Research and Development

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SEPA Project Summary

New Chemical Alternative for Ozone-Depleting Substances: HFC-236fa

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Hydrofluorocarbons (HFCs) form a class of chemicals having the potential to replace stratospheric ozone depleting substances such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). The report gives results of a preliminary evaluation of a new HFC (HFC-236fa or 1,1,1,3,3,3hexafluoropropane) as a possible alternative for CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane) refrigerant for chillers and as a possible fire suppressant replacement for halon-1301 (bromotrifluoromethane). Evaluation tests included examinations of flammability, stability, atmospheric lifetime, thermophysical properties, lubricant miscibility and solubility, materials compatibility, inhalation toxicity, refrigeration performance, heat transfer characteristics, and flame suppression. Results of these examinations indicate that HFC-236fa is a viable alternative for CFC-114 refrigerant and for halon-1301 or -1211 fire extinguishing agent. Its relatively long atmospheric lifetime may be a concern from a global warming perspective.

This Project Summary was developed by EPA's National Risk Management Research Laboratory's Air Pollution Prevention and Control Division, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Fully halogenated CFCs and their bromine-containing relatives (halons) are recognized as primary contributors to depletion of Earth's stratospheric ozone layer. As early as 1978, the U.S. Environmental Protection Agency (EPA) promulgated regulations banning the use of CFCs as aerosol propellants in all but a few exempted applications. In the mid-1980's, the EPA began considering additional regulatory restrictions on the use of CFCs and halons. In the course of this consideration, it became apparent that few, if any, alternative chemicals were readily available or had been proven applicable to the numerous CFC and halon uses which had grown dramatically in the time following the 1978 CFC aerosol ban.

Following the advice of an expert panel convened by the EPA, the Agency's Office of Research and Development undertook a program to systematically search for additional alternative chemicals to serve as backups if the few chemicals proposed by industry fell short of expectations. Over a 3-year period, 37 new compounds were prepared of sufficient stability and in sufficient yield and purity to obtain a limited set of relevant property measurements. All of these compounds were partially fluorinated hydrocarbons or ethers. Based on the thermophysical properties obtained for these compounds, EPA selected 12 chemicals (including HFC-236fa) for more extensive evaluation.

Evaluation Tests and Results

HFC-236fa contains no chlorine or bromine atoms and therefore has zero potential to deplete stratospheric ozone. Its reaction rate at 298 K with hydroxyl (OH) radical is 0.034 x 10⁻¹⁴ cm³ molecule⁻¹ sec⁻¹. This reaction rate translates into an atmospheric lifetime of approximately 192 years and a 100-year horizon global warming potential (GWP) of 6300 (relative to GWP for CO₂ = 1).

Theoretical analysis and experimental evaluations in a semihermetic compressor confirm that HFC-236fa can be considered as a replacement for CFC-114 in chillers. HFC-236fa was found to have a higher refrigerating capacity and coefficient of performance (COP) than CFC-114 at operating conditions typical of CFC-114 chillers. The experimental COP was higher than or equal to that of CFC-114 at condensing temperatures up to 70°C and declined somewhat at higher condensing temperatures.

HFC-236fa was included in a matrix of four HFCs and one hydrofluoroether examined for thermal and hydrolytic stability and materials compatibility. These tests showed that, with and without a polyolester (POE) lubricant present, several common elastomers gave acceptable overall performance in terms of change in weight, volume, linear swell, and hardness. Conversely, fluoropolymers such as Viton®, Kalrez®, and Teflon® were especially susceptible to absorption of HFCs, including HFC-236fa, resulting in unacceptable swelling. Hydrogenated nitrile butyl rubber and natural rubber showed excessive swelling when the POE oil was added to the refrigerants. Neoprene was deemed unsuitable due to shrinkage and embrittlement, with and without the lubricant present. Aluminum, steel, cast iron, copper, brass, and bronze were compatible with HFC-236fa and the POE lubricant. Of four molecular sieve bead desiccants tested, three were of three Angstrom average pore diameter and exhibited no apparent reactivity with HFC-236fa. The fourth desiccant had an average pore diameter of four Angstroms and showed

some evidence of degradation of HFC-236fa based on an increase in the fluoride ion content of the desiccant after the aging test.

HFC-236fa was found to be completely miscible with ISO-68 POE oil over the temperature range of -30 to +125°C. Lubricity tests indicated that the chemical was compatible with this type of lubricant and that the refrigerant/lubricant mixture provided good wear resistance.

Heat transfer coefficients of HFC-236fa were determined in test rigs configured to investigate refrigerant-side coefficients in centrifugal chillers. Coefficients were measured for two conventional finned tubes and three performance-enhanced tubes during shell-side condensation and pool boiling on the outside of a single horizontal tube. For pool boiling tests, a miscible POE lubricant was added to the HFC-236fa up to a lubricant concentration of 3 wt %. A comparison of shell-side heat transfer coefficients obtained for HFC-236fa with those obtained for CFC-114 under identical conditions showed HFC-236fa to have better heat transfer during condensation with a maximum increase of 40% relative to CFC-114. For pool boiling, HFC-236fa provided a maximum heat transfer increase of 80% relative to CFC-114.

HFC-236fa was found to be nonflammable by standards set by the American Society of Testing and Materials (ASTM). In laboratory cup-burner tests, a concentration of 5.6 volume % HFC-236fa in air was found to extinguish an n-heptane flame. This extinguishing concentration is equivalent (within experimental error) to that of a commercially available fire extinguishing agent; i.e., HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane).

Considerable toxicity testing was performed for HFC-236fa due in large part to the U. S. Navy's interest in retrofitting its shipboard CFC-114 chillers with HFC-236fa. Toxicity tests included acute inhalation, cardiac sensitization, genetic toxicity, developmental toxicity, and 90-day subchronic inhalation. The maximum concentration of HFC-236fa administered to rats and rabbits for the inhalation toxicity

evaluations was 50,000 ppm. The only notable compound-related effect was a diminished response or lack of response by the test animals to an alerting stimulus during exposure. Although rats exposed to 50,000 ppm were generally non-responsive and rats exposed to 20,000 ppm had a diminished response during the first week of exposure of a 2-week study, most animals exhibited normal alerting responses during the second week. Any diminished response effect was completely reversible upon cessation of exposure.

A maximum concentration of 200,000 ppm of HFC-236fa in air was used for the cardiac sensitization tests using six male beagle dogs as the subjects. Adverse effects, including two fatalities, were observed at concentrations at or above 150,000 ppm (15%). There were no adverse cardiac effects observed at or below 100,000 ppm (10%). Based on all toxicity tests performed, HFC-236fa should pose no significant toxicity problems at concentrations up to 100,000 ppm in air.

Conclusions

Performance testing under simulated chiller operating conditions indicates that HFC-236fa is as good as or superior to CFC-114. Preliminary material compatibility tests reveal that certain elastomers may not be suitable for use with HFC-236fa and/or POE-type lubricants. However. several elastomers exhibited good behavior, and no thermal or chemical instability problems were uncovered with the refrigerant. HFC-236fa is considered "safe" to use in refrigeration systems based on its confirmed nonflammability and low toxicity. While its high chemical stability is advantageous from an engineering standpoint, it renders the compound resistant to removal from the atmosphere, thereby imparting a long atmospheric lifetime to the chemical. This, coupled with a relatively high infrared absorptivity, yields a relatively high global warming potential for the compound.

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The complete report, entitled "New Chemical Alternative for Ozone-Depleting Substances: HFC-236fa," (Order No. PB97-186 308; Cost: \$21.50, subject to change) will be available only from:

National Technical Information Service 5285 Port Royal Road Springfield, VA 22161 Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

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