Stratospheric Ozone Protection: An EPA Engineering Perspective

William J. Rhodes

U.S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, North Carolina

Chlorine released into the atmosphere is a major factor in the depletion of the protective stratospheric ozone layer. The Montreal Protocol, as amended in 1990, and the Clean Air Act Amendments of 1990, address the limits and reduction schedules to be placed on chlorine- and bromine-containing chemicals. The status of technical solutions to the problem of chlorofluorocarbons, halons, methyl chloroform, and carbon tetrachloride in the major use areas of refrigeration, foam, aerosols, fire protection, and solvents is discussed here. The discussion includes the cooperative efforts involving academia, industry, U.S. governmental organizations, and other nations who are contributing solutions to these problems.

Previous articles have presented the scientific basis and legislation that are driving the need for solutions to the problem of emissions of certain chlorine and bromine chemicals. It is important to remember that until humans intervened in the process there was a natural dynamic balance between ozone formation and destruction resulting in the stratospheric ozone layer which has protected and nourished life on Earth.

Human activities have caused the emissions of chlorineand bromine-containing compounds, which have long lives and do not have destruction mechanisms, in the lower atmosphere. Fully halogenated chlorofluorocarbons (CFCs), having one or two carbon atoms, have lives ranging from almost 100 to several hundred years. When they reach the stratosphere, they are broken down by radiation which in turn releases chlorine atoms. A series of reactions takes place with chlorine acting as a catalyst that results in destruction of ozone and formation of diatomic oxygen. The chlorine from the fully halogenated CFCs is available to begin the ozone destruction cycle again. Similar reactions occur when chlorine or bromine is released from halons, carbon tetrachloride, methyl chloroform, and hydrochlorofluorocarbons (HCFCs).

Even partial destruction of the ozone layer allows additional ultraviolet-B (UV-B) rays to reach the Earth's surface. This increases the cases of skin cancers, cataracts, and suppression of immune systems, etc. Therefore, there is concern for any release of chemicals that contain chlorine or bromine with sufficiently long lives to survive in the stratosphere. At the time of the signing of the Montreal Protocol, the U.S. used its production of new CFCs and halons in approximately the following way (when actual quantities are weighted for the ozone depletion potential of each chemical): synthetic cellular foams, 28 percent; motor vehicle air-conditioning, 20 percent; refrigerants, 10 percent; solvents, 17 percent; fire extinguishers, 15 percent;

sterilization, 5 percent; and miscellaneous (including aerosols), 5 percent.

In addition to the stratospheric ozone situation, some of these same chemicals are of concern in the global warming arena. As with the dynamic equilibrium that existed with stratospheric ozone, there was a dynamic equilibrium which existed with regard to heat transfer. Below about seven micrometers wavelength, water in the atmosphere absorbs thermal radiation being emitted from Earth, and above about 12 micrometers wavelength, water and carbon dioxide both absorb thermal radiation. This left a gap in wavelengths, an open thermal window, where heat could and did escape from the Earth and its atmosphere. Gases from human activities, such as CFCs and halons, absorb thermal radiation in the range of 7 to 12 micrometers. This has the effect of closing the previously open thermal window, resulting in less heat escape from Earth through this mechanism and a potential increase in temperature.

Technology

The question facing technology is what to do with chemicals that are already in use and with long-lived equipment in operation that depends on these chemicals, and also new equipment. For existing chemicals, there is the decision whether to emit them or collect them. In the future, some of these decisions will be made for us as the regulations come into force. Now, if the chemicals are collected, the next decision to be made is what to do with them. Choices include recycling, chemical transformation, destruction, or long-term storage. For existing equipment, there is the potential that drop-in or near drop-in chemical replacements might be developed. Also, there is the potential that recycled chemicals might be available. Either of these would allow continued use of the equipment until its useful life has been achieved. For new equipment, there are the possibilities that new chemicals would be developed to use in the equipment or that entirely new technologies

Copyright 1991 - Air & Waste Management Association

might be developed that would satisfy the same need as the original equipment without using the old chemicals. In all of these situations, secondary environmental tradeoffs or impacts are important. Prudent actions would suggest that any solution for a stratospheric ozone problem not be implemented until consideration is given to other potential environmental problems that might be aggravated, to alternatives, and to the economics. This is not a formula to delay action, but one which should allow reasonable progress. As soon as necessary information is available, action should be taken.

To achieve maximum success, the Montreal Protocol restrictions^{2,3} must be adhered to by all nations. The U.S. method for achieving compliance is to enact appropriate regulations4 and implement the Clean Air Act Amendments.⁵ The Montreal Protocol and the Clean Air Act Amendments both indicate the need for developed countries to technically and financially assist developing countries. For this reason, the U.S. Environmental Protection Agency (EPA) program is sensitive to the needs of developing countries and provides incremental efforts in its research and development program to address the unique requirements of these countries. These efforts include technology transfer in the areas of safe aerosol propellants, refrigerant recycling, foam, and refrigeration systems. In addition, EPA is assisting in areas that would help reduce the incremental cost of a developing country's efforts not to utilize Montreal Protocol restricted chemicals. The Montreal Protocol agreement stipulates that developed countries will pay the incremental cost for developing countries to avoid using the Montreal Protocol restricted chemicals. Any savings in the incremental cost is an avoidance of cost to the developed countries; therefore, any reduction in incremental cost is a direct savings to the U.S. In addition, developing countries want assurance that they will have help in achieving the most beneficial solutions to their unique and common problems.

Recovery and Recycling

For the areas of motor vehicle air-conditioning and solvents, collection techniques for the chemicals are established. Collection devices for other refrigeration systems are now being evaluated or developed. The motor vehicle air-conditioning effort which has been completed involved industry, professional societies, and EPA cooperation to achieve rapid progress. In meetings, the automobile industry, the Mobile Air Conditioning Society, and EPA were able to agree on a way to determine the purity of recycled refrigerant that would be acceptable for maintaining warranties. The acceptable purity was to be what existed in properly operating vehicles that had about 15,000 miles (24,000 kilometers) of operation. EPA, in cooperation with the Mobile Air Conditioning Society, proceeded to test vehicles in several U.S. locations to determine the purity levels of the used refrigerants.6 In addition, EPA tested vehicles with other mileages to determine if time or mileage was a factor. Failed systems were also tested to determine a worst-case refrigerant. This worst-case refrigerant then served as a basis for the dirty fluid that would have to be cleaned by recycling machines to the level of purity specified for a recycled refrigerant.

With the test results, a committee consisting of the Mobile Air Conditioning Society; the Motor Vehicle Manufacturers Association of the United States; the Society of Automotive Engineers; the Automobile Importers of America, Inc.; the American Society of Heating, Refrigerating and Air-conditioning Engineers; manufacturers of recovery and recycle machines; and EPA agreed on the specifications which were announced in January 1989 as a voluntary standard less than 12 months after program initiation. Simultaneous with this work, Underwriters Laboratories

developed a certification program for recovery and recycle machines. As of October 4, 1991, 19 different machines have been certified with several others being sold under private brands or multiple listings. Table I lists primary and multi-listed machines. To obtain the most recent list, contact the Underwriters Laboratories. Most motor vehicle manufacturers have announced plans to require their factories and dealers to use certified machines even prior to any formal requirement to do so.

For home refrigerators/freezers, several methods have been proposed and are being used by some manufacturers and servicing personnel. These include bagging the contents using system pressure and vacuum pumps for withdrawal into containers. As of this writing, there has been no independent evaluation of the effectiveness of these techniques either in withdrawing the refrigerant or in contaminants left behind or removed. It would seem appropriate that a program similar to that involving motor vehicle air-conditioning be carried out in these other refrigerant areas. Such a program would require that sampling and analysis procedures be developed beyond those used in the motor vehicle air-conditioning work. The nonhermetic systems found in motor vehicle air-conditioning are expected to be cleaner than the hermetic systems found in other refrigeration systems. For example, contamination from motor burnout is expected to cause additional concerns.

Several procedures exist for these nonmotor vehicle systems, depending on the suspected level of contamination. For lightly contaminated refrigerant, a simple insystem filter/dryer can be used. Small portable units can also recover, store, and recycle refrigerant. These usually operate similar to the motor vehicle refrigerant recycling machines in terms of removing acid, moisture, and particulates and further purifying through vaporization. Where higher capacities are needed, larger skid- or truck-mounted units are available to accomplish similar purification. Where on-site cleanup is not practical or desirable, off-site facilities

Table I. Manufacturers/vendors of certified motor vehicle air-conditioning recycling machines.

- 1. AES NTRON, Exton, PA
- 2. Assembly Systems Corp., Eau Claire, WI
- 3. Belco Controls Inc., Regina, Saskatchewan, Canada
- Environmental Products Amalgamated Pty, Ltd., Shepparton, Victoria, Australia
- 5. Environmental Technologies Corp., Niles, MI
- 6. Everco Industries Inc., St. Louis, MO
- Four Seasons, Grapevine, TX
 IG-LO Inc., Lexington, KY
- 9. James Kamm Technologies Inc., Toledo, OH
- 10. MDI, Wheatridge, CO
- 11. Power Manufacturing, Rockwall, TX
- 12. Refrigerant Recovery Systems Inc., Tampa, FL
- 13. Refrigerant Technologies Inc., York, PA
- 14. Robinaire Division, Montpelier, OH
 - Also marketed by:
 - Bear Automotive Everco
 - General Motors
 - Kent-Moore
 - OTC Division of Sealed Power Corp.
- 15. Rolo, Jacksonville, FL
- 16. Sun Electric Corp., Crystal Lake, IL
- 17. Technical Chemical Company, Dallas, TX
- 18. White Industries, Fishers, IN
- 19. Wynn's Climate Systems Inc., Fort Worth, TX
- 20. Other marketers of certified machines:

Atlas Supply Co.

Ford Motor Co.

Four Seasons Manufacturing Co., Division of Standard Motor Products Inc.

MAC Tools Inc.

NAPA Temperature Products

Snap-on Tools Corp.

are available. It is hoped that voluntary agreements can be reached with each segment of the refrigeration industry similar to those for the motor vehicle area so that environmentally protective, reliable, safe, effective, and economic recovery, reclamation, and recycle machines will be utilized to extend the life of equipment that uses environmentally unsafe refrigerants without increasing their emissions.

Destruction or Transformation

After collecting a chemical that is on the Montreal Protocol or U.S. regulatory list as undesirable to release, there are several options. If allowed, the chemical could be emitted, but from an environmental view this is undesirable and from a regulatory view may be prohibited. Other options may include reuse in its original application, reuse in a different application, long-term storage, transformation to another chemical form for reuse, or destruction. Reuse of refrigerants has been discussed earlier. Reuse of other chemicals as solvents, fire extinguishants, or other uses is either being handled by the effected industry or has not yet been sufficiently researched. Long-term storage has not been seriously considered at this time; however, shortto mid-term storage has been considered as a means of establishing a bank of material which would extend the life of critical equipment such as certain safety applications, military applications, and other uses valued by society.

The only commercially available destruction system is thermal incineration. This is being done in some places by mixing up to five percent of chemicals to be destroyed with large quantities of other wastes. One company in England has contracted with a waste company to destroy unwanted halons. An environmental concern with thermal destruction is the unknown products of incomplete combustion. Although these could potentially be damaging, they have not been experimentally evaluated. Depending on the type of equipment, there could be problems from corrosive acids in the combustion gases that would attack the equipment.

Some other destruction mechanisms that have been evaluated at least at laboratory-scale are pyrolysis, photolysis, and dehalogenation with metal/metal oxide. An alternative to destruction that might be feasible and more desirable is chemical transformation. CFCs and halons might be good starting reactants for the production of other chemicals. These types of chemicals are used in the production of certain pharmaceuticals and polymers. An obvious disadvantage is the quantity of reactants that would be available which might not support an independent production facility. However, it might be possible to utilize these waste chemicals in an existing production facility. This concept needs to be explored more fully but it is a potential alternative to destruction and results in useful waste. A side benefit from such evaluations is the potential for production facilities of CFCs and halons in developing countries to be converted to produce alternative products without loss of the capital investment. This would reduce the incremental cost for countries in their avoidance of use of CFCs and halons and, therefore, reduce the U.S. monetary contribution.

Refrigeration

Home refrigerator/freezers. Home refrigerator/freezers now use CFC-12. Several types of replacements for this chemical are being evaluated. One philosophy is to find a replacement that will work in current equipment with as little change as possible and have fewer environmental problems than CFC-12. Since no single component has been found which satisfies the minimum change criterion, this leads to blends of chemicals that have similar necessary properties. One such blend announced by DuPont consists of HCFC-22, HFC-152a, and HCFC-124. This is expected to

be available for commercial use in 1993. Another philosophy is to find a replacement which is completely nonstratospheric ozone depleting. Pure chemicals which satisfy this criterion are HFC-134a and HFC-152a. However, these require changes in equipment, and each presents different concerns. HFC-134a is a global warming gas and is estimated in redesigned systems to have anywhere from a five to zero percent energy penalty, possibly further compounding global warming. There are concerns that use of HFC-134a might unnecessarily trade one environmental problem for another. Use of HFC-152a does not have the potential problems of HFC-134a with regard to global warming. In fact, it is estimated that its use will result in energy efficiency improvements of several percent. The potential problem of HFC-152a is how to handle it safely because it is flammable. This issue has led to an assessment of the risk of having small amounts of HFC-152a in the kitchen, compared to other risks that are acceptable in the home, and to a review of ways to minimize the risk. It is estimated that home refrigerator/freezers utilizing these HFCs could be available in the U.S. in 1993.

Other refrigerant systems are being actively explored which have greater promise for higher efficiencies. ^{10,11} These include systems which use single refrigerants or azeotropic mixtures. However, the uniqueness is not only in the refrigerants but also in the hardware. The hardware variations include systems which have two completely separate loops; one each for the freezer and fresh food sections, systems which share some components between the freezer and fresh food sections, and systems which switch back and forth between the freezer and fresh food sections, depending on load requirements.

Systems which use nonazeotropic refrigerant mixtures (NARMs) utilize a concept which was initially explored by Lorenz and Meutzner. 12 This modified system consists of one compressor, one condenser, two evaporators, and two intercoolers. The advantage of using an NARM in this system is that the mixture evaporates over a range of temperatures, and countercurrent heat exchangers may be used to reduce the temperature difference between the refrigerant and air streams. Therefore, in a refrigerator/ freezer which has two temperature zones, evaporation can take place in each section at a more thermodynamically advantageous temperature difference. The Lorenz concept is being evaluated by EPA, first through computer models to determine the potentials for different NARMs, and second through modified hardware to demonstrate the potential. Some of the chemical combinations include HCFC-22/-141b, HFC-32/HFC-152a/HCFC-141b, HCFC-22/ -123, and HFC-32/HCFC-142b. Continued progress in the Lorenz and the other more complicated systems requiring additional development should lead to commercially available models around 1995.

In addition to the refrigerant research and development area, work is also being conducted on improved cabinets for the refrigerator/freezer. The need to find a replacement for the CFC-11 used in the foam insulation created an opportunity for evaluating the cabinet design. One of the more promising concepts is the use of some form of vacuum insulation. 13 There are several competing types of advanced insulation at the present time. One type of vacuum superinsulation consists of fine powder contained in evacuated panels. The small size and shape of the powder limits the number of contact points for thermal conduction. Another type is a hard vacuum system consisting of an outer metal shell with the vacuum drawn inside. Currently these designs have unacceptable thermal conduction paths, and major improvements would appear to be necessary. A third type of vacuum panel is the silicon dioxide gel. This panel is formed as a gel, and then the water is removed leaving mostly evacuated space within the panel. A nonvacuum type insulation proposed by the Lawrence Berkeley Laboratory utilizes sheets of metal panels which are impermeable to gas and contain a gas such as argon or krypton.

Theoretical estimates are that a 50 percent reduction in energy use over the current refrigerator/freezer is possible from a combination of improved cabinet and refrigeration systems (including electronic control improvements). These savings might come from approximately half in each category (i.e., cabinet and system). Although a considerable amount of work needs to be done to achieve the full potential, a more modest gain should be achievable at a reasonable cost in the 1995 time frame.

Industrial/Commercial refrigeration. Efforts in this category are just beginning, and therefore are not as far advanced as in the home refrigerator/freezer area. Supermarket systems also have multiple evaporating temperatures which are generally classified as low- and mediumtemperature systems. Presently, available replacements include HCFC-22 in medium-temperature systems and ammonia where it can be safely used. Because compressor discharge temperatures are very high for HCFC-22, additional modifications are required in order to lower the temperature at which it can be effective. In systems where technical control can be maintained, ammonia may have more advantages than drawbacks. Even in retail food stores, it may be advantageous to use ammonia in a cascade system with ammonia located in an external building and glycol used as the refrigerant circulating through the facility. Implementation of these ammonia systems requires significant hardware changes, so other replacement technologies are also being reviewed. Similar to home refrigerator/freezers, HFC-134a, HFC-152a, and blends may have roles depending upon temperature requirements. The potential for using an azeotrope of HFC-32 and HFC-125 is being reviewed for low temperature applications. For low leak systems such as self-contained units, NARMs may be advantageous. Although some of the work being done for home refrigerator/freezers will benefit the industrial/commercial sector, there would appear to be a requirement to evaluate the specific needs of each industrial and commercial use and determine which refrigeration approach might be most suitable.

Space cooling. CFC-12 is now used in motor vehicle air-conditioning and is a major source of emissions. CFC-12 is both a stratospheric ozone depleting gas and a direct global warming gas. Any improvement that could be quickly introduced into the market would reduce the effects of CFC-12. In motor vehicle air-conditioning, the market is moving toward use of HFC-134a in 1993 or 1994. On the positive side, HFC-134a is not ozone depleting and can be used as a refrigerant to replace CFC-12. Also, HFC-134a has about 10 percent of the direct global warming potential of CFC-12. On the negative side, HFC-134a still has direct global warming potential and has lower energy efficiency than other potential replacements. In evaluating alternatives to motor vehicle air-conditioning, a product with lower energy efficiency was not considered critical since the application is used for short periods of time over only part of the year. Therefore, the lower energy efficiency of HFC-134a may not be critical. However, emissions could be a problem since they occur over the entire year.

To partially address intentional emissions during servicing in the short term, a good system for recovery, reclamation, and reuse of motor vehicle air-conditioning refrigerant for CFC-12 is now being established which could be modified to handle HFC-134a. To address unintentional emissions (e.g., fugitive emissions), improved hoses and fittings are required. Therefore, HFC-134a could satisfy interim needs in motor vehicle air-conditioning because emissions would not be harmful to the ozone problem, could be partly controlled to minimize global warming increases, and its lower energy efficiency may not be significant. Other refrigerants that might be used are blends and HFC-152a. Also,

other cooling concepts including innovative technologies might be practical.

Home central air-conditioning and heat pumps now use HCFC-22. Future replacements might include the same types of chemicals that have potential for motor vehicle air-conditioning use. Both the home air-conditioning and heat pump applications might see the use of NARMs and HFC-32 in mixtures.

Chillers are large space air conditioning units. There are several different types of chillers for which replacements are in different stages of development. Centrifugal chillers use CFC-11. Recent developments have produced a replacement chiller now being sold that uses HCFC-123. Because preliminary bioassay results have raised some interesting questions regarding exposure to HCFC-123, industry has reduced the interim acceptable exposure limits for HCFC-123 as a precaution. These lower limits do not appear to affect its acceptability for use in chillers. For CFC-12 reciprocating chillers, HFC-134a might be a replacement in the future. For the long term, more research needs to be done in these areas to ensure environmentally sound, efficient, reliable, and economic units.

Other nonvapor compression concepts might be advantageous for any of the stationary space cooling sources and should be evaluated. Some of these under development by various organizations include absorption systems and the Stirling cycle.

Foam

Insulation. There are several types of foam insulation, such as rigid polyisocyanurate boardstock, rigid polystyrene boardstock, and rigid polyurethane. Rigid polyisocyanurate and polystyrene boardstocks are used in building insulation. Rigid polyurethane can be laminated, sprayed, or poured in place (for example, in appliances). By changing formulations and the process for making the foam, lower quantities of CFC-11 can be used while still producing foam with essentially the same necessary characteristics. 14 This would appear to be a prudent intermediate step in phasingout CFCs. For the rigid polyisocyanurate boardstock, cooperative work is being done by EPA, Oak Ridge National Laboratory (ORNL), Polyisocyanurate Manufacturers Association, and the Society of Plastics Industries. Using commerical scale equipment, the work has produced insulation boards using HCFC-141b, HCFC-123, and a mixture of these chemicals as blowing agents. Testing of these boards at ORNL's roof thermal research apparatus has shown them to have a slight decrease in insulation capability compared to the CFC-11 which they are proposed to replace. However, the formulations for the HCFC boards were not optimized and it was recognized that further development by individual producers would probably improve the properties of the commercial product.

Noninsulation. There are several types of noninsulation foam which include flexible polyurethane, rigid polypropylene, rigid polyethylene, and rigid polystyrene sheet. Flexible polyurethane is made with CFC-11 and is used for cushioning. In many of these foam products, the amount of CFC-11 used can be reduced or eliminated by recovery and recycle of the blowing agent, by use of methylene chloride and methyl chloroform as blowing agents, and by changing the formulation to incorporate new polyols and softening agents. 14 One formulation change employs a mixture of formic acid and amine formates in conjunction with water as the blowing agent to double the amount of carbon dioxide generated and reduce the quantity of CFC-11 needed. In the future, improved polyol technology and alternative chemicals such as HCFC-141b and -123 might be applicable as replacements. In the long term, nonchlorine containing chemicals are needed to replace even the HCFCs.

Rigid polypropylene and rigid polyethylene are mostly made with CFC-11, -12, and -114 and used in life vests, packaging materials, computer cabinets, and armrests. Alternate blowing agents, such as butane and HCFC-22 and -142b, are being used for some products today to replace CFCs. Rigid polystyrene sheet is used in food packaging, egg cartons, cups, and plates and has been made with CFC-12 and in some cases CFC-11. Currently, these foams can be made with water-blown technologies or HCFC-22. In the future, there is the need to completely replace CFC-11, CFC-12, and HCFC-22. Possible near-term replacements are HCFC-123, -141b, and -142b. In the long term, HFC-125 or -134a might be applicable or other new chemicals or technologies might be developed.

Aerosols

Aerosol propellant technologies underwent major changes in the 1970s. With the first major opposition to CFCs, manufacturers changed from CFCs to other propellants. Over the years in these nonessential uses, the propellants of choice included hydrocarbons; compressed gases such as nitrogen, nitrous oxide, and carbon dioxide; dimethylether; and HFC-152a. The propellant utilized depended on the specific use and need of the product. However, environmental regulation allowed continued use of CFCs in applications that were considered essential. 15 These included formulations where the CFCs were part of the active ingredients or necessary as a solvent in the formulation. Today almost all of the previously exempted uses of CFCs have acceptable replacements which range from the abovementioned chemicals to nonaerosol propellants. Alternative pressurized packaging forms include bag-in-can, piston, and mechanical pressurizing systems. At this time, about the only products for which no totally acceptable substitute has been demonstrated are some cases where CFC-113 is used as a solvent in the product and CFC-12 is used in medicinals either as a solvent or as a propellant. 16,17

Fire Protection

Fire protection agents are used in two types of systems, streaming and total flooding. The agents of choice for many applications have been halons. For the streaming systems, Halon-1211 and -2402 are used. It has been found that these chemicals were being used almost exclusively for nontechnical reasons. 18 They were convenient, low cost, readily accepted, and worked well. With the current need to phase out these chemicals and with increasing prices. review of the alternative agents has resulted in findings that powder, foam, water sprays, and carbon dioxide are perfectly acceptable in given uses. For situations where one might want some different characteristics, DuPont and Great Lakes Chemical Corporation have announced chemical replacements which have either chlorine or bromine in them along with hydrogen and would be available in the next few years. Other HCFCs might also be available in this time frame.

Total flooding systems currently use Halon-1301. The flooding systems provide protection for various concerns such as fire suppression, explosion suppression, and explosion prevention. Much of the use of Halon-1301 has been in accidental or unnecessary releases. ¹⁹ These are the first areas in which to achieve conservation and reduce emissions. Strategies for reducing or eliminating Halon-1301 include rethinking the design of the protection system and using alternative chemicals or techniques for testing room integrity. In some cases, instead of using a total flooding system to protect an entire room of equipment, the system might be redesigned to have a smaller concentrated fire protection system near the actual location of the most

probable hazard and to isolate that from the remaining part of the room. This would require less agent. The larger part of the room could be protected by a water sprinkler or other system as a backup should the smaller in-place system not be sufficient in a given situation.

For some total flooding systems, work on additional agents may be necessary. Specialty uses such as aircraft and fuel pump rooms are of concern. 20 Whether these needs can be satisfied by alternative strategies, agents under development, or new agents remains to be seen. The situation requires that the agents be used in the presence of people, and therefore not only be fire protection agents but also be health protective. In cases such as fuel pump rooms, there is the concern that no explosion occur which might effect human life, might have ecological effects, and might effect availability of national fuel supplies. Chemical companies such as DuPont, Grace, Great Lakes Chemical, and 3M are working on replacements, any one of which might serve part of the need. EPA, through a series of extramural contracts, is working with the University of Tennessee, Clemson University, and New Mexico Engineering Research Institute on potential chemical replacements. Current efforts are synthesizing, purifying, and evaluating properties of the perfluorocarbons, hydrofluorocarbons, and fluoroethers. As information becomes available, the characteristics are compared to needs, and should any of the chemicals look promising, they would be produced in large enough quantities to allow further evaluation, including appropriate health effects testing. EPA is also working with companies from the North Slope such as British Petroleum, ARCO, and Alyeska Pipeline Service Company.

As existing halon total flooding systems are decommissioned for whatever reason, there is the opportunity to collect the halon. Halon collected in this way could be stored for any high priority use in the future. These might include military critical areas, museums, and historical documents. To ensure that the highest priorities are addressed, a halon bank would need to be established and administered impartially. Some thought has been given to this by the military.

Solvents

Solvents have been handled differently from most other chemicals. The solvents industry was quick to point out that the use of CFC-113 was mainly the result of military specifications. Armed with this information, industry and government diligently pursued potential solutions. Industry's attitude was that this was an opportunity to make some changes that could benefit them. With this attitude, industry did not look at a situation and try to find reasons why something could not be done, but instead was able to look for reasons why something better could come of a change. As a result, old technologies were re-evaluated and new technologies developed that were found in many situations to be as good as or better than CFC-113. For electric circuit assemblies, changes in soldering techniques such as low residue fluxes that do not require cleaning, controlled atmosphere soldering (e.g., inert gas blankets) that reduce contaminant formation, aqueous-based systems with and without high pressure or surfactants, alcohol blends, emulsions, and new HCFCs are all viable under various circumstances.21

Work performed in the 1930s on citrus-based terpenes resulted in systems capable of dissolving heavy petroleum greases. With changing environmental and cost factors these types of systems now appear to be viable for some applications. Mixtures of terpenes with surfactants are reported to be capable of removing contaminants from printed circuit boards more completely than CFC-113 and methanol mixtures. Aqueous-based systems, along with newer chemical replacements, are being certified for military applications through cooperative work with industry,

Table II. Solvent alternatives passing the Ad Hoc Solvents Working Group tests.

Manufacturer	Solvent	Material Type
Allied-Signal	Genesolv 2010	HCFC
Allied-Signal	Genesolv 2004	HCFC
DuPont	Axarel 38	Semi-aqueous
DuPont	Freon SMT	CFC-diluted
DuPont	Virtrel 34	HCFC
Kyzen Corp.	Ionox MC	Semi-aqueous
Martin Marietta	Marclean R	Semi-aqueous
Petroferm	Bioact EC-7	Semi-aqueous

EPA, and the military. Several solvents (listed in Table II) from five manufacturers have passed the test phase of the evaluation as of October 4, 1991. These tests were conducted under specific equipment and operating parameters. Since military specifications are the governing factor in industry choices, certification of solvents based on these tests will also have a major impact on industry. Changes in government procurements and specifications are being made as a result of these efforts. Industry, through the Industry Cooperative for Ozone Layer Protection (ICOLP), is actively and freely transferring its newly acquired information on solvents, technologies, and practices to other users. The technology transfer includes a globally accessible database called OZONET which can be reached through the General Electric Information Service network. As of this writing, members of ICOLP include AT&T, Boeing Company, Compaq Computer Corporation, Digital Equipment Corporation, Ford Motor Company, General Electric, Honeywell, Motorola, Northern Telecom, and Texas Instruments.

Conclusion

Industry, government, academia, and others are working toward replacing CFCs, halons, and HCFCs in our society. The U.S. is also working with developing countries to transfer the results of our work so as to accelerate utilization of chemicals that are not part of the Montreal Protocol restrictions. Most progress is being made where cooperation is the greatest. It appears that all areas where CFCs and halons have been used will eventually benefit from taking a fresh look at why and how they were used. These benefits are already being achieved and include lower costs, higher energy efficiency, and reduced environmental problems. It is important that solutions to stratospheric ozone depletion not exacerbate other environmental problems. All problems are not yet solved, but continued good attitudes and cooperation are making progress easier and more assured.

Disclaimer

Although this paper has been administratively reviewed within the Agency and approved for publication, it does not necessarily reflect EPA policy.

References

- Hoffman, J. S. "Assessing the Risks of Trace Gases that Can Modify the Stratosphere, Volume 1," Executive Summary, EPA-400/1-87/001a (NTIS PB88-231055), December 1987, Chapters 7–16.
- "Montreal Protocol on Substances that Deplete the Ozone -Final Act," United Nations Environment Programme,

- "Second Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer," UNEP/OzL-Pro. 2/3, London, June 29, 1990.
 U.S. EPA. "Protection of Stratospheric Ozone Final Rule,"
- Federal Register, 40 CFR Part 82, August 12, 1988. "Clean Air Act Amendments of 1990," 101st Congress, 2d
- Session, Public Law 101-549, November 15, 1990.

 6. Harmon, D. L.; Rhodes, W. J.; Weitzman, L. "Mobile Air Conditioner Refrigerant Evaluation," Paper No. 89-4.4 presented at 82nd Annual Meeting of Air and Waste Management Association, Anabasin, CA, June 1999.
- Association, Anaheim, CA, June 1989.
 7. Harmon, D. L.; Rhodes, W. J. "Recycle and Disposal Options for CFCs and Halons," Paper No. 90-138.4 presented at the 83rd Annual Meeting of Air and Waste Management Associa-
- tion, Pittsburgh, PA, June 1990.
 Dickerman, J. C.; Emmel, T. E.; Harris, G. E.; Hummel, K. E.
 "Technologies for CFC/Halon Destruction," EPA-600/7-89011 (NTIS PB90-116955). October 1989.
- "CFCs and Halons: Alternatives and the Scope for Recovery for Recycling and Destruction, 1990," A Report by Depart-ment of Trade and Industry, Coopers and Lybrand Deloitte, HMSO, London.
- Bare, J. C. "Preliminary Selection of Refrigerants for Dual-Circuit and Lorenz Refrigerator/Freezers," Paper No. 90-138.2 presented at the 83rd Annual Meeting of Air and Waste Management Association, Pittsburgh, PA, June 1990.
- Roke, L. "142b/22 Test Results: Food Storage Advantages with Two-Evaporator Refrigerants," in Proceedings of the International Conference on CFC and Halon Alternatives, October 1989.
- Lorenz, A.; Meutzner, K. "On Application of Non-Azeotropic Two-Component Refrigerants in Domestic Refrigerators and Home Freezers," in Transactions of the 1975 International
- Institute of Refrigeration Meeting, Moscow, USSR, 1975.

 13. Fine, H. A. "Advanced evacuated thermal insulations: the state of the art," J. Therm. Insulat. Vol. 12 (1989).
- "Technical Progress on Protecting the Ozone Layer: Flexible and Rigid Foams Technical Options Report," UNEP Foam Technical Options Committee meeting, June 30, 1989.
- Smith, N. D. "Reduction of CFC Usage in U.S. Exempted and Excluded Aerosols," Paper no. 90-138.5 presented at the 83rd Annual Meeting of Air and Waste Management Association,
- Pittsburgh, PA, June 1990.

 Nelson, T. P.; Wevill, S. L. "Alternative Formulations to Reduce CFC use in U.S. Exempted and Excluded Aerosol EPA-600/2-89-061 (NTIS PB90-149972), Novem-Products,
- Nelson, T. P.; Wevill, S. L. "Aerosol Industry Success in Reducing CFC Propellant Usage," EPA-600/2-89-062 (NTIS Nelson, T.
- PB90-143447), November 1989.

 18. Robinson, F. "Extinguishing Halons: A Direct Approach by an
- Australian Trade Union," in Proceedings of the International Conference on CFC and Halon Alternatives, October 1989. 19. Mossel, J. W.; Willmott, B. J. "Fire Protection Industry's Emission Reduction Efforts," in Proceedings of the International Conference on CFC and Halon Alternatives, October
- Rhodes, W. J.; Shapiro, P. S. "Success of EPA's Stratospheric Ozone Engineering Research," Paper no. 90-138.3 presented at the 83rd Annual Meeting of Air and Waste Management Association, Pittsburgh, PA, June 1990.
- Ahmadzai, H. "Progress on the Phase-out of CFC Use as a Solvent in the Engineering Industry World-wide," in Proceedings of the International Conference on CFC and Halon Alternatives. October 1989.
- Hayes, M. E. "Naturally Derived Biodegradable Cleaning Agents: Terpene-Based Substitutes for Halogenated Solvents," in Proceedings of the International Conference on CFC and Halon Alternatives, October 1989.

W. J. Rhodes is chief of the Stratospheric Ozone Protection Branch, Air and Energy Engineering Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency at Research Triangle Park, NC 27711. He has a Master of Chemical Engineering degree and leads a group in efforts to solve the problem of emissions of stratospheric ozone depleting chemicals. This manuscript was submitted for peer review on June 17, 1991. The revised manuscript was received on October 9, 1991.