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Research Update: ARTI Materials Compatibility and Lubricant Research (MCLR) Program

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ABSTRACT

Since September 1991, the Air-Conditioning and Refrigeration Technology Institute (ARTI) has been conducting materials compatibility and lubricants research on CFC and HCFC refrigerant alternatives. This work has been supported by a grant from the U.S. Department of Energy with co-funding from the Air-Conditioning and Refrigeration Institute (ARI). During the first two years of this program, ARTI has subcontracted and managed sixteen research projects totaling over $4 million. This research has included materials compatibility tests, refrigerant-lubricant interaction studies, measurement of thermophysical properties, and development of accelerated test methods. This paper summarizes results to date and discusses plans for future research for the Materials Compatibility and Lubricants Research (MCLR) program.

INTRODUCTION

Current commercial air-conditioning and refrigeration equipment generally operate reliably for 30 years or more, while home refrigerators and freezers are generally reliable for 20 years or more. This high reliability is the result of properly designed and manufactured products using materials that have proven compatibility with refrigerants and lubricants whose properties are well understood. These refrigerants, which were developed over 40 years ago, are stable, have good thermodynamic properties, low toxicity and are non-flammable. However, they are chlorofluorocarbons (CFCs). The inherent stability of CFCs allow leaked quantities to rise and linger in the atmosphere for many years and eventually attack the Earth's stratospheric ozone layer. Because of the long term health and environmental risks associated with this, international treaties have mandated the phaseout of CFC refrigerants. Newer refrigerant fluids, namely hydrochlorofluorocarbons (HCFCs), are less stable in the atmosphere and deplete ozone at a much lower rate. Because of their good thermodynamic properties and greatly reduced ozone depleting potential, HCFCs were seen as the interim alternatives to CFC refrigerants. However since these fluids still deplete the ozone layer, they also have been scheduled to be phased out of use as refrigerants. Hydrofluorocarbons (HFCs) which have a zero ozone depleting potential are seen as a likely long-term solution as alternative refrigerants.

As manufacturers began investigating these alternative fluids as refrigerants, they found that information was lacking on the thermophysical properties, materials compatibilities, and lubricant interactions with the new refrigerants. Faced with a relatively short lead time before these phaseouts, equipment manufacturers quickly realized that they, on their own, did not have enough time or resources to adequately evaluate and test these alternatives to ensure reliable products.

In 1989 the Air-Conditioning and Refrigeration Institute (ARI) addressed this challenge head on and formed the Materials Compatibility and Lubricants Research (MCLR) Advisory Committee. The purpose of this committee was to define and monitor research which was needed to accelerate the introduction of alternative refrigerants. The MCLR Advisory Committee was made up of representatives from equipment manufacturers, chemical producers, and government agencies. Members were selected based on their knowledge and experience with refrigerants, lubricants and materials compatibility. ARI and the MCLR Advisory Committee succeeded in gaining a research grant from the U.S. Department of Energy which was awarded in September 1991. ARI established the Air-Conditioning and Refrigeration Technology Institute (ARTI) as an independent corporation to receive the grant and to manage the research with the advice of the MCLR Advisory Committee. On 30 September 1992, the grant was amended and additional funding was awarded to support Phase II of the MCLR program. In September 1993, the Department of Energy issued a letter of intent to approve ARTI's request for additional funding to support Phase III of the program. With final approval of Phase III the cumulative budget of the MCLR program will reach $6.45 million.

Most of the Phase I research projects have been completed. Phase II projects have been underway since October 1992. Several Phase III research projects are ready to begin as soon as the Department of Energy awards funds for this phase. Planning is currently underway to define future research needs.

Results from all MCLR research projects are available to the public. Technical reports may be obtained through the National Technical Information Service (NTIS) of the U.S. Commerce Department and also through the ARTI Refrigerant Database administrator.

PHASE I RESEARCH

Phase I research focused on measuring thermophysical properties, studying refrigerant-lubricant interactions and determining materials compatibility of alternative refrigerants and lubricants. Projects evaluated ten alternative refrigerants (HCFC-22, HCFC-123, HCFC-124, HCFC-142b, HFC-32, HFC-125, HFC-134, HFC-134a, HFC-143a and HFC-152a) and a number of lubricants including mineral oil, alkylbenzene, polyglycols and polyolesters.

Thermophysical Properties

The Thermophysics Division of the National Institute of Standards and Technology has completed measurements and correlations of HFC-32, HCFC-123, HCFC-124 and HFC-125 [Kayser, 1993]. This data filled gaps that existed in data sets. The data were fitted to the Carnahan-Starling-DeSantis-Morrison (CSDM) and the modified Benedict-Webb-Rubin (MBWR) equations of state. The data was integrated into the NIST REFPROP program which is widely used in computer simulations to predict refrigerant thermophysical properties which can be used to measure cycle performance in existing and new equipment designs.

Theoretical Evaluations of R-22 and R-502 Alternatives

This project provided performance evaluations of nine HCFC-22 and three R-502 alternatives using the computer model, CYCLE-11. The computer simulations yielded the following relative COP for the test refrigerants [Domanski & Didion, 1993]:

Refrigerant (Composition: Wt %)	COP Relative to Baseline Refrigerant	Relative Volumetric Capacity
HCFC-22 Alternatives:		
R32/125 (60/40)	0.97	1.55
R32/125/134a/290 (20/55/20/5)	0.93	1.18
R32/125/134a (10/70/20)	0.93	1.04
R290	0.94	0.83
R32/125/134a (30/10/60)	0.98	0.98
R32/227ea (35/65)	0.84	1.03
R32/134a (30/70)	0.99	0.93
R32/134a (25/75)	0.99	0.88
R134a	0.98	0.59
R-502 Alternatives:		
R32/125/143a (10/45/45)	0.97	1.13
R125/143a (45/55)	0.93	0.94
R125/143a/134a (44/52/4)	0.93	0.92

Chemical and Thermal Stability of Refrigerants and Lubricants

Twenty-three refrigerant-lubricant combinations were tested for stability in sealed tube tests. Results indicted that HFC-32, HFC-125, HFC-134a and HFC-143a with polyolester lubricants were all as stable as HCFC-22 with mineral oil after thermal aging at 160°C (320°F) for 14 days. It was also noted that polyolester and polyglycol lubricants exhibited increased acid numbers and evidence of decomposition after aging at temperatures of 200°C (320°F) [Huttenlocher, 1992].

Miscibility of Lubricants in Refrigerants

Ten refrigerants were tested with a number of lubricants at eight refrigerant-lubricant concentrations over temperature ranges from -50 to 90°C (-58 to 194°F) for most of the refrigerants and from -50 to 60°C for high pressure refrigerants. Each of the tested refrigerants were miscible with at least one test lubricant, except for HFC-143a, which was partially miscible with each of the lubricants. [Pate et al, 1993].

Compatibility with Motor Materials

Twenty-four hermetic motor materials were tested for compatibility with eleven refrigerants and seventeen refrigerant-lubricant mixtures. Physical properties, such as dielectric strength, burnout resistance, bond strength, beak load strength and weight change, were evaluated before and after exposure to the test fluids. Results indicated that materials currently used in hermetic motors were as least as compatible with polyolester lubricants and HFC-32, HFC-125, HFC-134a and HFC-143a as they were with HCFC-22 and mineral oil [Doerr et al, 1993].

Compatibility with Elastomers

Ninety-five elastomeric materials were tested for compatibility with ten refrigerants and seven lubricants. Twenty-five of these elastomers were further tested for compatibility with seventeen refrigerant-lubricant mixtures. Elastomer swelling and tensile strength were used to determine compatibility. Results of testing indicated that most of the commercial elastomer test materials were compatible with HFC-32, HFC-125, HFC-134a and HFC-143a with polyolester lubricants [Hamed et al, 1993].

Compatibility with Engineering Plastics

Twenty-three engineering plastics were tested for compatibility with ten refrigerants and seven lubricants. Dimensional changes, weight changes and tensile strength were used as measures of performance. Results indicated that all of the test plastics were degraded to some degree by the various refrigerants or lubricants. In general the HFC test refrigerants affected the materials less than the HCFC refrigerants. ABS, polypheylene oxide and polycarbonate plastics were incompatible with most of the test refrigerants [Cavestri et al, 1993].

PHASE II RESEARCH

Phase II research focused on additional compatibility testing and the development accelerated test methods.

Compatibility with Desiccants

This project just began in August, 1993. It will examine the compatibility of several standard desiccant materials with thirteen refrigerant-lubricant mixtures.

Electrohydrodynamic (EHD) Enhancement of Pool and In-Tube Boiling of Alternative Refrigerants

The objectives of this project were to construct a test rig for measuring improvements in boiling and condensation heat transfer performance when utilizing EHD enhancement technologies and to conduct limited EHD enhancement experiments with HCFC-123 and

HFC-134a. The experiments showed that for pool boiling, higher applied electric potentials resulted in higher EHD-induced effects that promoted refrigerant bubble break-up and increased bubble departure speeds - collectively leading to higher transfer rates. For pool-boiling with HCFC-123 and HFC-134a, heat transfer rates for EHD enhancements runs increased from five to eight fold, depending on the presence or absence of lubricant and the use of mesh or straight-wire electrodes [Ohadi et al, 1993].

Accelerated Screening Methods for Determining Chemical and Thermal Stability

The objective of this project is to develop a new method for determining the chemical and thermal stability of refrigerant-lubricant mixtures. The current method for determining CFC refrigerant stability is ASHRAE 97-1989 - sealed tube test. This test method measures breakdown products using a relatively simple chemical analysis. This technique was good for CFC refrigerants whose breakdown products were well known. However, HFC breakdown products are more complicated and require a more elaborate chemical analysis. A new method under investigation uses *in situ* measurement of the electrical conductivity of the refrigerant-lubricant mixture to detect decomposition. Initial results of tests with this method show good correlation with other stability measurement techniques. This new method may enable researchers to determine stability within a few hours of testing, without extensive chemical analysis [Kauffman, 1993].

Accelerated Test Methods for Predicting The Life of Motor Materials

The objective of this project is to develop a method for determining the life of motor insulating materials and varnishes used in hermetic motors using alternative refrigerants and lubricants. Several degradation models and test procedures were investigated and a new test method was proposed which combines the advantages of the IEEE motorette test and the plug reversal test into a single more practical method. The new test method utilizes a stator simulator unit which consists of a laminated steel core containing two coil winding separated by phase-to-phase insulation and slot wedge insulating materials. The stator simulation unit is placed in an autoclave with a refrigerant lubricant mixture. Plug-reversal in-rush currents are simulated by intermittent 30 Amp AC pulses applied to the lead wires of the stator simulation unit. The test subjects the stator simulation unit to the electrical, thermal and magnetic forces similar to those in the plug-reversal test, using a much smaller and more reliable test rig [Ellis and Ferguson, 1993].

Accelerated Screening Methods for Predicting Lubricant Performance

The objective of this project is to devise a bench type device for conducting lubricity tests that simulates conditions in refrigeration and air-conditioning compressors. Current methods for lubricity testing are limited since they do not closely simulate the wear contacts in real systems and are not normally tested in a pressurized refrigerant-lubricant environment. This project will determine if lubricant performance data obtained from a high pressure tribometer more accurately predict tribological behavior of critical contacts in compressors than the current test methods using simpler equipment [Cusano, 1993].

PHASE III RESEARCH

Phase III research is focusing on retrofit and long term compatibility issues, refrigerant flammability test methods and procedures, and issues concerning the fractionation of zeotropic refrigerant blends. Top priority projects for Phase III are described below:

Compatibility of Manufacturing Process Fluids with HFC Refrigerants and Ester Lubricants

During the manufacturing process, air-conditioning and refrigeration components are exposed to a number of process fluids, residual amounts of which remain in the equipment. While experience has shown that many of these process fluids are compatible with CFC refrigerants and mineral oil, their compatibility with alternative refrigerants and lubricants are unknown. This project will screen 50 common manufacturing process fluids for compatibility with R-134a and a polyolester lubricant.

Long-Term Compatibility of Polyolester Lubricants with HFC Refrigerants

The long-term behavior of polyolester lubricants and HFC refrigerants, particularly thermal stability and resistance to hydrolysis, must be investigated to determine the long-term compatibility of these refrigerant-lubricant mixtures. This project will investigate the long-term compatibility of four HFC refrigerant blends and six different fully formulated polyolester lubricants. The effects of air and moisture contaminants on their long-term stability will also be studied.

Compatibility Problems Resulting from the Products of Motor Burnouts

The high temperatures generated through electrical arcing during motor burnouts are known to break down CFC refrigerants and oils to create acidic, noxious and some toxic by-products. Little is known about the by-products that will be generated by motor burnouts in systems using HFC refrigerants. This project will determine the by-products from various HFC refrigerant and polyolester lubricant mixtures during simulated motor burnouts. The effort will also include a literature survey to determine the potential toxicity and corrosive effects of these by-products.

Investigation into the Fractionation of Refrigerant Blends

A number of zeotropic blends are currently considered as possible alternatives for HCFC-22 and R-502. By nature, zeotropic blends change composition in both the vapor and liquid phases during condensation and evaporation. Fully understanding the fractionation of zeotropic blends is important in the design of optimal and safe refrigeration systems. It is also important in determining proper servicing procedures for these systems. This project will investigate fractionation of two HFC refrigerant blends with respect to solubility in the lubricant, successive charging from storage/shipping containers, composition shifts within various components of refrigeration systems and from leaks.

Investigation of Flushing and Clean-out Methods to Ensure System Compatibility

To ensure reliability, a system which has suffered a motor burnout must be flushed and cleaned of corrosive by-products before the system is placed back in service. To operate efficiently, CFC refrigerant-mineral oil systems retrofitted with alternative refrigerant-lubricant mixtures must have the residual mineral oil flushed from the system. The past practice of using CFC-11 as a flushing and clean-out fluid is no longer acceptable. Other current methods are expensive. This project will identify and verify the effectiveness of an economical and environmentally acceptable flushing and clean-out method.

Methods Development for Measuring and Classifying Flammability/Combustibility of Refrigerants

Many potential alternatives for HCFC-22 and R-502 are HFC refrigerant blends which contain flammable refrigerant components (e.g. HFC-32 or HFC-143a). The current test procedure used to classify refrigerants for flammability is based on subjective visual observations. These procedures do not specify humidity conditions. Both of these shortcomings affect test repeatability and make flammability classification of marginally flammable refrigerants difficult. This project will address improving ASTM Standard E681, identifying appropriate test conditions for air conditioning and refrigeration applications, and develop improved methods for detecting combustibility of refrigerants.

Thermophysical Properties

This project will expand on previous work performed by the National Institute of Standards and Technology. Thermophysical measurements will be made on HFC-245ca, HFC-41 and a number of binary and ternary HFC-refrigerant blends. The binary and ternary refrigerant measurements will be used to verify mixing parameters used in equation of state models and computer simulation routines.

Chemical and Thermal Stability of Phase III Refrigerants and Lubricants

Several new refrigerants and refrigerant blends which are potential alternatives are now available in sufficient quantities for testing. This project will perform chemical and thermal stability tests of these new alternatives refrigerants and lubricants. These test will be similar to those performed on refrigerants and lubricants during Phase I.

Miscibility of Phase III Refrigerants and Lubricants

This project will conduct miscibility studies of polyolester lubricants with newer refrigerants and refrigerant blends. These studies will be similar to those conduct on Phase I refrigerants and lubricants.

FUTURE RESEARCH

The development of Phase IV research needs is currently underway. Research under consideration include the identification and testing of viable alternatives for low temperature refrigerant applications, determining acceptable contaminant levels for recycled refrigerants, lubricant dynamics on the performance of refrigeration systems, and follow-on work to develop accelerated test methods.

SUMMARY

Much has been accomplished in the first two years of the MCLR program. Much more is yet to be accomplished. Thermophysical properties measurement and model correlations have been expanded for most of the current contenders for CFC and HCFC alternatives. These equation-of-state models enable manufacturers to examine theoretical efficiencies of a number of pure refrigerants and refrigerant blends, assisting them in selecting potential alternatives and optimizing systems for their use. Miscibility, viscosity, solubility and materials compatibility testing of these leading contenders have also been done or are nearing completion. New test methods are under development which will enable researchers to more fully evaluate and quickly screen newer refrigerants and lubricants as they become available.

Work which still remains to be done includes compatibility studies in addressing system retrofits and use of reclaimed refrigerants; the search for an adequate long-term substitute for low pressure refrigerants; fully understanding fractionation of zeotropic refrigerant blends to determine their safety and performance impacts on equipment and to determine proper servicing procedures for systems using these blends; development of a better flammability testing procedure for classifying marginally flammable refrigerants and refrigerant blends.

Much of the data already provided by the MCLR program have been useful to manufacturers in determining their selection of alternative refrigerants, lubricants and materials to be used in new equipment designs, as well as in determining the compatibility of current materials after retrofitting systems with alternative refrigerants. So far material compatibility results have been favorable for HFC refrigerants tested.

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