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REFRIGERANTS CONTAINING FLUOROIODOCARBONS (FICS)

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Abstract

This paper describes recent progress on a new group of refrigerants that appear likely to provide drop-in replacements for several CFCs, HCFCs, and HFCs. These new refrigerants are blends of fluoroiodocarbons (FICs) with hydrocarbons, ethers, HFCs, perfluorocarbons, and/or alkyl chlorides. FIC-based refrigerant blends appear to be nonflammable, non-ozone-depleting, near-azeotropic, compatible with mineral oil and other lubricants, and have very low acute toxicities. Extensive computer modeling and initial laboratory tests indicate that they provide acceptable energy efficiency and capacity with physical properties suitable for use in existing equipment. Recent results on performance, toxicity, thermal stability, materials compatibility, cost, and availability of FICs and FIC-containing blends are reviewed. Likely candidate FIC-based refrigerants to provide potential drop-in replacements for R-11, R-12, and R-22 are discussed.

Introduction

This paper addresses the status of some of the key issues regarding use of FIC containing refrigerants. Issues addressed include expected performance, reactivity of iodides, toxicity, flammability, thermal stability, materials compatibility, lubricant miscibility, electrical properties, leak detection, reclamation, cost and availability, as well as additional validation testing and approvals required. Environmental issues addressed include ozone-depletion potential (ODP), global warming potential (GWP), and volatile organic compound (VOC) issues (*e.g.*, smog formation). Current top candidate refrigerants are discussed and their calculated properties are presented.

FICs contain fluorine, iodine, and carbon. They are outstanding fire extinguishants, comparable to halons. They have negligible ODPs and GWPs because of their rapid photolysis in the troposphere. The best current estimate for the atmospheric lifetime of CF_3I is 1.15 days. FICs are not VOCs and do not contribute to smog formation. Several FICs have very low acute toxicity and highly desirable physical properties for refrigeration (e.g., trifluoroiodimethane, CF_3I, bp -22.5°C, and heptafluoro-1-iodopropane, $CF_3CF_2CF_2I$, also abbreviated 1-C_3F_7I, bp 40°C).

Although FICs have been described on rare occations in the chemical literature since the 1940s, their usage has been quite limited and they have been a relatively obscure group of chemicals. Their primariy application has been in chemical synthesis and in chemical lasers (Ref. 1).

Perhaps the major reason iodides have not been more fully investigated is that *in general* iodides are more reactive than bromides or chlorides. However, the FICs selected here have unusual stability and low toxicity because they have at least two fluorine atoms attached to the carbon bonded to the iodine atom. The presence of these fluorine atoms greatly stabilizes the molecules, making them hundreds to thousands of times less reactive and less toxic than would otherwise be the case.

In searching for alternative chemicals, the authors have consistently sought the "ideal" chemical for a given purpose, rather than "making do" with currently available products. About 11 million are chemicals reported in the literature, the vast majority of which cannot be purchased even in research quantities and have no toxicity data whatsoever reported. A shortage of information on a chemical of interest was not considered a fatal flaw. The amount of information known can be changed, whereas physical and environmental properties cannot. It is fortunate indeed that FICs are available in research quantities and have some toxicity data available. Previous papers have introduced FIC-containing refrigerants (Ref. 2), solvents (Ref. 3), and firefighting agents (Refs. 1, 4-6). An upcoming presentation will discuss their potential as high-R-value foam blowing agents (Ref. 7).

The authors have U.S. and international patents pending on a wide range of FIC technologies. The Ikon Corporation has been formed to promote testing, development, manufacture, and use of FIC

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technologies; provide know-how and technical support; license FIC technologies; and make available the benefits of FIC technologies worldwide. The Ikon™ trademark is pending.

Top Candidate Replacements

Tables 1 and 2 show calculated properties and performance of current refrigerants (for reference) and candidate FIC-containing replacements. Vapor-pressure curves of candidate replacements compared to reference refrigerants are shown in Figures 1 and 2.

Table 1. Calculated Properties of Selected Alternative Blends

BLEND NAME	COMPONENT NO.	COMPONENT NAME	VAPOR MOL FRACT. 40°F	LIQUID MOL FRACT. 40°F	VAPOR MOL FRACT. 100°F	LIQUID MOL FRACT. 100°F
R-11A	1	Diethyl Ether	.4699	.3999	.4635	.3998
	2	1-C_3F_7I	.5310	.6001	.5365	.6002
R-12C	1	HFC-152a	.4813	.4693	.4792	.4669
	2	CF_3I	.5192	.5307	.5208	.5331
R-22A	1	HFC-134a	.3062	.2996	.3049	.2951
	2	HFC-152a	.4043	.3997	.4013	.3987
	3	CF_3I	.2900	.3006	.2937	.3063

Table 2. Comparative Performance per Ton (40°F Evaporator, 100°F Condenser)

BLEND NAME	EVAP. PRESS. PSIA	COND. PRESS. PSIA	NET REFR. EFFECT, BTU/LB	MASS FLOW LBS/MIN	SUCTION GAS SPEC. VOL. Ft³/Lb	HORSE-POWER Per Ton	COMPR. CFM/Ton
R-11	7.02	23.5	68.1	2.94	5.43	0.62	15.95
Ikon-11A[a]	6.271	20.772	44.5	4.61	3.71	0.61	16.71
R-12	51.7	131.9	50.3	3.97	0.77	0.66	3.07
Ikon-12C[a]	49.3	135.7	81.8	2.47	1.17	0.66	2.88
R-22	83.2	210.6	68.9	2.90	0.66	0.68	1.91
Ikon-22A[a]	46.24	129.48	59.3	3.1	.887	0.7	2.99

a. Calculated values shown.

For R-11, a blend of diethyl ether and 1-iodoheptafluoropropane (Ikon-11A refrigerant) provides an efficient alternative. Similar efficiencies, volume flow rates and evaporator pressures indicate a potentially viable application. The higher mass flow rate and lower refrigerating effect are compensated by the higher vapor density and resulting compression efficiency.

For R-12, Ikon-12C refrigerant is a probable alternative. Composed of HFC-152a and CF_3I, it is almost a duplicate of the extrinsic properties of CFC-12. Comparable efficiency, capacity, and vapor pressure indicate a likely "drop-in" match. The polarity of the CF_3I and the high hydrogen content of the HFC-152a enable very high miscibility with mineral oil lubricants.

For R-22, Ikon-22A refrigerant provides an alternative worth considering. The higher vapor density and lower discharge pressures indicate that a possible application exists such that some property enhancements may compensate for compromises in refrigerating effect.

Expected Performance

Although they have desirable vapor pressures, FICs alone have undesirably low heats of vaporization. Current efforts have focused on identification of possible near-azeotropic or azeotropic blends with higher capacity refrigerants; some of which may be flammable in an unadulterated condition. Blending agents considered include hydrocarbons (*e.g.*, propane, cyclopropane, butane, pentane), ethers (*e.g.*, dimethyl ether, methyl ether, methyl trifluoromethyl ether, perfluorodimethyl ether), HFCs (*e.g.*, 23, 32, 125, 134a, 143a,152a, 227ea), perfluorocarbons (*e.g.*, perfluoromethane, perfluoroethane, perfluoropropane, perfluorobutane) and alkyl chlorides (*e.g.*, methyl chloride and ethyl chloride). Alkyl chlorides have not been ranked highly at this time because of their incompatibility with aluminum and less desirable toxicities.

Extensive computer modeling of thermodynamic properties and refrigeration performance of FIC-containing refrigerants has been carried out. Calculations based on the Soave-Redlich-Kwong equation of state indicate that candidate FIC-based refrigerants may be expected to have energy efficiencies and capacities comparable to CFCs. Improved refrigerating effect is achieved by using higher capacity flammable refrigerants (e.g., high-hydrogen-content HFCs, hydrocarbons, ethers) blended with FICs to make them nonflammable. Promising candidates are shown in Tables 1 and 2, with selected calculated properties.

Demonstration of Two Drop-in Replacements for R-12

Two FIC-containing blends have been successfully demonstrated as drop-in replacements for R-12 in a small domestic refrigerator. The refrigerator was instrumented to show temperature, pressure, and power consumption. The R-12 was evacuated and replaced with the experimental blends with no changes in the mineral oil lubricant or components. The first blend demonstrated consisted of CF_3I and HFC-152a (52:48 by moles, 75:25 by weight, called Ikon-12c refrigerant). This blend was run for over 2500 hours. The energy efficiency and capacity were equal to or slightly greater than those observed with R-12 and no operational problems were encountered. In another test, a blend of HFC-152a, CF_3I, and HFC-134a (30:40:30 by moles, called Ikon-12d) was placed in the refrigerator. This blend had slightly higher capacity than Ikon-12c, but also had a slightly higher discharge temperature. No operational difficulties were encountered.

Flammability

FICs have been shown by at least three research groups to be outstanding extinguishants, comparable to halons (Ref. 1). They inert hydrocarbons at about 3% concentration by volume of FIC in air. By adding sufficient FIC to a flammable refrigerant (one from which it does not fractionate), the mixture is rendered nonflammable at all points during its evaporation. The authors only use blends that will not fractionate and will not be flammable at any point during evaporation.

Toxicity

Acute studies of CF_3I have been conducted under the direction of Major Gary Jepson at Armstrong Labs at Wright-Patterson AFB. In these tests CF_3I was shown to have very low acute toxicity (Ref. 11). Acute toxicity testing of 1-C_3F_7I is underway. Published data indicates a 2-hour mice LC_{50} of more than 250,000 ppm (Ref. 12). To validate blends, a cardiotoxicity test on the blend is required, as well as acute toxicity data on all components (Ref. 13). A cardiotoxicity test is relatively fast and inexpensive. Current data indicate little or no tendency towards cardiac sensitization by CF_3I or 1-C_3F_7I.

Environmental Effects

The ODPs of FICs will be very close to zero. Because FICs undergo rapid photolysis in sunlight, they have very short atmospheric lifetimes and only a minute fraction of the material released at ground level will reach the stratosphere. The best current estimate for the atmospheric lifetime of CF_3I is 1.15 days (Ref. 14). The authors have estimated the ODPs of FICs at less than 1×10^{-15}, based on a transit time of 90 days. This calculation does not take account of any rapid mixing of part of the troposphere with the stratosphere, and more accurate calculations of ODP are underway at Lawrence Livermore National Labs (LLNL) and the National Oceanographic and Atmospheric Administration (NOAA). Additional measurements of rate constants for atmospheric reactions of FICs are planned.

The GWP of CF_3I has been determined to be about 5 times that of carbon dioxide, corresponding to about 10^{-5} relative to the standard CFC-11 = 1.0 (Ref. 14). This is an extremely low number, about 20,000 times lower than that of R-11 or R-12. The EPA has publicly stated that it will favor low-GWP materials.

Some refrigerants, such as hydrocarbons, are classified as VOCs. Tropospheric (ground-level) ozone is one of the most dangerous components of smog. Addition of iodine to smog at levels near 0.1 ppm has been shown to decrease levels of undesirable tropospheric ozone and carbon monoxide (Refs. 8-10). Thus FICs appear to be "anti-VOCs," and their release would be expected to improve air quality in urban areas. They appear to provide the best of all possible worlds; destroying "bad" tropospheric ozone while leaving "good" stratospheric ozone intact. Testing is underway to quantify "anti-VOC" effects of FICs.

Lubricant Miscibility

The fact that Ikon-12c was placed into service for 2500 hours in a domestic refrigerator with no change of the mineral oil lubricant or materials provides empirical evidence that it is miscible with mineral oil and does not adversely affect component materials. In published results of FIC solvent testing, the four- and six-carbon FICs were found to be miscible with all common organic solvents (Ref. 3). FICs are therefore expected to be compatible with all common lubricants including mineral oil, alkylbenzenes, polyalkylene glycols (PAGs), and polyol esters (POEs).

Thermal Stability

Thermal stability testing of pure CF_3I (without additives or stabilizers) by the New Mexico Engineering Research Institute (NMERI) and the National Institute for Standards and Technology (NIST) have indicated that it is stable at 80°, 110°, and 170°F for 60 days, and that it decomposes when maintained at 340°F for 30 days (Ref. 15). Intermediate temperature testing, and testing with stabilizers such as copper metal, is planned. Possible stabilizers for FICs identified to date include copper metal, silver metal, activated charcoal, and nitromethane. None of the conditions encountered in normal refrigeration applications would approach conditions leading to thermal degradation of the refrigerants proposed here with the exception of a motor burnout. In such cases, the refrigerant is generally reclaimed and/or replaced as a standard service procedure.

Leak Detection

Because of the properties of iodine, refrigerants containing FICs are expected to be very easy to detect by all common methods, including halide torches and electronic leak detectors. Small quantities of CF_3I may be added to dry nitrogen as a tracer gas for quick pressure testing/leak detection. Other methods that do not depend on the identity of the refrigerant, such as helium leak detection, visual inspection, standing vacuum test (static vacuum check), soap bubble test, and ultrasonic leak detection will still be useful.

Materials Compatibility

Reported compatibility information on selected CFCs, HCFCs, HFCs, halons, and FICs with polymers was compared, and this comparison indicates that FICs will have acceptable materials compatibility, comparable to that of CFCs, HFCs, HFCs, and halons (Refs. 3 and 16).

Ability to "Top-up" Systems

It is not anticipated that any compatibility problems will arise between Ikon-12c refrigerant and other CFC, HCFC, and HFC refrigerants or lubricants. They are expected to be miscible in all proportions and should not undergo any chemical reactions. Computer modeling shows that the performance should not be affected significantly. However, as discussed in the section on reclamation of used refrigerants, separation of mixed refrigerants for reclamation may be complicated slightly.

Cost and Availability

Chemicals that are custom-made in research quantities are of necessity much more expensive (by factors of 30 or more) than those made in bulk. One year ago CF_3I was, like other FICs, available only in research quantities and relatively expensive (about $600/lb). Today it is available from two pilot plants in quantities of up to several thousand pounds at $50-100/lb. The ultimate cost is expected to be $5-10/lb, and blends will be even less expensive. Availability in hundred thousand pound quantities is planned for mid-1994.

Reclamation of Used Refrigerant

It is expected that pure Ikon refrigerants can be recovered, recycled, and reclaimed like any other refrigerants. Ikon-12c refrigerant has been deliberately designed to have virtually identical vapor pressure to R-12 and not to separate into components on distillation. Because of these properties, Ikon-12c refrigerant may be difficult (but not impossible) to separate (*e.g.*, for reclamation) from R-12 once they are mixed. Separation may be achievable through membrane diffusion or selective adsorption (e.g., preparative gas chromatography). Because Ikon-12c refrigerant has virtually identical performance to R-12, there may be no advantage to separating them, and it is possible that virtually any mixture of the two will perform well. Another option is to keep "topping up" R-12 systems with Ikon-12c refrigerant over time until by dilution virtually all the R-12 is gone.

Approvals Required

Under the Significant New Alternatives Program (SNAP) a chemical can be submitted for EPA approval with acute toxicity data plus all available information on ODP and GWP. Once it achieves approval under the SNAP program it can be produced and sold while other tests (such as subchronic and chronic toxicity) are underway. Approval (or rejection) of a new chemical under the SNAP program takes about 6 months after submission. Testing, classification, and approval by both Underwriters Laboratories (UL) and the Air-Conditioning and Refrigeration Institute (ARI) will be sought provided market conditions warrant those actions.

Additional Validation Work Required

Additional validation work on FIC-based refrigerants is required in the areas of performance, lubricant miscibility, materials compatibility, thermal stability, and toxicity.

Conclusions

FIC-based refrigerants show promise as high-performance, nonflammable, nontoxic, environmentally safe drop-in replacement refrigerants. Much validation work remains to be done. We estimate that, if work proceeds promptly and with adequate support, SNAP approval and bulk production of FIC-containing refrigerants such as Ikon-12c could be achieved in about 12-24 months. The Ikon Corporation is seeking licensees to support further development and marketing of FIC refrigerants worldwide.

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Figures

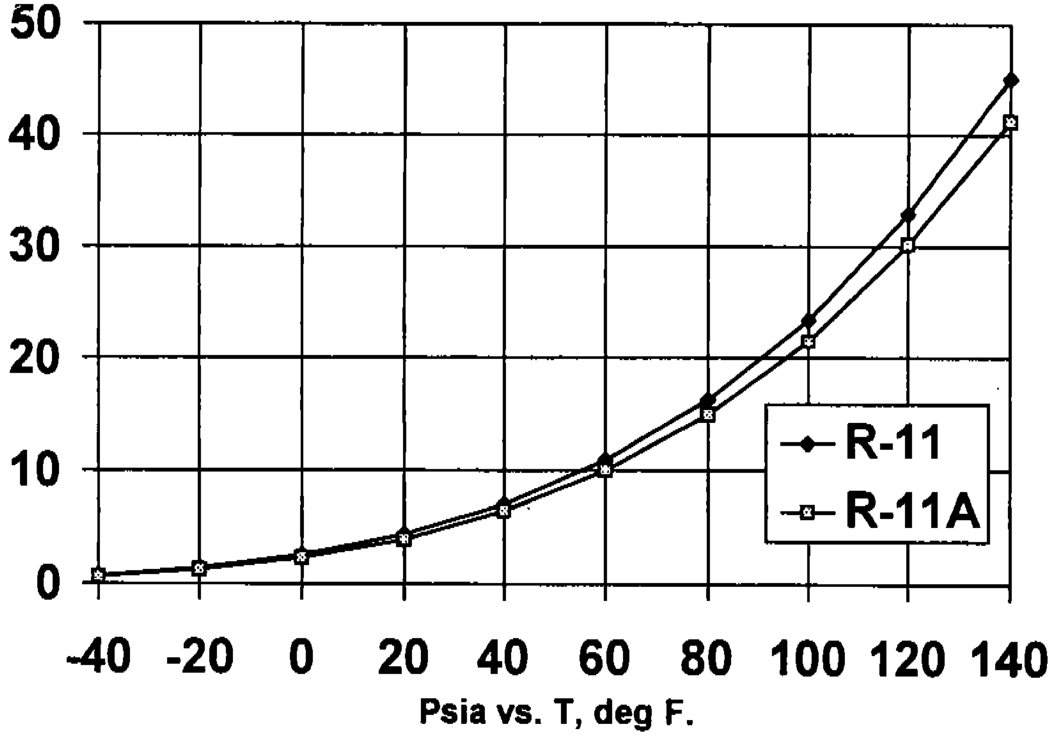

Figure 1. Vapor pressure curves of R-11 and Ikon-R11A refrigerants

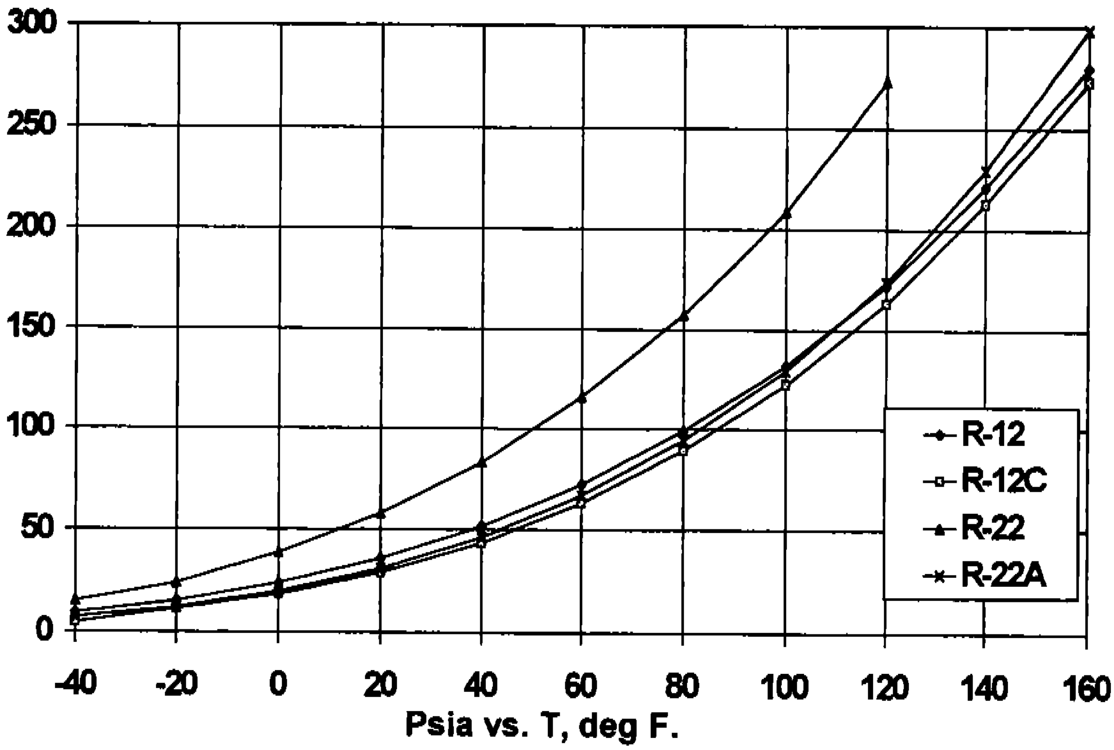

Figure 2. Vapor pressure curves of R-12, Ikon-12A, R-22, and Ikon-22A refrigerants