only properly trained technicians handle flammable refrigerant substitutes when maintaining, servicing, repairing, or disposing of household and retail food refrigerators and freezers, very low temperature freezers, non-mechanical heat transfer equipment (e.g., thermosiphons), and room air conditioners. In addition, EPA recommends that if hydrocarbon refrigerant substitutes are vented, released, or disposed of (rather than recovered), as would be allowed in most of the specified end-uses in this rule, the release should be in a well ventilated area, such as outside of a building.

LINDE

R744 Refrigerant Grade CO_2

http://www.r744.com/web/assets/companybrochure/file/252_Linde_R744.pdf

Introduction

R744 is a high purity carbon dioxide (CO_2) based refrigerant gas with a typical moisture content less than 10 parts per million. The low moisture content enables the refrigerant to work more effectively and more importantly, have less corrosive impact on your refrigeration systems.

Background

Carbon dioxide has been used as a refrigerant since the mid to late 19th century. With the introduction of fluorocarbons in the 1930s, CO_2 fell out of use by the 1950s. However, due to its low environmental impact, CO_2 is now regaining popularity from refrigeration system designers when an alternative to fluorocarbons is being sought. CO_2 suitable for use as a refrigerant is commonly named R744 in the refrigeration and air conditioning industry.

Advantages of R744

R744 is now regaining popularity due to a number of advantages:

- Low toxicity
- Non-flammability
- Zero ozone depletion potential
- Very low global warming potential (GWP=1)
- Excellent thermodynamic properties and low energy requirements