Exhibit 11

Fluoroethers and Other Next-Generation Fluids

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ABSTRACT

Hydrofluorocarbons (HFCs) have been predominantly chosen as the zero ozone depletion potential (ODP) alternatives for chlorofluorocarbon (CFC) refrigerants. Since there might be other types of zero ODP compounds more preferable than HFCs as working fluids, several organizations have investigated fluorinated ethers, alcohols, amines, silicon, and sulfur compounds. Evaluation criteria included toxicity, nonflammability, stability, atmospheric lifetime, refrigeration performance, and manufacturing feasibility and cost. Although a few of the compounds have predicted refrigeration performance close to HFCs, at this stage of the evaluations none appears to have a balance of refrigerant fluid requirements to challenge HFCs.

INTRODUCTION

Hydrofluorocarbons (HFCs) have been chosen as the zero ozone depletion potential (ODP) alternatives for chlorofluorocarbon (CFC) refrigerants; however, there are several reasons to continue searching for other types of zero ODP compounds as working fluids: other compounds might have better refrigeration performance, lower atmospheric lifetimes, or lower manufacturing cost or some toxicity problem might have been discovered during testing of HFCs. These HFC alternative fluids have been termed "next-generation fluids" beyond HFCs

The fluids of this investigation have some fluorine content, as fluorine atoms impart characteristics of stability and nonflammability. Fluorinated ethers, alcohols, amines, silicon, and sulfur compounds were investigated. The following sections will include a literature review, description and listing of the compounds, and a summary of findings for toxicity, stability, atmospheric lifetimes, refrigeration performance, and manufacturing considerations. Each next-generation fluid mentioned in the text will be included in a master table of compounds (Table 1). References for each fluid and property value are included in the table.

BEFORE THE MONTREAL PROTOCOL

The earliest patent for fluorinated ethers as refrigerants was issued to Booth (1937), claiming halogenated methyl ether compounds in general and specifically 142aE ($CHClFOCH_2F$), 143E (CHF_2OCH_2F), and 133aE (CF_3OCClH_2).

Eiseman (1968) received a patent on a process for refrigeration with fluorinated ethers having the formula $CF_3OC_nH_mF_{(2n-m+1)}$ where n = 1-2 and m = 1-3. These compounds had a relatively higher heat of vaporization compared to commercial refrigerants such as R-12 (a CFC), R-23 (an HFC), and R-22 (an HCFC) and compared to perfluorinated ethers such as 116E (CF_3OCF_3). Compounds mentioned in the claims were 143aE (CF_3OCH_3), 227eaE ($CF_3OCHFCF_3$), 236faE ($CF_3OCH_2CF_3$), 125E (CF_3OCHF_2), and 227caE$\alpha\beta$ ($CF_3OCF_2CHF_2$).

Simons et al. (1977) received a patent in 1977 on aerosol applications of 134E (CHF_2OCHF_2), 116E, and 125E. In the patent text was information on biological testing of these compounds, concluding that 134E and 116E had less biological activity than 125E.

Powell (1985) received a patent with allowed claims for a high-temperature heat pump operating with hydrofluorocarbon R-245ca ($CHF_2CF_2CH_2F$), 254cbE$\beta\gamma$ ($CHF_2CF_2OCH_3$), or fluoroamines of several different formulae. One fluoroamine claimed was trifluoroethylamine, $NH_2(CH_2CF_3)$. Powell's objective

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was to provide stable fluids for heat pumps operating at high output temperatures.

The chlorofluorocarbon/ozone controversy began to receive more attention at this time, evidenced by the Vienna Convention for the Protection of the Ozone Layer finalized and adopted in March 1985 (UNEP 1985). Multinational discussions continued after the Vienna Convention, culminating in the signing of the Montreal Protocol in September 1987. The agreement limited production of specified chlorofluorocarbons (UNEP 1987).

Chlorofluorocarbon alternatives were researched in the mid-1970s after publication of Molina and Rowland's 1974 paper on ozone layer depletion potential by chlorofluorocarbons. Great effort was expended trying to validate the theory, and the only significant impact on CFCs was banning their use in "nonessential" aerosols in 1978 (*Federal Register* 1978) by the United States, followed by similar actions in Sweden, Norway, and Canada.

The 1985 Vienna Convention signaled renewed ozone depletion concern, and some researchers in industry, academic, and governmental laboratories quietly began reconsideration of CFC alternatives. One example (Smith 1992) was the United States Environmental Protection Agency (EPA) convening a group of experts in the spring of 1987 to assess the potential for finding suitable CFC alternatives. Recommendations included back-up replacements if the primary candidates were deemed unacceptable (Bare 1993).

AFTER THE MONTREAL PROTOCOL

Research into CFC alternatives became more active after the Montreal Protocol was signed in 1987 and even more emphasized after publication of data on ozone layer thinning in 1988 (*New York Times* 1988). The need to consider a wide range of alternatives including fluorinated ethers was expressed at the 1988 Workshop on Property Data Needs for Ozone-Safe Refrigerants at the National Institute of Standards and Technology in Gaithersburg, Maryland (Hill 1988). Accordingly, the scope of worldwide alternatives research included HCFC and HFC compounds and also other compounds, such as fluorinated ethers, alcohols, amines, sulfur- and silicon-containing compounds, hydrocarbons, ammonia, and carbon dioxide. The criteria of toxicity and nonflammability limited the application possibilities for hydrocarbons and ammonia.

In 1988 the EPA and EPRI funded a project with two universities to synthesize fluorinated propanes, butanes, and ethers, which might be CFC alternatives (Smith 1992). Of 34 compounds synthesized, 11 were the fluorinated ethers: 116E, 125E, 134E, 143E, 143aE, 227caE$\alpha\beta$ ($CF_3OCF_2CHF_2$), 218E2 ($CF_3OCF_2OCF_3$), c216E (cyclo-$CF_2CF_2OCF_2$-), c225eE$\alpha\beta$ (cyclo-$CHFCF_2OCF_2$-), c234fE$\alpha\beta$ (cyclo-$CH_2CF_2OCF_2$-), and c216E2 (cyclo-$CF_2OCF_2OCF_2$-). Two of these ethers were selected for further study: 143aE as a replacement for R-12 and 125E as a replacement for R-115.

William L. Kopko presented a paper at the 1989 American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) CFC Technology Conference at Gaithersburg, Maryland (Kopko 1989), in which he suggested several fluorinated ethers be investigated as CFC refrigerant alternatives: 134E as a substitute for R-114, 123bE (CHF_2OCFCl_2) as a substitute for R-113, and 143E as a substitute for R-11.

Vineyard and Sand of ORNL and Statt of the U.S. Department of Energy (DOE) in 1989 compiled an extensive list of potential refrigerant mixture compounds and properties (Vineyard et al. 1989), including the fluorinated ethers 116E, 125E, 143aE, 218E ($CF_3OCF_2CF_3$), 227eaE ($CF_3OCHFCF_3$), 134E, 236faE ($CF_3OCH_2CF_3$), 143E, 227caE$\alpha\beta$, and 254cbE$\alpha\beta$ ($CHF_2OCF_2CH_3$).

PATENT ACTIVITY

Research on CFC alternatives beyond HFCs and HCFCs was under way by refrigerant manufacturers in the late 1980s as evidenced by patent activity that became public information. O'Neill and Holdsworth (1990) received a patent on 134E as a refrigerant on October 9, 1990; the patent filing date was February 28, 1989. Fellows et al. (1990) received a patent on a mixture of R-22 and 125E on August 14, 1990; the patent had been filed on September 26, 1989. Several patent applications had the priority date of September 6, 1989 (Omure et al. 1991a, 1991b, 1991c, 1991d, 1991e), for fluorinated ethers, amines, and sulfur-containing compounds as refrigerants. Compounds included were 116E, 125E, CF_3SF_5, $C_2F_5NF_2$, and $(CF_3)_2NF$. Omure's company continued with patent applications having priority dates of August 30, 1990 (Teraoka et al. 1992) and August 31, 1990 (Hara et al. 1992; Inagaki et al. 1992) for additional CFC alternatives. These included CH_3-N=CH_2, $CF_2(NF)_2$, CHF_2NF_2, F_2S=O, FSSF, CF_3SH, CH_3SiH_2F, a series of C2-C4 fluoroethers, and a series of C2-C4 sulfur-containing compounds. Graphs of energy efficiency and capacity for these compounds vs. R-12, R-22, and R-502 were presented. Adcock (1993) received a patent on fluorinated oxetanes having the structures cyclo-CF_2CFHCF_2-O- and cyclo-$CF_2CH_2CF_2$-O-; his United States filing date was December 9, 1991. Patron and Sievert (1995) received a patent on two fluorinated ethers as refrigerants: 236caE and 236eaE$\beta\gamma$ having boiling points of 28.5°C and 23.2°C. Their filing date was January 25, 1993. There have been additional patents granted for refrigerant mixtures containing fluorinated ethers and other fluorinated compounds, and a selected few can be reviewed in Klug et al. (1997); and Powell et al. (1994).

RESEARCH INSTITUTE OF INNOVATIVE TECHNOLOGY FOR THE EARTH

The Japanese government provided money in 1990 for a five-year program targeted at fluorinated compounds containing oxygen, nitrogen, or silicon under the name Development of Advanced Refrigerants for Compression Heat Pumps (Sekiya and Misaki 1996). The money was administered by the New Energy Development Organization (NEDO), and the project was assigned to the Research Institute of Innovative Technology for the Earth (RITE). There was additional cooperative research with the National Institute of Materials and Chemicals Research (NIMC). Ten Japanese companies provided their personnel for research on this project at RITE. The project had many activities, including initial research for compound selection, synthesis, measurement of properties, evaluation of safety and environmental impact, and overall assessment of suitability.

About 500 compounds were considered, with 70 being synthesized for additional property characterization (Sekiya and Misaki 1996). A partial listing of the compounds being studied was provided by Suga (1993), which included 16 fluorinated alcohols and 28 fluorinated ethers. Only one of the fluorinated alcohols had a boiling point low enough to be considered for a refrigerant application. This was $(CF_3)_3COH$, having a boiling point of 45°C and being a potential replacement for R-113 (48°C boiling point). The 28 fluorinated ethers were all three-carbon linear compounds. The purpose of the listing was to illustrate the effect of molecular structure (location and number of hydrogen and fluorine atoms) on estimated atmospheric lifetimes.

Selected targeted compounds by RITE were reported by Misaki and Sekiya (1994). The article included 19 fluorinated ethers, five fluorinated compounds containing nitrogen, and five containing silicon. These compounds are listed in Table 1. All of the fluorinated ethers were of three or four carbon chain length. Initial data on toxicity, flammability, and atmospheric lifetimes were provided (see Table 1).

Three fluorinated ether compounds targeted by RITE were described by Misaki and Sekiya (1995). These were 245cbE$\beta\gamma$ ($CF_3CF_2OCH_3$), 347sE$\gamma\delta$ ($CF_3CF_2CF_2OCH_3$), and 347mmyE$\beta\gamma$ ($(CF_3)_2CFOCH_3$), having boiling points of 5.6°C, 34.2°C, and 29.4°C, respectively. Atmospheric lifetimes were five to six years for all three compounds. The paper had data on thermophysical properties, thermal stability, flammability, toxicity, and atmospheric lifetime of the compounds. Some of these data are in Table 1. Patent applications for these compounds were filed in Japan in March 1995 (Ito et al. 1996; Nagasaki et al. 1996; Suga et al. 1996).

As reported in two different publications (Sekiya and Misaki 1996; Misaki and Sekiya 1996), these three compounds have been selected for further study of toxicity, practical application tests, and improved synthesis procedures.

As an observation by the authors of this paper, the Japanese project was an impressive cooperative effort of researchers from many different companies and academic and governmental laboratories. In addition to the three compounds selected for further study as low environmental impact refrigerants, basic knowledge of molecular structure effects on properties was developed during the five-year research project. This knowledge will be useful in studies of future refrigerants.

INVESTIGATIONS FOR REFRIGERANT SUITABILITY—TOXICITY

Toxicity data in Table 1 have been taken from literature sources and from acute toxicity testing of selected fluorinated compounds. References for data sources are shown in parentheses for each compound. The "approximate lethal concentration" (ALC) is the exposure level at which deaths occur in a group of rats. NOEL is a "no observed effect level." A convulsant is defined as a central nervous system (CNS) stimulant usually observed as tremors. An anesthetic is defined as "CNS depression," observed as weakness, lethargy, dizziness, and/or sleepiness.

Data show there is wide variation in the toxicity of alternatives. Some have very low toxicity, such as 236eaE$\beta\gamma$, which has been extensively tested and is a commercial anesthetic. Some compounds, such as 143aE, 347mfcE$\alpha\beta$, and 356mffE$\beta\gamma$, have a high degree of acute toxicity. Different isomers, such as the 347 series fluoroethers, have varying toxicity. Although there are data from Simons et al. (1977) indicating some concern about 125E biological effects, more recent data indicates >100,000 ppm ALC (Haskell 1992-1996). The fluorosulphides tested showed low acute toxicity; however, these compounds were fully fluorinated. It is expected that the reactive fluorinated sulfur compounds $F_2S{=}O$ and FSSF would have toxic effects. There are very little toxicity data on the fluoroamine compounds.

Any promising next-generation refrigerant must undergo extensive toxicity testing. Future toxicity screening costs could possibly be reduced if more information were available on toxicity of functional groups present in the fluorinated ethers, amines, silicon, and sulfur compounds.

INVESTIGATIONS FOR REFRIGERANT SUITABILITY—THERMAL STABILITY

Thermal stability is a critical factor in determining long-term viability of a refrigerant. Data from the literature and from tests (DuPont 1992-1996) are included in Table 1. For the tests, 5g of refrigerant were placed in sealed tubes containing various combinations of lubricant, copper, aluminum, and steel coupons. Tubes were held at 175°C for two weeks, then checked for decomposition and metal attack. Stability tests also were run by RITE (Misaki and Sekiya 1994, 1996) at 120°C and 175°C.

According to O'Neill (1993), the stability of fluorinated ethers in contact with glass is unpredictable. He reported the following compounds unstable in glass: CH_2FOCH_3 (161E), CHF_2OCH_3 (152aE), and CHF_2OCH_2F (143E). CHF_2OCHF_2 (134E) was stable in glass after impurities such as 143E and 152aE were removed. O'Neill further reported that 134E reacts with polyglycol lubricants but not with polyolester lubricants.

Doerr et al. (1993) made an extensive study of $CF_3CH_2OCHF_2$ (245faE$\beta\gamma$), finding it to be thermally stable in the presence of metals but reacting with glass to produce high pressures. The reaction was accelerated in the presence of oxygen or peroxides.

Doerr speculated on stability of fluorinated ether compounds, observing that perfluoroethers and totally halogenated ethers usually are stable and concluding that fluoroether molecules, with either all fluorines or all hydrogens on the carbon attached to the oxygen, should offer the greatest stability. This seems to be the case for the three fluoroethers selected by RITE (Misaki and Sekiya 1996) for future study: $CF_3CF_2OCH_3$, $CF_3CF_2CF_2OCH_3$, and $(CF_3)_2CFOCH_3$. However, this generalization must be used with caution, as Sako et al. (1994) reported thermal decomposition of $CHF_2CF_2OCH_3$ during laboratory measurements of critical properties. The presence of unstable impurities also could be a factor.

Stability of the silicon, sulfur, and nitrogen-containing compounds in Table 1 is not as well defined. Generally, it is known that S-F and Si-H bonds can be reactive (DuPont 1997), so refrigerant stability tests must be run on any next-generation candidates having these atoms.

INVESTIGATIONS FOR REFRIGERANT SUITABILITY—TROPOSPHERIC LIFETIME

A major goal in studying next-generation alternatives is to determine whether other types of non-ozone-depleting molecules could have lower tropospheric lifetimes than HFCs and possibly less environmental impact. Unfortunately, obtaining experimental lifetime values is difficult (Cooper and Cunningham 1992) and can require sample quantities that are not always available.

Cooper and Cunningham (1992, 1993) used empirical structure-activity relationships to estimate tropospheric lifetimes of HFCs and fluorinated ethers containing two and three carbon atoms. As expected, they found shorter lifetimes as the number of hydrogen atoms increased. The effect of inserting an oxygen into an HFC molecule usually was toward shorter lifetimes, but not in all cases. Shorter lifetimes were calculated for molecules containing the structural units CH_3O-, CH_2FO-, -CH_2O-, and -CHFO-. Fluorinated ethers that did not contain at least one of those structural units were predicted to have longer lifetimes than the HFC counterparts. Two examples illustrate this: R-134/134E and R-125/125E. The HFC molecular formulae are CHF_2CHF_2 and CHF_2CF_3, respectively. The four structural units previously mentioned will not be present in 134E or 125E; therefore, these fluoroethers could have longer lifetimes than their HFC counterparts. This is the case, as the tropospheric lifetimes are 12 and 23 years respectively, for R-134 and 134E (Calm 1995) and 36 and 171 years for R-125 and 125E (DeMore 1994).

All available lifetime values are in Table 1. Few data are available for the other classes of next-generation compounds. RITE (Misaki and Sekiya 1994) estimated lifetimes of 0.1 to 3.1 years for four compounds containing nitrogen.

INVESTIGATIONS FOR REFRIGERANT SUITABILITY—FLAMMABILITY

The flammability classification of a compound has a significant impact on its potential as a refrigerant. The United States organizations Underwriters Laboratories and ASHRAE recently cooperated to clearly define criteria for testing and flammability definition of a refrigerant (Iracki 1997). This has included revisions to test procedure ASTM D-681 (1985). None of the compounds in this review have been subjected to the new test procedure; however, some guidelines can be used for initial screening of potential flammability. Previous flammability test data have shown the need for substantially more fluorine on a molecule than hydrogen for a compound to be nonflammable. The ratio F/(F+H) should be 0.67 0.70 or higher to ensure nonflammability. Flammability ratios are shown in Table 1. Molecules with ratios around 0.60 may or may not be flammable. Position of the fluorine and hydrogen on the molecule will have some effect on flammability. Fluorinated sulfur compounds were found to be surprisingly flammable. The perfluorinated molecules CF_3SCF_3 and $CF_3CF_2SCF_2CF_3$ were flammable at 100°C in ASTM D-681 test apparatus.

INVESTIGATIONS FOR REFRIGERANT SUITABILTY—REFRIGERANT CYCLE PERFORMANCE

Modeling refrigerant thermodynamic cycle performance gives an indication of whether a next-generation refrigerant can provide similar efficiency and capacity compared to CFCs, HCFCs, or HFCs. Figures 1, 2, and 3 show calculated relative refrigerant performance for potential nonflammable alternatives to R-22, R 134a, R-114, R-11, and R 123 at conditions of 130°F (54.4°C) condenser, 45°F (7.2°C) evaporator, 10°F (5.56°C) subcooling, and 65°F (18.3°C) return gas temperature. An equation of state model was used to predict cycle performance, with model coefficients estimated based on compound structure and boiling point. The data points in Figures 1, 2, and 3 show the following:

- None of the alternatives matched performance for R 22 or R-134a.
- Three nitrogen-containing compounds had modeled capacity values near R-22 and R-134a.
- As boiling points and molecular size increase, performance of alternative molecules is more comparable to existing refrigerants such as R-114 and R-123, resulting in more potential alternatives.
- Some of the potential R-114 alternatives for future study might be 134E, 245cbEβγ, and sulfur-containing compounds.

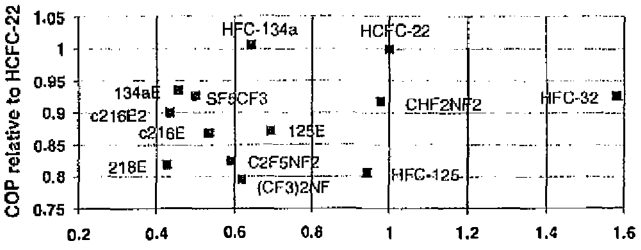

Figure 1 *Performance vs. R-22 and R-134a.*

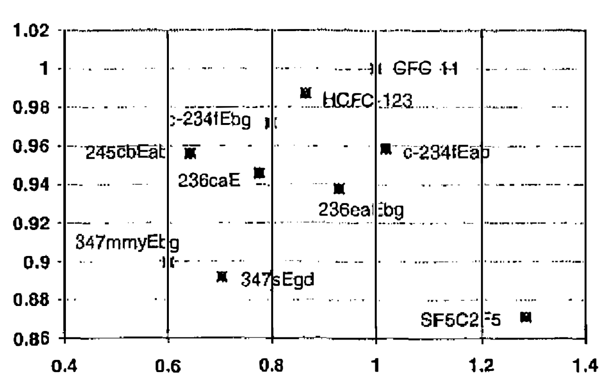

Figure 2 *Performance vs. R-11 and R-123.*

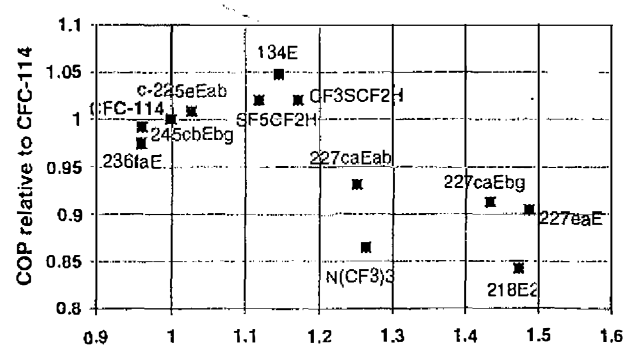

Figure 3 *Performance vs. R-114.*

- Some of the potential R-11 alternatives for future study might be 236eaEβγ, 347mmyEβγ, and 347sEγδ.
- Perfluorinated molecules such as 218E, 218E2, c216E, c216E2, SF_5CF_3, and $N(CF_3)_3$ performed poorly.

RITE performance data (Misaki and Sekiya 1996) were similar to estimates for 347mmyEβγ and 347sEγδ in Figure 2 and for 245cbEβγ in Figure 3. Performance data also were comparable to data reported by DeVotta et al. (1993a) for 134E, 218E2, c216E, and $N(CF_3)_3$, as well as 245caEαβ (DeVotta et al. 1993b). Several compounds, such as 143E, 143aE, 152E, CF_3SCF_3, and 245faEβγ were not included in the analysis due to toxicity, stability, or flammability concerns.

MANUFACTURING AND COST CONSIDERATIONS

Another critical factor in selecting a new alternative is the practicality and cost of manufacturing on a large scale. Sekiya and Misaki (1996) described synthesis routes to several types of alternatives in their paper. In studying fluoroethers, fluoroamines, and fluorinated sulphur compounds, several difficulties, such as synthesis routes, reaction rates, and compound purity, were encountered in simply synthesizing small quantities of compounds. In most cases, candidates under consideration were larger, more complex molecules requiring multistep synthesis routes. Compound costs increase as the number of fluorine and carbon atoms increase, and the refrigerants industry has already seen this in manufacturing costs of HFCs. There can be additional costs for adding oxygen, nitrogen, or sulphur atoms. As expected, initial manufacturing cost estimates for selected next-generation alternatives show higher costs than HFCs.

CONCLUSIONS

1. Several potential next-generation alternatives have been identified for future study, with relatively more candidates being available for R-11 and R-114

replacement studies than for R-134a and R-22 replacement.

2. An enormous amount of effort and expense is required for identifying, synthesizing, and running the many types of tests (stability, toxicity, tropospheric lifetime, properties, performance) to qualify a new refrigerant.

3. At this point in the studies, none of the next-generation candidates appears to have a balance of refrigerant fluid performance, safety/environmental properties, and manufacturing feasibility/cost to challenge HFCs.

4. There are opportunities to add to our understanding of fluorinated compound toxicity, stability, tropospheric lifetime, and flammability by relating these properties to molecular structure.

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