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Abstract

In response to international protocol agreements and national regulatory actions promoted by the increasing concern for ozone depletion and the greenhouse effect, R134a has emerged as a leading candidate for R12 substitution in automotive air conditioners, centrifugal chillers and residential refrigerators and freezers. Chemical companies are engaged in extensive developments to establish cost-effective processes for producing R134a of the required purity and toxicological testing is underway to evaluate physiological safety. This paper will consider compressor and refrigeration system questions that need to be addressed before R134a is accepted as a commercially viable substitute for R12. The following major questions will be discussed:

(A) Refrigerant R134a quality, the likely contaminants and their significance

(B) Physical, chemical and transport properties; what is needed and why

(C) Solution behavior with lubricants including solubility, viscosity and low temperature properties such as flow point

(D) R134a chemical compatibility with lubricants and materials of construction

(E) Effect on elastomers

(F) Permeation of R134a through typical seal and gasket materials

(G) Solubility of water and hydrolytic stability

Important gaps in published information about R134a refrigeration system applications will be identified. Sharing available information from knowledgeable sources such as refrigerant suppliers and equipment manufacturers can reduce the risk inherent in the introduction of a new refrigerant.

LE R134a UN PRODUIT DE REMPLACEMENT DU R12

RESUME : Comme suite aux accords du protocole international et aux mesures réglementaires nationales en raison de l'inquiétude croissante au sujet de l'appauvrissement en ozone et de l'effet de serre, le R134a est apparu comme le principal candidat au remplacement du R12 dans les conditionneurs d'air d'automobiles, les refroidisseurs à compresseur centrifuge et les réfrigérateurs et congélateurs ménagers. Des sociétés chimiques ont entrepris des actions considérables pour mettre au point des procédés rentables de production de R134a avec la pureté nécessaire et des essais toxicologiques sont en cours pour évaluer sa sécurité physiologique. Ce rapport considérera les questions concernant le compresseur et le système frigorifique auxquelles il faut répondre avant que le R134a devienne un substitut commercialisable du R12. Les principales questions suivantes seront examinées :

(A) Qualité du R134a, contaminants possibles et leur importance

(B) Propriétés physiques, chimiques et de transport ; ce qui est nécessaire et pourquoi

(C) Comportement des solutions avec les lubrifiants, notamment la solubilité, la viscosité et les propriétés à basse température telles que le point de fluage

(D) Comptabilité chimique avec les lubrifiants et les matériaux de construction

(E) Effet sur les élastomères

(F) Perméation de R134a à travers les matériaux classiques de joints et de garnitures d'étanchéité

(G) Solubilité dans l'eau et stabilité hydrolytique

D'importantes lacunes dans la littérature sur les applications des systèmes frigorifiques à R134a seront identifiées. L'échange de renseignements disponibles en provenance de sources bien informées telles que les fournisseurs de frigorigènes et les constructeurs peut réduire le risque inhérent à l'introduction d'un nouveau frigorigène.

CF134a AS A SUBSTITUTE REFRIGERANT FOR CFC12

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INTRODUCTION

The recent Montreal Protocol on Substances That Deplete The Ozone Layer (1) resulted in proposed ruling by the United States Environmental Protection Agency limiting the manufacture of CFCs 11, 12, 113, 114 and 115 to 1986 production levels. The production freeze is to be followed by further reduction in quantities of these refrigerants produced in 1993 and 1998. In March of this year a major producer of CFCs announced that it planned an orderly transition to the total phase-out of fully halogenated CFC production and that R&D efforts would concentrate on the development of environmentally acceptable new refrigerants (2). CFC12, one of the target materials, is widely used as refrigerant in a variety of applications including home refrigerators and freezers (7%), automotive air conditioning (39%), centrifugal and reciprocal chillers (6%) as well as for food freezing (3%) and miscellaneous foam blowing and solvent (45%) uses. Total 1986 usage has been estimated as 318 million pounds.

The leading candidate for CFC12 substitution is CF134a, a material that contains no ozone depleting chlorine. Its properties are strikingly similar to those of CFC12. Extensive research and development is underway to establish cost-effective processes for producing CF134a of the required purity and to validate toxicological acceptability. In a parallel effort, equipment manufacturers are engaged in evaluating performance of their products when CF134a is substituted for CFC12. Notwithstanding this high level of interest, technical information concerning CF134a as a working fluid is incomplete and not widely disseminated. The primary purpose of this paper is to review some of the published and unpublished information about CF134a as vapor compression refrigerant and to highlight technology gaps that require attention. Although this report emphasizes U.S. production and application of these refrigerants, the issues are of a global nature and resolution of the problem will require unprecedented international cooperation.

WHY CF134a ??

Major factors responsible for the selection of CF134a as the leading substitute for CFC12 are its benign atmospheric behavior (3,4) and thermodynamic properties that are similar to those of CFC12. The structure of CF134a (CF3CH2F or 1,1,1,2 tetrafluoroethane) has been studied in detail to determine bond angles, bond lengths, bond strength, thermal stability and dipole moment (5-8). As a vapor compression refrigerant, a 1971 patent 9) disclosed an azeotrope with CFC12 which was proposed for use in automotive air conditioning systems. Interest in CF134a developed rapidly as concerns about ozone depletion became widespread in the mid-seventies.

At a January 1988 conference in Washington D.C. on substitutes and alternatives to CFCs and Halons (10), major refrigerant producers reviewed status of CF134a production process development and forecast future availability. At present, a two step synthesis is required followed by complex separations to attain purity levels required for refrigeration applications. Test samples of CF134a available for evaluation purposes have varied in purity. The most recent samples available to the writer have been determined as 99.7 mole percent CF134a. Physical property information available from different refrigerant producers of CF134a are generally in good agreement. P-V-T data of engineering quality have been determined, they are available on a private basis from refrigerant producers and are soon to be published. A study to determine thermodynamic properties of CF134a more accurately at the Bureau of Standards has been approved and should be underway at the time of this meeting.

Although the results of initial biological testing of CF134a have been favorable,approval for general use as a refrigerant will require extensive animal tests to be conducted over a five year period. Funding for this evaluation work is being provided on a cost sharing basis by refrigerant producers from the United States and abroad.

With the above as background information, we will now address the main topic of this paper; properties and characteristics of CF134a that are of special interest and significance for vapor compression refrigeration system applications.

REFRIGERANT SYSTEM CHEMISTRY

Utilization of a new refrigerant in commercial products requires information about material compatibility and lubricant-refrigerant mixture properties. For widely used refrigerants, this information is generally known and readily available in references such as the ASHRAE Handbook Systems Volume chapters on Refrigerant System Chemistry and Lubricants In Refrigerant Systems (11). Chemical stability and compatibility of the refrigerant with the lubricant and with other materials to which it is exposed is of primary importance. The composition and structure of the CF134a molecule provides important clues concerning its chemical behavior. A high degree of chemical stability is predicted from the absence of C-Cl bonds, which are known to be weaker than C-F bonds. This predicted stability is borne out by shock wave decomposition studies (12) and by extensive sealed tube accelerated aging studies with a variety of material combinations investigated by the writer. The CF3CH2F molecule is relatively polar compared to CFC12 and CFC22 as revealed by the dipole moments for these substances; CF134a = 1.82 Debye Units (13), CFC22 = 1.40 DU, CFC12 = 0.51 DU (14). The higher polarity of CF134a contributes to low solubility in non-polar lubricants such as the mineral oils and synthetic hydrocarbons presently used as refrigeration compressor lubricants.

CF134a properties, along with those of the selected lubricant, determine suitability of the mixture as a refrigerant system working fluid. Stability, material compatibility, solubility, viscosity, lubricity and low temperature behavior are important considerations. Selected working fluid properties are highlighted in the following discussion to encourage other investigators to share in building the necessary background.

Chemical Stability of CF134a

Chemical stability includes consideration of thermal stability in the absence and presence of other materials such as lubricants, metals of construction, polymers used as motor insulation, seals and gaskets and refrigeration drier materials. Shock tube studies (12) revealed that thermal decomposition ranged from 0.1% at 1170K to 46% at 1410K. Between 1170K and 1300K the major reaction product was CF2CHF, resulting from the elimination of HF. Above 1300K, other products were observed in increasing amounts with increasing temperature. The significant observation is that temperatures well above those realized in refrigeration compressors and systems are required for thermal decomposition of CF134a.

We have conducted many glass sealed tube tests at accelerated conditions in the presence of metals (steel, copper, aluminum) and with a variety of mineral and synthetic oils. Gas samples from sealed tubes after aging times as long as 21 days at 175C were analyzed by gas chromatography with thermal conductivity detector and by infrared analysis in 6 and 10 centimeter path length cells. No indications of CF134a decomposition or reaction were observed.

Experiments with a variety of lubricating oils were carried out in an attempt to define the CF134a/lubricant chemistry, as has been done with CFC12 and CFC22. Although no refrigerant reaction products were detected, significant decomposition of some of the lubricants was observed. Additional studies at more severe conditions and perhaps with other metal or inorganic catalysts would be of interest but chemical stability of CF134a is not likely to be a limiting consideration in refrigeration applications.

One negative consequence of the high stability of CF134a is the lack of response to the gas by electronic leak detectors. Functioning of these instruments is based on ionization of the halocarbon between charged electrodes and it would appear that higher energy levels are required to break the C-F bonds. Lack of a reliable detection method for low concentrations of CF134a must be resolved to avoid serious problems for producers, equipment manufacturers and service engineers.

Mutual Solubility With Lubricants

Mutual solubility of refrigerant and lubricant over the entire range of temperature, pressure and composition is considered a positive factor, if not a necessity, by most refrigeration engineers. Solubility helps to insure that lubricant is supplied to compressor bearings and enhances oil return from the refrigeration system. CFC12 is soluble in all proportions with mineral lubricating oils and the equipment using this refrigerant, be it refrigerators, freezers, automotive air conditioners or large centrifugal chillers has been design to operate with a one phase working fluid. It is well known that CFC22 is considerably less soluble in mineral base lubricating oils and that under saturated conditions, two liquid phases coexist for many of the lubricants. The critical solution temperature; that is, the temperature above which all compositions merge into a single liquid phase, can be quite different from one lubricant to another. The degree of solubility depends on composition of the lubricant including type of hydrocarbon, molecular weight and molecular weight distribution. Many of the air conditioners using CFC22 operate over a temperature range where immiscibility can occur in some part of the system. However, it is important to recognize that phase separation represents limited mutual solubility and that even with phase separation, each liquid phase can contain substantial quantities of both components and thereby support basic functional requirements such as lubrication and oil return.

Our extensive solubility investigations of CF134a and refrigeration grade mineral oils confirm informal reports by others that they are mutually insoluble, independent of the composition or viscosity of the mineral oil. Insolubility is also observed for CF134a - alkylbenzene mixtures,; further demonstration of the unusual solubility behavior of this refrigerant since alkylbenzenes are known to be good solvents for CFC22. The term insoluble is used to convey the observation that the degree of solubility approaches zero. Mixtures of mineral oil and CF134a can be characterized as totally immiscible even at temperatures as high as 65C (150F). Although equipment performance consequences of this insolubility are not yet fully known, it is unlikely that they will be favorable. Successful application of R134a as "drop-in" substitute for CFC12 requires the development of new or modified lubricants, beyond those presently considered for this application. The alternative to developing a new lubricant for CF134a is hardware design modification and extensive engineering evauation and field testing to prove out new designs using present refrigeration lubricants. The inherent high cost and high risk associated with this option lend favor to continued intensive search for a new lubricating fluid that is soluble in CF134a and meets all the other refrigeration lubricant requirements; excellent stability and lubricity, compatibility with elastomers and/or polymers and outstanding low temperature properties. Since many different chemical fluids are available or can be synthesized, a large number of candidates are available for evaluation. Recent refrigeration oil trends are toward products formulated to meet special requirements of refrigeration compressors and systems (15). Thus it is not unlikely that the special needs imposed by the use of CF134a will simply accelerate the development of "tailored" fluids for this application.

Although we are not prepared to discuss results for specific synthetic lubricants, some general information can be shared. Solubility of CF134a in synthetic lubricants varies from soluble to partially soluble to insoluble. Although solution theory is not sufficiently advanced to predict solubility from component structural and property information for these complex mixtures, some general guidelines are emerging. Certain of the more popular candidate synthetic lubricants exhibit unconventional solubility behavior, including decreasing solubility with increasing temperature. This unconventional solubility behavior can lead to serious difficulties in management of the working fluid in refrigeration systems operating over a wide range of temperature, pressure and compressor parameters. Other synthetic lubricants evaluated to date do not exhibit this solubility inversion, but each has one or several properties that will need to be improved before extensive compressor evaluation is warranted. Cost considerations will undoutedly enter into the selection process since some of the better candidates are much more expensive than the current refrigeration lubricants.

Lubricity

The primary function of the lubricant in vapor compression systems is to lubricate compressor bearings over a broad range of operating conditions and throughout many cycles of compressor start-up. When a new refrigerant such as CF134a is introduced, it is important to anticipate differences in performance arising from the effects of the new refrigerant on properties of the oil/refrigerant mixture. Two types of lubrication influence bearing performance; a) boundary lubrication occuring during compressor start-up or as experienced in reciprocal motion and b) hydrodynamic lubrication where a fluid film separates bearing elements in continuous motion. To meet boundary lubrication requirements, refrigeration lubricants should exceed 525 to 550 pounds in failure load when evaluated by Falex test according to ASTM D 3233-73 (16). For lubricants that do not meet this criterion, extreme pressure additives in 1 to 2% volume concentration are often blended into the base oil. The contribution of the refrigerant to boundary lubrication is recognized, if not well defined. In the writer's experience, replicate failure load tests conducted with refrigerant saturated lubricant are more consistent than results for the neat lubricant. Failure loads of lubricants saturated with CFC22 and CFC12 are significantly higher than those for the lubricant without refrigerant (17). This improvement may result from the exclusion of oxygen and moisture or from refrigerant decomposition at local hot spots from metal contact between bearing surfaces. Metal halide solid films, such as iron chloride, formed at local hot spots can function effectively as solid lubricants. If the refrigerant is CF134a rather than CFC12 or CFC22, the greater stability may prevent metal halide formation and thus enhance boundary lubrication problems. Falex failure load determinations with a variety of experimental lubricants saturated with CF134a have, in fact, produced results ranging from acceptable to outstanding. Compressor tests with CF134a will be required to verify correlation with these bench test results.

Effectiveness of hydrodynamic lubrication depends on viscosity of the working fluid. Minimum fluid viscosities of 5 to 10 centipoise at the highest compressor bearing temperatures are required to assure a margin of safety (18). When halocarbon refrigerants are soluble in the lubricant, viscosity of the mixture is reduced, thereby compounding the effect of high temperature. With CF134a as refrigerant, viscosity, and hence hydrodynamic lubrication, will be determined by nature of the lubricant as well as compressor design. If the lubricant is insoluble in CF134a, no contribution to viscosity reduction can occur. If a soluble lubricant is used, hydrodynamic lubrication will more nearly resemble the behavior of CFC12/lubricant working solutions. Very little information is available on solubilities and viscosities of CF134a/lubricant mixtures. Studies to correct this deficiency should be initiated once leading candidate lubricants have been identified.

SUMMARY

Commercial application of a new refrigerant requires knowledge of its thermodynamic, transport and refrigeration system properties. This paper has reviewed some of the basic refrigeration system properties of CF134a; stability, solubility and lubricity. Clearly, much additional information that is system-specific will need to be developed for each major application; automotive, home appliance or centrifugal chillers. For example, in automotive applications, seals, gaskets and permeation problems must be addressed. Compressor design in terms of materials, compressor speeds and temperatures are different for each application. Refrigerator and freezer products are essentially free of leakage problems but are sensitive to compatibility with hermetic motor insulation materials and driers. Factory sealed units for appliances are designed to operate reliably for more than 15 years and this can only be achieved if the material combinations used are thermally stable and non-reactive. The compatibility of CF134a with refrigeration drier materials such as molecular sieves and aluminas and the solubility and distribution of moisture with this refrigerant are important consideration for all of these systems.

A great deal of additional technology is required before successful commercialization of CF134a will be realized including refrigerant process development, toxicological validation, lubricant development, material screening tests and refrigeration product engineering. These tasks must be addressed with parallel efforts if the ambitious target dates for phasing-out CFC12 are to be met. Sharing of basic information will avoid duplication of expensive and time-consuming work but the process for such collaboration has not yet been established.

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