

**DOCUMENTATION OF NEWLY DEVELOPED METHODS
TO ASSESS MATERIAL COMPATIBILITY
IN REFRIGERATION AND AIR-CONDITIONING APPLICATIONS**

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**DOCUMENTATION OF NEWLY DEVELOPED METHODS TO ASSESS MATERIAL
COMPATIBILITY IN REFRIGERATION AND AIR-CONDITIONING APPLICATIONS**
ARTI MCLR Project Number 660-50000

ABSTRACT

This document summarizes the experimental methods used during the materials compatibility and lubricants research program (MCLR). The MCLR program was jointly sponsored by the U.S. Department of Energy and the air-conditioning and refrigeration industry. The individual projects were managed by the Air-Conditioning and Refrigeration Technology Institute. The projects presented in this report are: Chemical and Thermal Stability of Refrigerant/Lubricant Mixtures with Metals, Miscibility of Lubricants with Refrigerants, Compatibility of Refrigerants and Lubricants with Motor Materials, Compatibility of Refrigerants and Lubricants with Elastomers, Compatibility of Refrigerants and Lubricants with Engineering Plastics and Sealed Tube Comparisons of the Compatibility of Desiccants with Refrigerants and Lubricants.

SCOPE

The scope of this project was to document the experimental procedures used in six projects in the MCLR program. These included, chemical and thermal stability, miscibility, compatibility with motor materials, elastomers, plastics and desiccants.

1. INTRODUCTION

1.1 Background:

The forthcoming phaseout of CFC and HCFC compounds¹ has required the air conditioning and refrigeration (AC&R) industry to conduct extensive research on alternative refrigerants and their physical, chemical and toxicological properties. The AC&R industry recognizes that a major deterrent to the application of alternative refrigerants in equipment is the lack of data covering lubricants and materials compatibility. This paper documents experimental procedures used by contractors during the materials compatibility and lubricants research (MCLR) program.* This program, as its name suggests, was designed to examine the compatibility of new refrigerants and lubricants with the other materials used to construct AC&R equipment.

Refrigerants have changed very little over the last 40 years, so the qualification of materials used with currently established refrigerants has been in place for many decades. With the advent of the ozone depletion and global warming issues, the accelerated phase-out of CFC refrigerants does not allow sufficient time for manufacturers to evaluate the effects of alternative refrigerants, and associated lubricants, on the reliability, durability, and function of the equipment where they will be used. New lubricants and alternative materials need to be developed and qualified for compatibility with alternative refrigerants.

The methods described in this paper were performed by multiple investigators under the U.S. Department of Energy grant: DE-FG02-91CE23810: Materials Compatibility and Lubricants Research (MCLR) on CFC-Refrigerant Substitutes. These researchers, along with many others, submitted proposals in response to work statements issued for specific projects under this grant. The selected researchers were chosen in a competitive fashion by an advisory committee consisting of industry experts. The committee considered primarily the technical merit of the proposals when awarding the research funds. The researchers funded in the MCLR program were selected because their proposed methods were judged by the advisory committee to be the best available at the time the research was performed.

* The MCLR program is funded by an on-going research grant administered by the Air-Conditioning and Refrigeration Technology Institute (ARTI), a not-for-profit organization for scientific research in the public interest. The program was implemented on September 30, 1991. The total value of the program is estimated to be over \$10 million. Support for the MCLR program comes jointly from the U.S. Department of Energy via grant number DE-FG02-91CE23810 and from significant monetary and in-kind contributions from the air-conditioning and refrigeration industry.

The following chapters describe, in detail, methods to measure relatively short term compatibility of materials under specific conditions of temperature and pressure. Some insight into long-term compatibility can be gained by comparing results of tests with alternative refrigerants and lubricants with the results of tests with the CFC and mineral oil used successfully in the past. Although these methods have proven effective in the past for predicting long term results, other severe situations, such as contamination or extended extreme conditions of operation can negatively affect the reliability of air-conditioning and refrigeration systems.

References are provided within each section to provide readers with some perspective of other similar work which has been performed. This is not intended as an exhaustive literature search, but consists of a small sample of the type of information available. More information on these and many other topics is available through the Refrigerant Database⁵ and other sources. The Refrigerant Database itself is funded under the MCLR program and contains a wealth of information on many topics pertinent to the AC&R industry.

1.2 Experimental Standards:

The starting materials used in all of the compatibility experiments presented in this paper must adhere to certain standards if the results of the tests are to be comparable. Since water is the primary contaminant in refrigeration systems, refrigerants must contain less than 10 ppm water by weight. The other impurities which might be present in the refrigerant must be consistent with ARI Standard 700.² For example, the amount of any other refrigerants found as impurities must be less than 0.5% by weight. If newly synthesized experimental refrigerants do not meet these purity standards, differences must be noted when reporting the results of an experiment. If the purity of the refrigerant sample is not specified by the manufacturer, or is doubted for any reason, it must be verified in separate quantitative experiments.

Acceptable moisture levels must also be specified for lubricants. Hydrocarbon oils such as mineral oil and alkylbenzenes must have less than 30 ppm water and a total acid number less than 0.01 mg KOH/g. Polyglycols and polyolesters must contain less than 50 ppm water and have an acid number less than 0.05 mg KOH/g. Many new synthetic lubricants are hygroscopic,³⁻⁴ therefore, exposure to atmospheric water vapor must be carefully regulated. The lubricants used for these material compatibility tests did not contain additives except those necessary to ensure storage stability. Additionally, the lubricants contain less than 1 ppm iron and copper.

Analytical verification of the lubricant purity was performed before any compatibility experiments were undertaken.

High pressures will arise at the elevated temperatures present during some of the compatibility tests. Furthermore, toxic and/or corrosive chemicals may be produced during the thermal aging process or might be used during the analysis of the resulting mixtures. Also, toxicological properties of some of the refrigerants and lubricants used in these experiments had not been fully investigated. Therefore, it is crucial that proper safety measures and equipment are used at all times.

1.3 References:

- ¹ "Handbook for the Montreal Protocol on Substances that Deplete the Ozone Layer", United Nations Environmental Programme, Nairobi (1991).
- ² ARI Standard 700-93, Air-Conditioning and Refrigeration Institute, Arlington (1993).
- ³ S.G. Sundaresan and W.R. Finkenstadt, "Polyalkylene Glycol and Polyol Ester Lubricant Candidates for use with HFC-134a in Refrigeration Compressors", *ASHRAE Trans.*, **98(1)**, 796 (1992).
- ⁴ K.S. Sanvordenker, "Durability of HFC 134a Compressors-the Role of the Lubricant", *Proc. Int'l. Appl. Tech. Conf.* (1991).
- ⁵ J.M. Calm, "Status and Use of the Refrigerant Database", *ASHRAE J.*, **35(11)**, 50 (1993).

2. CHEMICAL AND THERMAL STABILITY OF REFRIGERANT/LUBRICANT MIXTURES WITH METALS

2.1 Purpose and Use:

The purpose of this method is to measure the chemical and thermal stability of refrigerant/lubricant mixtures in the presence of metal catalysts. These measurements will occur under well defined experimental conditions. The elevated temperatures present in this experiment are used to accelerate any decomposition reactions which occur. Since it is known that chemical reactions of refrigerants with lubricants can be catalyzed by metals,¹ these tests are necessary to determine if new combinations of materials are suitable for incorporation into next generation cooling equipment.

2.2 Introduction:

Many new chemicals have been proposed as alternative refrigerants. One of the properties which they must possess to be a successful substitute is chemical and thermal stability. For a new refrigerant to gain widespread acceptance it must have exceptional chemical and thermal stability even though it is in contact with other materials such as metals and lubricants.

Stability is usually determined in the laboratory by aging a refrigerant/lubricant mixture in a sealed tube in the presence of a metal at high temperature.²⁻⁴ Recent studies have shown that the sealed tube test can also be used successfully with most fluorinated refrigerants⁵. Care must be used however, since for certain refrigerant species, problems can exist.⁶ The fluids aged in these sealed tubes are analyzed by standard chemical means to quantify the extent of decomposition of both the refrigerant and lubricant. Various methods of analysis are used on the refrigerant and lubricant. The procedures for fluorinated refrigerants and synthetic lubricants are slightly different from the ones used for chlorinated refrigerants and mineral oil lubricants.⁷ These analysis methods can include visual inspection, gas chromatography, ion selective electrode potentiometry, titrations, infrared spectroscopy, size exclusion chromatography, or other analytical methods.

Recently, other methods have been proposed to measure the stability of these materials *in-situ*.^{8,9} These include, conductivity, colorimetric spectroscopy, and thermal analytical techniques. The conductivity method seems to have the most promise as a new technique and is currently under development to provide an

accelerated method for screening chemical and thermal stability.⁹ This method still must prove itself to correlate with the standard, reliable sealed tube test before it will be widely accepted.

2.3 Documented Test Method: Spauschus Associates, Inc.¹⁰

2.3.1 experimental conditions

Stability tests for the refrigerant/lubricant/metal combinations were performed in sealed glass tubes. These tests are described in detail in ASHRAE Standard 97-1989.⁴ Heavy walled glass tubes were used to withstand the high pressures which were present during the testing. It has been demonstrated that glass tubes of this type provide an inert environment in which to study the chemistry of refrigerant decomposition.⁵ The aging of the tubes took place at three different temperatures (usually 150, 175 and 200°C [300, 350, 390°F]).

2.3.2 experimental

2.3.2.1 materials: Tubes were cleaned with toluene and dried at 150°C (300°F). The total internal volume of each tube is about 7.5-8 cm³ (0.5 in³). The metal catalyst used was cut into coupons 6.3 mm (0.25") wide and 32 mm (1.25") long. The coupon was made of valve steel, but any metal of interest could have been used. Metal coupons were cleaned in hexane and stored in this solvent as well. The absence of water in the sealed tube and in its components is critical to the reliability of the testing procedure.

2.3.2.2 procedure: The metal coupons were first placed into a glass tube with one end sealed. The tube was then necked about 15 cm (6") from the sealed end. Necking of the tube prior to the addition of the lubricant minimizes thermal breakdown of the lubricant from heating the tube. After this, 1.0 ml of lubricant was added through a calibrated syringe. Next, the tube was cooled to liquid nitrogen temperatures to facilitate the addition of the refrigerant. An equal weight of the refrigerant was condensed from a gas manifold into the cooled tube. Each tube was then sealed, annealed and inspected. The tubes were sealed by heating the necked down area of the tube until the atmospheric pressure caused it to collapse. An example of a completed sealed tube before aging is shown in Figure 1. At least three tubes were prepared for each test (each refrigerant, lubricant, metal, temperature combination). Satisfactory tubes were placed inside

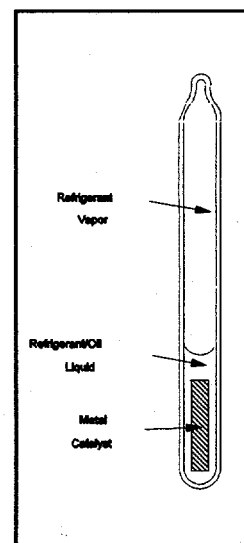


Figure 1: Schematic of sealed tube used to test chemical and thermal stability with metals.

an oven for 14 days at a constant temperature. The tubes were contained in bored out holes in a metal housing to protect the other tubes in case one fractured. The aging temperatures used in the experiment ranged from 105 to 200°C depending on the refrigerant.

2.3.3 analysis

2.3.3.1 visual: After the tubes were removed from the oven the first evaluation to be performed was a simple visual analysis of the tube and its contents. If a precipitate was formed in the tube, it was noted, as was the appearance of the metal coupon. The change in the color of the liquid phase was measured by comparison with the standards in ASTM Standard D1500. For a permanent record, a photograph was taken which includes three elements: an unaged metal coupon, an aged metal coupon outside of the tube, and the sealed tube itself. This picture was taken immediately after the coupon was exposed to the atmosphere since the ambient water vapor will interact with the halogens present to corrode the metal, sometimes with great rapidity.

2.3.3.2 vapor phase analysis: The vapor present in the sealed tubes after aging was analyzed in a gas chromatograph (GC).¹¹ The purpose of this analysis was to estimate the extent of decomposition of the refrigerant. The recovery of the vapor was accomplished in the following manner. The tube contents were first frozen with liquid nitrogen, then the tip of the sealed tube was broken off, and coupled to a gas manifold. Finally the contents of the tube were warmed until all of the volatile components were released into the manifold. Samples of this gas were then injected into a GC column.

The details of the operation of the GC are defined by the specific instrument and the skill of the operator. A column was chosen which provided reasonable separation between the refrigerant and any possible breakdown products. In this case, a Gow-Mac 550P thermal conductivity detector instrument using a 2.44m Poropak "Q" column was used. The helium carrier gas flow rate was 27 ml/min and the column and injector temperatures were both 120°C. A 500 μ l sample was used and the detector temperature was 200°C using a current of 150 mA. In a general case, retention times should be recorded for each element contained in the aged samples, and for a standard unaged sample of neat refrigerant as well. The products of any decomposition which occurred during the aging process, if gaseous, may be detected by examining the retention times of the species eluting from the column. Comparison of the relative peak areas for each species in the gas chromatograph can lead to an estimate of the amount of refrigerant which has reacted.

2.3.3.3 halide ion: The tube contents were frozen in liquid nitrogen and the tubes were broken at the top. The open end was immediately submerged in a beaker containing the extraction solvent; deionized water, slightly acidified with nitric acid. The tube walls were rinsed thoroughly with the extraction solvent to recover as much of the liquid sample as possible. This solution then undergoes a series of quantitative and qualitative analytical tests.

The concentration of halide ions (Cl⁻, F⁻) present in the lubricant solution after aging was determined by a standard potentiometric method using the appropriate ion selective electrodes for chloride and fluoride anions.^{7,11} Since C-Cl bonds are far more labile than C-F bonds, HCFC refrigerant decomposition can be detected by observing only the chloride ions in solution. When analyzing HFC's, it is necessary to detect fluoride ions. The measurements of halide ion are recorded to $\pm 0.1 \mu\text{g}$ (100 ppb).

The ion selective electrodes are first calibrated by using standard solutions of chlorine or fluorine. After calibration of the electrodes, the unknown concentration of ion can be read directly from the potentiometer (pH meter). Multiplying this concentration by the total original volume of the solvent provides the number of ions present in the lubricant solution. If one then assumes that each ion detected is equivalent to one molecule of refrigerant reacted then the percentage of refrigerant which reacted is obtained from;

$$\text{percent reaction} = (\text{moles halide detected}) / (\text{original moles refrigerant}). \quad (1)$$

This approximation is valid as long as the total reactivity of the refrigerant is relatively low, and the halide ion doesn't further react with the lubricant/metal mixture. This analysis is performed using the contents of two of the sealed tubes (two trials), the third sealed tube is used to analyze the lubricant.

2.3.3.4 lubricant acidity: In this case, the tube contents were submerged in a beaker containing a neutral extraction solvent; toluene/isopropanol/water. The tube walls were rinsed thoroughly with the extraction solvent to recover as much of the liquid sample as possible.

Certain lubricants are amenable to titrometric analysis to detect the total amount of acid present in the refrigerant/lubricant mixture. For polyol ester (POE) type lubricants, potentiometric titration following the procedures presented in ASTM Method D664, was used to determine the total acid number. The total acid number was recorded to the nearest $\pm 0.01 \text{ mg KOH/g}$ lubricant.

2.3.3.5 lubricant structure: Qualitative changes in the molecular structure of the lubricants can be observed by several methods, depending on the precise lubricant species. For POE lubricants, infrared (IR) spectroscopy is an effective technique.¹¹ IR spectra were taken by simply placing a liquid sample of oil between NaCl plates in a IR spectrometer. Comparison of these IR spectra taken before and after thermal aging can illustrate if changes have occurred in the molecular structure of the lubricant.

Polyalkylene glycol (PAG) lubricants were, in this case, examined using size exclusion chromatography (SEC).¹¹ This technique again will provide a general view of any changes in the structure of the lubricant. SEC will provide information on the change in the molecular weight distribution of the polymer after aging. Chromatograms were obtained using chloroform as the mobile phase. Two 3m length sets of phenogel linear mix columns with a 2 mm interior diameter were used. Detection of the components of interest in the eluent was accomplished using the refractive index.

2.3.4 reporting

All experimental data should be reported for each mixture. The initial components of the mixtures and their purity is first noted. After the aging process, the visual appearance of the metal coupon and the appearance and color of the solution is recorded. A gas chromatograph of the vapor component in each case is measured. Halide ion concentrations for each mixture are measured as well, and the percentage of refrigerant reacted is calculated and reported. If the lubricant is a POE, the total acid number is determined and the IR spectrum is measured for both unused and aged oil samples. If the lubricant is a PAG, a size exclusion chromatogram is obtained for both unused and used oil samples. The numerical results are arranged in tabular form, the other resources (chromatographs, spectra, etc.) are included in the final report. Table I shows a sample of some chemical and thermal stability data acquired in this fashion for a mixture of R-134a and a POE which was aged for 14 days at 150, 175 and 200° C.

Table I: Typical data acquired when measuring the chemical and thermal stability of refrigerants and lubricants (from reference 10).

Sealed Tube Contents: valve steel strip
1.0g of POE lubricant
1.0 g of R-134a

Visual Appearance			Chemical Analysis				
Temp (°C)	Oil Color	Steel Color	GC Data	F. (µg)	%R-134a Reacted	Oil TAN	Oil IR
150	no change at 3.0	no change	--	1.6	0.001	0.94	split C=O band
175	from 3.0 to 3.5	darkened	--	1.0	0.001	0.63	same
200	from 3.0 to 4.5	blackened	0.56% CO ₂	6.8	0.004	0.99	..and.. C-O band

2.4 References

- ¹ K.S. Sanvordenker, "Mechanism of Oil-R-12 Reactions-the Role of Iron Catalyst in Glass Sealed Tubes", *ASHRAE Trans.*, **91(1a)**, 356 (1985); A. Factor and P.M. Miranda, "An Investigation of the Mechanism of the R-12-Oil-Steel Reaction", *Wear*, **150**, 41 (1991).
- ² D.E. Kvalnes and H.M. Parmelee, "Behavior of Freon-12 and Freon-22 in Sealed Tube Tests", *Ref. Eng.*, **65(11)**, 4 (1957).
- ³ G.C. Doderer and H.O. Spauschus, "A Sealed Tube-Gas Chromatograph Method for Measuring the Reaction of R-12 with Oil", *ASHRAE Trans.*, **72(2)**, IV.4.1 (1966).
- ⁴ ANSI/ASHRAE Standard 97-1989, "Sealed Tube Method to Test the Chemical Stability of Material for Use Within Refrigeration Systems", ASHRAE, Atlanta (1989).
- ⁵ H.O. Spauschus, G. Freeman and T.L. Starr, "Surface Analysis of Glass from Sealed Tubes After Aging with 134a", ASHRAE Annual Meeting, June (1992).

- ⁶ R.G. Doerr, R. Schafer, D. Lambert and D. Steinke, "Stability Studies of E-245, Fluoroether $\text{CF}_3\text{CH}_2\text{OCHF}_2$ ", Int. CFC and Halon Alt. Conf., December (1991).
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3 MISCIBILITY OF LUBRICANTS WITH REFRIGERANTS

3.1 Purpose and Use

The purpose of this documented procedure is to measure the miscibility of refrigerants with lubricants. Preliminary screening of miscibility was done under varying conditions of temperature and relative refrigerant/lubricant concentrations. These measurements were performed under controlled, repeatable experimental conditions to allow further developments in this area.

3.2 Introduction

Mineral oils and alkylbenzene lubricants effective in air conditioning and refrigeration equipment operated with CFCs and HCFCs. These lubricants had sufficient miscibility with the CFCs and HCFCs to provide sufficient oil return such that heat transfer was not reduced. Mineral oils and alkylbenzene lubricants do not have sufficient miscibility with HFCs to operate acceptably in most systems. New synthetic lubricants with a wide range of miscibilities were offered for use with HFC alternatives. The knowledge of the miscibility over a large range of temperatures and relative refrigerant/lubricant concentrations are needed to select lubricants for air conditioning and refrigeration systems employing alternative refrigerants.¹

Miscibility determinations are usually performed in the following manner.²⁻³ First, sealed vessels with known concentrations of refrigerant and lubricant are prepared and placed in a constant temperature bath. Then, the phases occurring in the cylinders are observed as a function of temperature to visually determine the miscibility of the two fluids.

3.3 Documented Test Method: Iowa State University⁴

3.3.1 experimental conditions

Miscibility tests for the refrigerant/lubricant combinations were

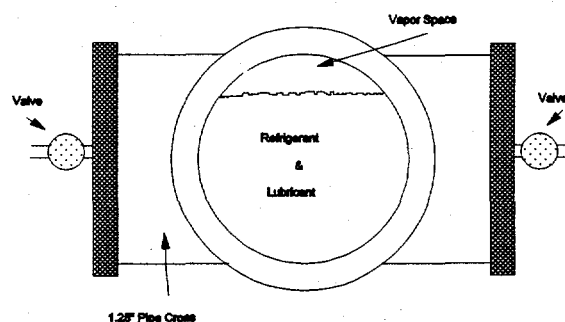


Figure 2: Schematic diagram of a test cell for determination of temperature dependent refrigerant-lubricant miscibility.

performed in sealed test cells. The test cells were designed to allow both maximum visibility of the test mixture and easy cleaning. Each cell was constructed from a 3.2 cm (1.25 inch) diameter pipe cross which has sight windows which screw into opposing ports as shown in Figure 2. Valves necessary for charging the refrigerant and evacuating the cell are screwed into the other two ports. There is a small vapor space in each cell. This causes a slight difficulty since the density of the vapor changes as the temperature and pressure change inside the cell. This will cause the amount of refrigerant in the liquid phase to also change slightly. The effect of this problem is minimized by keeping the vapor volume restricted to a small fraction of the total cell volume. It should be noted that this same problem also exists any sealed-tube system as well.

The thermal baths in which the test cells were contained were simply large insulated liquid baths with thermostatted heating and/or cooling systems to produce temperatures from -50 to 90°C (-60 to 195 F). Two separate baths were used to span this temperature range. The cold bath covered a temperature range from -50 to 10°C (-60 to 50 F), and was filled with a 65/35 mixture of ethylene glycol and water. The ethylene glycol used in the bath contains no additives. This provided maximum visibility of the test cells. The hot bath was used from 10 to 90°C (50 to 195 F), and was composed of water with a rust inhibitor added. The thermal baths were both insulated, partly with styrofoam and partly by air spaces between the glass liquid containers and plexiglass viewing windows. Condensation was prevented on the cold bath windows by purging the internal air spaces with dry nitrogen. Temperatures in the baths were measured by two resistance temperature detectors (RTD). These devices provided a linear response from -51 to 149°C (-60 to 300 F). One test cell present in the bath had the temperature of its internal fluid measured directly using a thermocouple. The total capacity of either of the thermal baths was 12 test cells.

3.3.2 experimental procedure

The experimental procedure used to observe miscibility in the above apparatus was as follows. The cells began with both front and rear viewing windows removed for cleaning. After cleaning, (with R-113) the cell and windows were weighed. The rear window was then installed. Lubricant was injected into the cell through the open front port. The front window was then installed. A vacuum pump was used to evacuate the cell through one of the valves on the sides, removing all of the remaining air and water. If the cell leaked at this point, the fittings were retightened. The cell was weighed once again to determine the amount of lubricant added.

The refrigerant was then introduced through a valve on the side of the cell. The refrigerant was contained in a manifold which could be evacuated. The total vapor

volume was limited to about 15% of the cell volume to reduce the problem of the changing vapor density as a function of temperature. The weight was determined a final time to measure the amount of the refrigerant present, and the cell was ready for testing. The mass fraction of refrigerant present in solution is calculated from the measured masses of the refrigerant and lubricant which were present in the cell. This nominal value was not corrected for the amount of refrigerant in the vapor phase.

Test cells were then placed into the thermal baths where they were heated or cooled over the desired temperature range. The bath temperature was considered to be stable when both of the RTDs in the bath read within 0.5°C of the set temperature. The cell temperature was assumed to be in equilibrium with the bath when the thermocouple in the cell agreed with the two RTDs to within 0.5°C. When this state was reached the physical appearance of the solution in the test cells was observed and recorded. If there was cloudiness present, a precipitate or floc formed or separation into two layers occurred, it was noted. A mixture was considered miscible if none of these conditions were present and only a single phase was present.

Table II: Miscibility of R-32 with several lubricants.

R-32				
	Nominal Refrigerant Concentration			
lubricant (ISO grade)	10%	20%	50%	90%
naphthenic mineral oil (32)	0°C	I	I	I
alkylbenzene (32)	20°C	I	I	I
polypropylene glycol diol (32)	M	M	M	M
POE-mixed acid (32)	M	M	-40°C	-20°C

notes: M- miscible over the complete test temperature range
 I- immiscible over the complete test temperature range
 x°C- the mixture was immiscible below this temperature

This process is repeated until all the desired temperatures have been measured. The cells are drained through one of the valves and then rinsed three times with R-113.

The front and back windows are removed and the cell is rinsed once again with R-113 to remove all remaining lubricant. The windows and seals were then cleaned and the cell was ready to be refilled.

3.3.3 reporting

The visual observations of the miscibility cells should be reported in tabular form. A table for each refrigerant/lubricant combination was constructed which contains the visual observation of the test cell as a function of temperature and refrigerant concentration. The temperatures were varied from -50 to 60°C in steps of approximately ten degrees. If desired, miscibility plots can then be prepared for the partially miscible systems. Table II shows an

example of the miscibility data obtained for R-32 and several lubricants. Figure 3 shows an example of a miscibility plot for R-32 and a mixed acid POE (ISO 32).

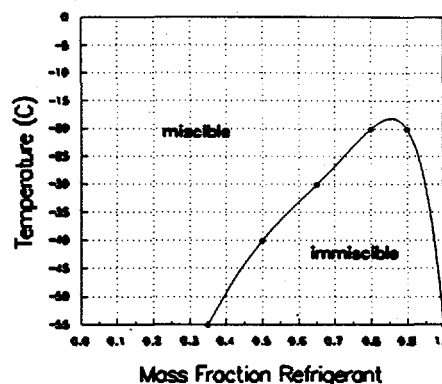


Figure 3: Miscibility plot for R-32/ISO 32 POE mixed acid mixtures.

3.4 References

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- ³ K.S. Sanvordenker "Experimental Evaluation of an R-32/134a Blend as a Near Drop-In Substitute for R-22", *ASHRAE Trans.*, 99(2), 1993.
- ⁴ M.B. Pate, S.C. Zoz and L.J. Berkenbosch, "Miscibility of Lubricants with Refrigerants", Report DOE/CE/23810-6, Air-Conditioning and Refrigeration Technology Institute, Arlington, VA, 1993.

4 COMPATIBILITY OF REFRIGERANTS AND LUBRICANTS WITH MOTOR MATERIALS

4.1 Purpose and Use

This procedure presents methods for determining the compatibility of various types of motor materials with refrigerants and refrigerant/lubricant mixtures. The methods of aging the materials are described as well as the various tests on the materials to determine the extent of their deterioration. Comparison of the status of the materials with that of standard systems which are known to be successful provides insight into the long term durability of each of the components.

4.2 Introduction

Hermetically sealed compressors have long been successfully employed in the HVAC&R industry. With the conversion away from CFC refrigerants however, questions regarding the compatibility of the new refrigerants and lubricants with motor materials have arisen. Since there are many different types of motor materials exposed to the refrigerant/lubricant, many opportunities for chemical incompatibilities exist. Historically, compatibility of hermetic motor materials with refrigerants and lubricants has been accomplished in sealed test vessels. All of the different types of materials need to be tested including wire,¹ varnish,² insulation³ and others. The compatibility of these components can be estimated via sealed cylinder tests at elevated temperatures. These results must be taken carefully however as the method of the aging can have an effect upon the results.² Analysis of the materials after aging, and comparison with known successful hermetic system components allows a qualitative evaluation of the compatibility to be performed. The procedure described below is not intended to estimate the lifetime of a motor, but to screen components strictly for material compatibility. Other testing methods have been developed to estimate hermetic motor lifetimes, and new methods are being developed.⁴

4.3 Documented Test Method: The Trane Company⁵

4.3.1 experimental conditions

Aging of the motor materials/refrigerant(/lubricant) mixtures occurred in four pressure vessels constructed from type 316 stainless steel. Each vessel contained some of the motor materials to be tested along with a refrigerant and/or lubricant. The exposures were conducted under conditions of high pressure and elevated temperature to

accelerate the decomposition process. After exposure, quantitative and qualitative testing of the materials was performed to determine their compatibility.

4.3.2 experimental

4.3.2.1 *materials*

4.3.2.1.1 *magnet wire*: The magnet wire was prepared in several different forms before it was tested. It was formed in either helical coils, single strands, or twisted pairs. The wires were tested both uncoated and with six different varnish coatings. The twisted pairs were constructed using a motorized dielectric twist fabricator.⁶

4.3.2.1.2 *varnishes*: Varnishes were tested in two different physical forms, as solid varnish disks and also as a thin film coated on magnet wire. The varnish disks were formed in the following manner. Enough liquid was placed into a pre-weighed aluminum dish to produce a cured disk which was approximately 1.2 mm (0.05 inches) thick (in this case, 3-6 grams). The curing process used was a slight variation on the manufacturers specifications. In most cases, a two part cure was used. The initial cure is needed to prevent formation of solvent bubbles in the varnish disk and is then followed by a final cure specified by the supplier.

The varnishing procedure for the magnet wires is the varnish dip bake process. First, the magnet wires (in any forms) were preheated to 175°C (350°F) for 2 hours prior to varnishing. Then the magnet wires were cooled to about 93°C (200°F). These warm wires were then dipped into the varnish and removed at a rate of 10 cm (4 inches) per minute. They were allowed to drip until no further dripping was observed. The helical coil magnet wires were checked to be certain they were not plugged with varnish. The wires were then suspended in an oven for a step cure of two hours at 100°C(212°F). The oven temperature was then increased to 163°C(325°F) and the wires were cured another ten hours. Finally, the wires were inverted and the entire process; heating, cooling, dipping, curing was repeated once again. The samples were then ready for use.

4.3.2.1.3 *insulation*: The samples were prepared two different ways depending on which test was performed. For dielectric strength, the sheet insulation was cut into samples of a couple of square inches, sleeving insulation samples of approximately 0.5 g were used. For tensile and elongation tests, the samples were cut into 0.5 by 6 inch samples.

4.3.2.1.4 *tape/tie cord/lead wire*: The tape, tie cord and lead wire samples used in the testing were all approximately 15 cm (6 inches) in length.

4.3.2.2 procedure: The different types of motor materials which were tested included varnishes, magnet wires, sheet insulations, spiral wrapped sleeving insulations, lead wires, tapes and tie cords. The analytical tests performed on each of these materials will be described in detail in the following sections after a general description of the procedure.

The first experimental evaluations which were performed measured the thermal stability of the refrigerant/lubricant mixtures. These tests were necessary to confirm that the test fluids themselves were stable at the temperatures planned for the motor materials tests. Every refrigerant/lubricant combination was placed into a 125 ml stainless steel pressure chamber and exposed at 127°C (260°F) for 500 hours at 2109 kPa (300 psi). The refrigerant purity was measured both before and after aging by gas chromatography. In this way, decomposition of the refrigerant could be easily detected. The lubricants were analyzed for total acid number and moisture content both before and after aging. A large increase in either the acid number or water content indicates decomposition of the lubricant.

Preparation of the compatibility test vessels was accomplished in the following manner. All of the motor material samples to be tested with each fluid were loaded into the four test vessels. Sheet insulation materials were always kept separate from varnished items and any items which suffered from large amounts of mass extraction were tested together in a vessel separate from the other materials. Exposures to pure refrigerant solutions were accomplished using equal masses of refrigerant which were large enough to cover all of the materials in the test vessel. Exposures were conducted for 500 hours at temperatures ranging from 60 to 121°C (140 to 250 F) depending on the refrigerant. In the case of refrigerant/lubricant mixtures, lubricant was added first to nearly cover the materials in the vessel. Then, the vessel was sealed and evacuated for 30 minutes. Finally, refrigerant was added to the vessel such that the pressure would be 2109 kPa (300 psi) at 121°C (250 F). After heating the bombs at 121°C (250 F) for 24 hours, the pressure was measured. Refrigerant was then either added or removed to maintain the target pressure. The pressure was checked at time intervals of 48, 168, 336 and 500 hours and was maintained at 2109 kPa (300 psi) throughout the exposure time.

The procedural sequence for the materials aging experiments was as follows. First, the starting motor materials were prepared, weighed and the appropriate properties were measured. Then they were placed into the vessels with a test fluid and aged for 500 hours at the specified temperature (121°C most of the time). Following removal from the test vessel, sample weights and measurements were taken again and recorded. Then, the materials were baked at 150°C (300 F) for 24 hours in air to release any absorbed refrigerant. Finally, measurements were again taken to

determine the effects of the absorbed refrigerant.

4.3.3 analysis

4.3.3.1 refrigerant: A gas chromatograph was used to analyze the purity of the refrigerant. The details of the operation of the instrument are defined by the specific instrument and the skill of the operator. A column was chosen which provides reasonable separation between the refrigerant and any possible breakdown products. In this case, a Varian 3700 flame ionization detector instrument using a 3.1m 5% Fluorocol column was used. The helium carrier gas flow rate was 30 ml/min, the injector temperature was 200°C (390 F) and the column temperature was 50°C (120 F). A 250 μ l sample was used and the detector temperature was 250°C (480 F). The gas samples were removed directly from the high pressure test bombs into a gas handling manifold before being analyzed.

4.3.3.2 lubricant: Lubricant acid number was titrimetrically determined using the method described in ASTM D-974. The total acid number was recorded to the nearest \pm 0.001 mg KOH/g lubricant. The water content in the lubricant was also measured by titration. In this case, a measured amount of lubricant was injected into a Fisher Scientific Coulometer K-F Titrimeter Model 447. After the coulometric titration was performed, the moisture in the lubricant was calculated and recorded to the nearest part per million.

4.3.3.3 magnet wire: The compatibility of the magnet wires (coated and uncoated) was evaluated using several techniques. A visual comparison of the exposed samples to the unexposed ones was made, and any differences were noted. The weight change of the magnet wire was measured by weighing the wire before and after exposure and taking the difference. Single strand magnet wires with and without varnish were checked for flexibility using ASTM D-1676, sections 141 to 148. Twisted Pairs of magnet wires were evaluated for burnout strength using ASTM D-1676, sections 13 to 21. They were also checked for dielectric strength using ASTM D-1676, sections 69 to 75.

4.3.3.4 varnish: The varnish disks after exposure were visually compared to an unexposed disk to see if a visible changes had occurred. Again, the weight difference was obtained from the before and after exposure weights. The exposed varnish disks were also qualitatively compared to the unexposed disks to see if there was a change in the flexibility. Finally, the varnished helical coil wires were checked for varnish bond strength using ASTM D-2519.

4.3.3.5 sheet insulation: The sheet insulation samples were visually compared to unexposed samples and the differences were noted. The weight difference was

obtained as described previously. The tensile strength of the samples was measured following ASTM D-882. The elongation was determined by measuring the increase in the head distance as the sample was stretched under tensile load to failure. Dielectric strength was determined using the standard method ASTM D-149.

4.3.3.6 *sleeving insulation*: The sleeving insulation samples were evaluated for both visual appearance and weight change as previously described.

4.3.3.7 *tape*: The tape samples were evaluated for visual appearance and weight change as previously described. The percent elongation was determined by measuring the increase in the head distance as previously described. The tapes were tested for break load using ASTM D-882. The same procedure was used as for the sheet insulation except that the break load achieved was reported instead of calculating a tensile strength.

4.3.3.8 *tie cord*: The tie cord samples were evaluated for visual appearance and weight change as previously described. The percent elongation was determined by measuring the increase in the head distance as previously described. The tie cords were tested for break load using ASTM D-882. The same procedure was used as for the case of the tape listed above.

4.3.3.9 *lead wire*: The lead wire samples were evaluated for visual appearance and weight change as previously described. The dielectric strength of the lead wires was measured by the following procedure. A four inch piece of copper wire was attached to a freshly prepared 1.25 x 2.5 cm (1/2 x 1 inch) piece of aluminum foil. The aluminum foil was then wrapped around the center of the lead wire. The copper wire was connected to one pole of a dielectric tester and the lead wire to the other pole. The voltage applied was increased at 500 V/sec until breakdown occurred. The breakdown voltage was then recorded.

4.3.4 reporting

The data acquired in this experiment is quite voluminous. For each test fluid there exists many experimental observations for each separate motor material. Furthermore, data is recorded for each material three different times; before aging, after 500 hours aging, and after the 24 hour bakeout.

Quantitative data was tabulated in the following manner. All weights were determined to 0.0001 grams, tensile strengths and break loads were determined to 0.02 kg. The burnout strength was measured in units of ± 1 sec, and percent elongations were determined to the nearest 1 %. The breakdown voltages in the dielectric strength tests were determined to the nearest 0.01 kV.

All of the qualitative and quantitative data is assembled into tables for each type of motor material and each test fluid. Each table contains the data for one type of material (magnet wire, tie cord, tape,...) and a single test fluid. Complete tables

Table III: Summary of the results from the aging of varnished, twisted pair magnet wires in R-143a.

R-143a with varnished twisted pair magnet wires (24 hrs. at 150°C)			
varnish type	% change weight	% change dielectric strength	% change burnout strength
U-475	0.012	-10.26	-41.36
Y-390	0.011	-30.98	1.06
ER-610	0.016	-14.57	-24.90
Y-833	-0.002	-2.78	-16.40
923	-0.066	26.18	12.06
ISO-800	0.011	8.43	-8.81

should contain the properties of the materials before and after aging, and also after the 24 hour bakeout. A sample data table summarizing the results of testing of R-143a with varnished, twisted pair wires is contained in Table III.

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- ⁶ Two motorized dielectric twist specimen fabricators were used, model MW-3 was used for the film coated magnet wire, model MW-3B was used for the other wires, the manufacturer was A/Z Tech Inc., Fort Wayne IN.

5. COMPATIBILITY OF REFRIGERANTS AND LUBRICANTS WITH ELASTOMERS

5.1 Purpose and Use

This procedure presents techniques to evaluate the compatibility of refrigerants and lubricants with various elastomers. The methods of aging the elastomeric species are described as well as the various tests performed on them to determine the extent of their interaction with the solvents. The data obtained from these tests will lead to a better understanding of the compatibility of elastomers with refrigerants and lubricants in actual AC&R systems.

5.2 Introduction

Elastomeric materials are commonly found in air conditioning and refrigeration equipment. If the system is to function properly it is vital that these components retain their integrity throughout the equipment's long lifetime. To ensure the reliability of newly manufactured systems, the long term compatibility of the elastomers with the new refrigerant fluids must be at least as good as the current combinations. The compatibility of elastomers with refrigerants is usually determined by submerging the elastomer in a fluid and assessing its behavior.¹⁻⁴ The indications of compatibility usually measured include hardness, tensile strength, weight, elongation and volume. The compatibility of elastomers with alternative refrigerants and lubricants can be estimated by comparing test results with the results of similar tests on the previous refrigerant/lubricant mixture.

5.3 Documented Test Method: University of Akron⁵

5.3.1 experimental conditions

Exposure of the elastomers to the test fluids was accomplished in two types of sealed test vessels. The vessels used for the refrigerant and refrigerant/lubricant mixture exposures were pressure sealed to contain the volatile refrigerant vapor. Vessels used for the lubricant exposures did not require such seals since they were performed at atmospheric pressure. The conditions of the aging process varied from room temperature (25°C) to 100°C, and from ambient pressure to 2100kPa (300 psi) depending on the test fluid. After 14 days of aging, qualitative and quantitative observations of the elastomers were performed to help to estimate the compatibility of the materials.

5.3.2 experimental

5.3.2.1 *materials*: To allow for a greater flexibility in the testing, a large number (95) of elastomers were mixed and cured on site. The base polymer was milled to break down the elastomer. Then, additives were blended in as desired. These materials were then all combined until a homogeneous mixture was formed. The mixtures were then cured into sheets according to the chemical producer guidelines. All cures of mixed elastomers took place to the 95% level. The cure characteristics of each compound were verified using an oscillating disk rheometer (ODR). Elastomers were further characterized by thermogravimetric analysis (TGA). The resulting elastomeric sheet materials were cut into round (2 cm) disk samples for use in the aging vessels. Commercial gasket materials, shipped from the suppliers, were also tested. Thermoplastic elastomers were tested as received if they were in sheet form, or were injection molded into sheets when they were received in pellet form.

5.3.2.2 *procedure*: There were three separate compatibility combinations examined. The elastomers were exposed to neat refrigerants, neat lubricants and refrigerant/lubricant mixtures. The weight, thickness, diameter, tensile strength and hardness of each elastomer was measured before the exposure testing was initiated.

The aging of elastomers with lubricants was performed in small 2 oz. glass jars. Two samples of the elastomer were placed in the jar, the lubricant was then added to cover the samples. The jar was then placed in an oven where it was heated to 60°C (140 F) for 14 days. Diameter measurements were made on one of the samples after one day of aging. Weight, thickness and diameter measurements were made on both samples after 14 days of aging. The lubricant adhering to the surface of the elastomer is removed from the elastomer by simply wiping it off thoroughly with a paper towel. Then, within 24 hours after removal from the test jars, the diameter, weight and hardness were remeasured. These additional tests were performed to evaluate effects of absorbed refrigerant.

The elastomer swell in neat refrigerant and refrigerant/lubricant solutions was measured in a pressure tight test vessel. A diagram of the test vessel is shown in Figure 4. The elastomers were placed into the test vessel. Stainless steel screens were placed between the samples so they could be differentiated from each other. The weight of the screens kept the elastomers under the level of the liquid refrigerant. The test vessel was closed using a hydraulic press to compress the die springs. The springs load a teflon O-ring which forms a high pressure seal.

The test vessel was then filled with refrigerant. After the cell was evacuated, refrigerant was allowed to flow in until the level of liquid refrigerant was above that of the samples. The final pressure reached in the cell therefore depended on the specific refrigerant being used, and was different for each refrigerant. The aging was then allowed to occur uninterrupted for 14 days at room temperature. In situ diameter changes were measured after one, three and 14 days using a traveling microscope. Two hours after removal from the test vessel, the diameter was again measured. One day after removal, both the diameter and the weight were remeasured.

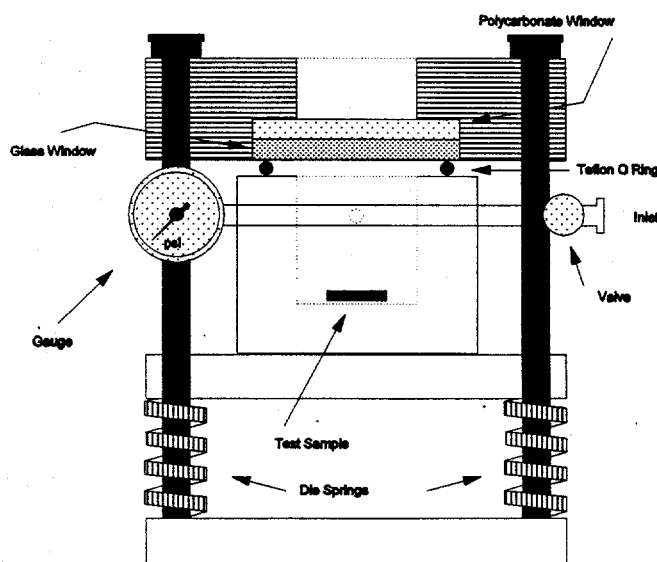


Figure 4: Test vessel for measurement of elastomer swelling in high pressure refrigerant or refrigerant/lubricant solutions.

Testing of refrigerant-lubricant mixtures was accomplished in a similar manner. To conduct the tests at constant pressure, different concentrations of refrigerant were needed. The tests were conducted at a temperature of 100°C and a pressure in the 1900-2100 kPa (275-300 psi) range. The concentration of refrigerant to use in the mixture was determined by constructing calibration diagrams of pressure vs. weight percent refrigerant. From these plots, the percentage of refrigerant in lubricant to produce the desired pressure was determined. The test vessels were prepared by adding the sample and the lubricant, evacuating the cell, and finally adding the calculated amount of refrigerant. The test vessel was placed in a heated bath where it aged at 100°C for 14 days. After the samples were removed from the test vessel the samples were weighed and measured, additionally, the tensile strength was determined. The decomposition of the polymeric material can be evaluated by comparing the tensile strength from the unaged and the aged samples.

5.3.3 analysis

5.3.3.1 dimensions: Weights were measured on an analytical balance and were recorded to the nearest 0.01 g. Thickness measurements were acquired using a thickness gauge to 0.01 cm. Diameter measurements were performed using a traveling microscope which measured distances to 0.01 cm. In situ measurements in the pressure sealed vessel were accomplished through the optical window shown in Figure 3.

5.3.3.2 hardness: Hardness was determined on a standard Shore A hardness durometer. A sample size of 2.5 X 5 cm (1 x 2") was necessary for accurate measurements, therefore it was difficult to measure the hardness of some of the 2 cm diameter elastomer samples.

5.3.3.3 tensile strength: Tensile strength was determined on a commercial instrument by standard methods. Tensile samples were cut from sheet materials using a die and punch.

5.3.4 reporting:

The experimental data should be contained in a table for each elastomer. It should include the measured weight change and diameter change from the initial conditions. All of the time dependent data should be included, as it can offer insights to the mechanism of any problems which may be observed. An example of the type of data which should be acquired is in Table IV, which shows how various refrigerants affect one commercially available neoprene type elastomer.

Table IV: Summary of data obtained from aging neoprene with several refrigerants for 14 days at room temperature.

Neoprene	measurements during aging				after removal from fluid		
	diameter change (%)			weight change (%)	diameter change (%)		weight change (%)
Fluid	1 day	3 day	14 day	14 day	2 hour	1 day	1 day
R-22	6.5	5.3	5.5	16.6	1.7	-0.5	0.5
R-32	2.0	1.6	0.8	2.8	-0.3	-1.4	-1.4
R-123	10.1	8.8	9.1	29.4	5.9	1.1	8.4
R-125	-0.4	0.1	-0.2	0.4	-0.7	-0.4	0.0

5.4 References

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6. COMPATIBILITY OF REFRIGERANTS AND LUBRICANTS WITH ENGINEERING PLASTICS

6.1 Purpose and Use

The procedure presented below provides methods for assessing the compatibility of refrigerants and lubricants with various types of plastic materials. The aging methods are described as well as the various tests which were performed to determine the extent of deterioration of the plastics. The data obtained from these tests can be used to estimate the compatibility of plastics with refrigerants and lubricants in a refrigeration system.

6.2 Introduction

Polymeric plastic materials are used in air conditioning and refrigeration systems. These materials must be compatible with the circulating refrigerant/lubricant fluid to preserve the proper operating conditions in the system. Under the high temperatures and long residence times which are present in a real system, plastics can decompose and deform quite readily. To be able to estimate the compatibility of plastics with the new refrigerants and lubricants, sealed vessel stability tests and dynamic creep tests were carried out.

Typically, compatibility with plastics and other polymeric materials is determined by sealing the material of interest in a vessel with a refrigerant and/or a lubricant. After the vessel is aged at an elevated temperature, the polymeric material is analyzed for decomposition.¹⁻⁴ Various methods can be used to determine the extent of the effect of the refrigerant and/or lubricant on the plastic material.

6.3 Documented Test Method: Imagination Resources, Inc.⁵

6.3.1 experimental conditions

Test samples of plastics were exposed to three different types of fluids 1) refrigerants, 2) lubricants, or 3) refrigerant/lubricant mixtures. Exposure of plastics to test fluids took place in sealed test vessels. After 14 days exposure time, the plastics were evaluated for tensile strength and percent elongation. Temperatures used during the exposures were from room temperature to 60°C, pressures ranged from atmospheric to 2100 kPa (300 psig). Dynamic, time resolved, creep measurements were determined for mixtures of 40% refrigerant in lubricant (by

weight) at room temperature for a 14 day test period.

6.3.2 experimental

6.3.2.1 materials: Since standardized tests were to be performed on the plastics, they were injection molded into specific size samples. This procedure was accomplished with a steel injection mold suitable for thermoplastic/thermoset plastics. Four ejector pins, located at opposite ends of the mold were used to improve the straightness of the molded test bars. The quality of the mold finish in the gage area of the test bar was 6F. To minimize slippage of the bars during testing, nine 0.005" molded nipples were also included on each side of the extension tabs. A sample test bar is shown in Figure 5. Thermoplastic materials were molded without any further modifications to the test mold.

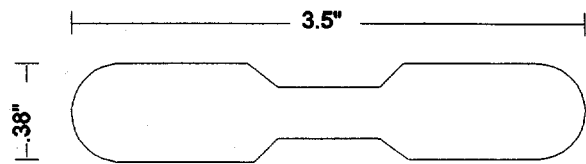


Figure 5: Shape of the test bars used for quantitative testing of plastic materials.

Slight modifications to the injection mold were necessary to mold thermoset phenolic materials. These materials require longer residence times under higher pressure and temperature. The mold itself was designed to accommodate both types of plastics. Allowance was made for the larger heater necessary for a phenolic thermoset curing procedure.

Some plastics cannot be molded in this manner as they require more specialized equipment. In such cases, test bars were fabricated using other methods. They were cut from sheets of the material, or, compression molded to the specified standard shape by the manufacturer.

6.3.3.2 procedure:

6.3.2.2.1 sealed vessel testing: The plastic materials were exposed to three different types of test fluids, lubricants alone, refrigerants alone and refrigerant/lubricant mixtures. Before any exposures of the plastics began, the physical properties were recorded, including measurements of the size, weight, tensile strength and percent elongation.

The exposures to neat lubricants took place at two temperatures, 60°C (140 F) and 100°C (210 F). The plastic material was immersed in the test lubricant in screw cap sealed vials under a nitrogen atmosphere for 14 days. Several visual observations were made after this period. The solution was checked for particulates and the plastic bar was checked for cracking, crazing or softening. Also, the color change (if any) was observed and all of the dimensions of the test bar were measured

(length, width, thickness). After the test piece was blotted dry of the lubricant, the weight was also measured.

Exposures of plastics to refrigerants were performed in stainless steel pressure tubes with a metering needle valve. The tubes were evacuated to 20-30 millitorr for several minutes and then chilled in ice water before they were filled with refrigerant. Approximately 20 grams of refrigerant was used in each trial. Aging was conducted at both room temperature and 60°C (140 F). After the 14 day exposure time, the refrigerant was exhausted (as liquid) into cooled, pre-weighed test tubes. The residues, if any, were concentrated by boiling off the refrigerant. The same observations on the physical state of the plastics were made as for the lubricant case. After a 24 hour waiting period, the weight was remeasured to determine the amount of refrigerant which outgassed from the plastic specimens.

The exposures of plastics to refrigerant/lubricant mixtures were all performed at 190-2100 kPa (275-300 psig) pressure. The amount of lubricant used was approximately equal to the mass of the plastic test sample. The test bars were aged in the refrigerant/lubricant mixture for 14 days at 150°C. After removal from the solution, the physical dimensions and weight of the test bars were again measured. The test bars were also pulled for tensile strength, and the percent elongation was determined.

6.3.2.2.2 *dynamic creep testing:* In an effort to understand the long term compatibility of plastics under stress, the creep behavior was determined for samples exposed to refrigerant/lubricant mixtures. The creep test was designed to evaluate the short-term resistance of the plastic materials to stress corrosion cracking. Creep was measured by applying a force to the plastic sample and following the amount of extension with time. In these experiments, creep was studied for plastics submerged in a mixture containing a lubricant with 40% by weight of the selected refrigerant at room temperature. The correct amount of refrigerant to add was determined with a calibration curve of refrigerant concentration vs. pressure at 150°C.

Figure 6 shows a schematic of the test apparatus developed for these measurements. The plastic test bars were held in screw clamped stainless steel jaws. The clamping procedure consisted of first centering the test piece between the jaws and firmly squeezing the plastic tabs. One hour after the initial tightening, the jaws are retightened to take up any cold flow which may have taken place in the jaw area. Before applying the load to the plastic, the test bars are immersed in the lubricant in a 100 millitorr vacuum for several hours to remove any air. A previously determined amount of liquid refrigerant is then added to the bottom of the test cylinder through a needle valve.

Static force was applied to the sample at 25% of the previously measured ultimate tensile load. This load was sufficient to provide a large range of creep in a 14 day test period. The load was applied by slowly releasing a dead weight. When the plastic part was loaded, it rapidly deformed. This deformation was measured at selected time intervals during the exposure. The distance the tensile plunger travels downward was measured by a linear variable displacement transducer (LVDT). Measurements continued as the plastic test piece continued to deform, or failure occurred.

Ideally, creep tests require months or years to complete. In this case, creep data was obtained in only 14 days. This scheduling was necessary to complete the project in a reasonable amount of time. However, it is possible that the greatly accelerated schedule caused this experiment to measure short-term creep instead of long-term creep, which is actually the quantity of interest. However, the test did meet the objective of determining the resistance to stress corrosion cracking.

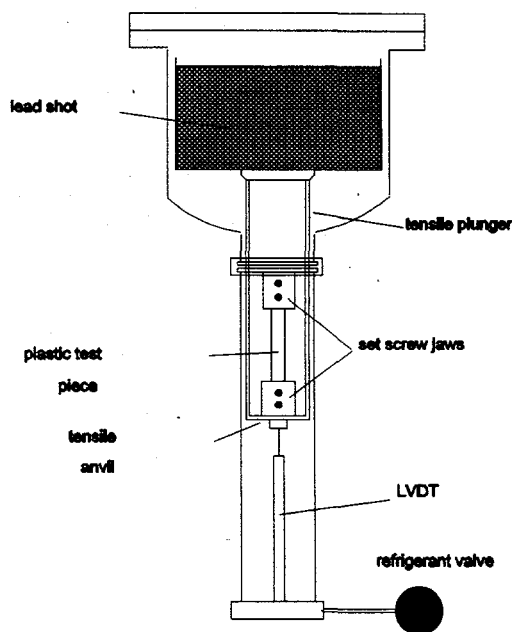


Figure 6: Test apparatus for determining creep behavior of plastics exposed to refrigerant/lubricant mixtures.

6.3.3 analysis of data:

6.3.3.1 *dimensions:* Visual analysis of the appearance of the exposed plastics was determined as described. The size of the test bars were measured using micrometers to 0.2 mm. Weights were determined on an analytical balance to 0.01 grams.

6.3.3.2 *tensile properties:* Tensile tests were conducted using an Instron Model 1122. The plastic test pieces were placed vertically in the test grips. The crosshead movement was set at the specified ASTM D 678 pull rates (between 0.2 and 1.2 mm/min). Percent elongation and ultimate tensile were both determined from the measurements made on the Instron device. Percent elongation is the total change in the length divided by the 25.4 mm (1") length of the reduced section. The change in length is determined by the amount the crosshead moves from the original position

until the plastic bar breaks. Ultimate tensile is the maximum recorded load divided by the original cross sectional area of the plastic test piece.

6.3.3.3 creep measurements: In the creep measurements, the elongation of the plastic test bar was measured as a function of time. Since these measurements require great precision and take 14 days, extremely sensitive, long term noise free electronics were required. The measuring device was sensitive to changes in length of 4×10^{-3} mm (1.5×10^{-4} inches).

Specifically, the stress (σ) applied to the test bar is,

$$\sigma = F/A. \quad (2)$$

Where F is the applied force and A is the cross sectional area across which the force is applied. The measured quantity which changes in time is the strain (ϵ), this is the normalized deformation per unit length,

$$\epsilon = \Delta L/L. \quad (3)$$

Where ΔL is the measured amount of deformation which occurs when a force is applied to the material and L is the length of the material. Typically, stress/strain data are reported in terms of the modulus of the material. The creep modulus (E) is defined by,

$$E = \sigma/\epsilon. \quad (4)$$

Since both σ and ϵ are determined from experimental measurements, the modulus is easily determined.

Table V: Compatibility data obtained when a phenolic plastic is aged at 150°C for 14 days.

test fluid	total acid number	tensile % change	elongation % change
air		8.4	-24.8
POE-Branched (no refrigerant)	19.9	5.0	-33.0
POE-Branched (dehydrated, no refrigerant)	1.7	5.1	-30.0

6.3.4 reporting

Data were reported for the two separate experiments. First, the physical properties were compared before and after exposure to the three different types of test fluids. Visual observations of the color and condition of the test bars were made. Measurements of the tensile strength and percent elongation before and after exposure were also reported. Table V shows an annotated example of the type of data which were obtained.

Second, time dependent creep data were reported for the plastics exposed to a 40% refrigerant/lubricant mixture. These take the form of reporting the modulus of the plastic as a function of exposure time. Figure 7 shows sample creep data obtained for several different plastics in a R-134a/branched acid POE mixture.

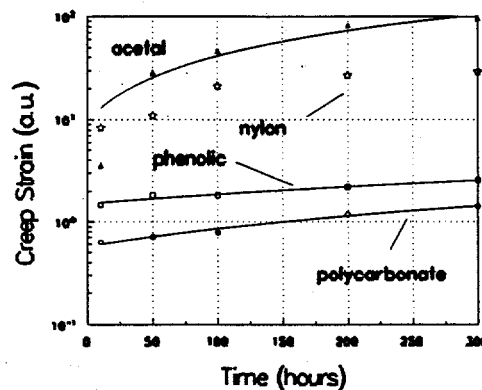


Figure 7: Creep data for several different plastics in a R-134a/POE mixture.

6.4 References

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7. SEALED TUBE COMPARISONS OF THE COMPATIBILITY OF DESICCANTS WITH REFRIGERANTS AND LUBRICANTS

7.1 Purpose and Use

This procedure presents techniques to evaluate the compatibility of refrigerants and lubricants with various desiccant materials. The methods of aging the desiccant materials are described as well as the various tests performed to determine the level of decomposition of the desiccants, refrigerants and lubricants. These tests will provide data which will lead to a better understanding of how refrigerants and lubricants will interact with desiccant materials in working systems.

7.2 Introduction

Desiccant materials are used in filter driers to remove water and other contaminants from the circulating refrigerant/lubricant. The proper selection of the desiccant material in the drier is essential to long-life of the refrigeration equipment. These materials are normally evaluated by exposing the desiccant to a refrigerant and/or lubricant at an elevated temperature. After aging, testing on the desiccant is performed to determine its effectiveness.¹⁻⁴ Testing is also done on the refrigerant and lubricant to see if they have chemically decomposed.

7.3 Documented Test Method: Spauschus Associates, Inc.⁵

7.3.1 experimental conditions

Exposure of the desiccant materials to the test fluids (refrigerant/lubricant mixtures) was performed in sealed glass tubes following ASHRAE/ANSI Standard 97-1989. The tubes contained desiccant, a metal catalyst, refrigerant and lubricant and were heated at 149°C (300 F) for 28 days before being analyzed. Tubes were prepared with two levels of moisture, 1000 ppm and less than 50 ppm.

7.3.2 experimental

7.3.2.1 sample preparation: The glass test tubes were cleaned by rinsing with deionized water, followed by two rinses with methanol and a final rinse with toluene. The tubes were dried at 175°C.

The metal catalyst coupons were prepared by punching 3.3 x 19.3 mm coupons from thin sheets of steel, aluminum and copper. The coupons were held together by an aluminum wire such that the steel and copper were separated by the aluminum.

The desiccant samples were activated at 260°C for four hours prior to sealing in the tubes. Desiccant samples in bead form were weighed to within one bead of 0.5 grams. Core-type desiccants were cut into small pellets prior to activation. Three or more pellets were chosen and weighed to yield the specified 0.5 grams.

7.3.2.2 experimental procedure: The desiccant and metal catalyst coupons were placed in the tube. A small wad of glass wool was inserted on top of the desiccant to keep the lubricant and desiccant from violently boiling when the tube was later opened for analysis. The tube then was necked down to a size through which a standard cannula will fit. Next, 1.0 ml of oil was added accurately using a syringe and cannula. The tube was then evacuated to 30 microns. Next, accurate charging of the refrigerant, and moisture (if required) was performed using a calibrated gas handling system. Finally, the tube neck was sealed and annealed. This procedure minimized oil contamination of the seal area and produced a minimally stressed glass seal. Three tubes were made for each moisture condition, desiccant and refrigerant/lubricant combination.

Each test tube was placed into a drilled hole in a large aluminum block which was heated in an air-circulating oven at 149°C (300 F) for 28 days. The aluminum block served to protect the tubes in the event that one breaks and also provided a large thermal mass to maintain a stable temperature throughout the aging process.

7.3.3 analysis

7.3.3.1 visual: Visual inspections were made on each tube after 14 days and 28 days of aging. Each tube was compared to standard color references, which provided a numerical value for the amount of color change, from colorless to black. Similarly, formation of solid particulates and copper plating on the steel catalyst were noted. The appearance of the metal catalysts and the desiccant were also noted.

7.3.3.2 refrigerant: The quantitative degree of refrigerant decomposition was determined by gas chromatographic (GC) analysis on the vapor phase from one tube of each group of three. The vapor phase was captured in an evacuated gas handling system and introduced to the GC helium effluent stream via a gas sampling valve. The GC used was a thermal conductivity detector instrument with a Poropak "Q" column

of 2.44 m length. The method utilized is the same as described in Chapter 2 of this report.⁶

Aged sealed tubes to be analyzed were connected to the gas handling manifold with a "tube breaker" assembly. After freezing of the tube contents in liquid nitrogen, the tube tips (previously scratched with a file) were broken off. The tubes were then warmed slowly and all volatile tube contents were expanded into a gas manifold. A sample of gas from the manifold was injected through a gas sampling valve into the GC column. The vapor pressure of the gas sample normally was in the 100 to 200 millitorr range, depending on the vapor pressure of the test refrigerant.

The GC was operated under the following conditions:

Column and injector temperatures: 120°C (250 F)	Carrier gas: helium
Detector temperature: 200°C (390 F)	Gas flow rate: 27 ml/min
Detector current: 150 mA	Sample size: 500 µl

Quantitative GC results were obtained on a digital integrator. Percent decomposition was calculated from the peak area ratios for each species. This assumes that the detector had equivalent sensitivity to all of the species of interest. Decomposition was only calculated in those cases in which the decomposition product was identifiable in the chromatogram. Additional peaks occurred in some chromatograms from decomposition of the lubricant, species such as CO and CO₂. These should not be considered as refrigerant decomposition products.

7.3.3.3 lubricant: The total acid number was determined for one tube from each group of three. The procedure used follows that for ASTM 664. The method is slightly modified to accommodate the small 1ml sample size from the sealed tubes by reducing the alcoholic KOH titrant concentration from 0.1 Normal to 0.01 Normal. This yields sufficient sensitivity to determine acid numbers down to 0.1 with the 1 ml sample size.

7.3.3.4 halide and acid anions: Anion concentrations are determined for the tube liquid phase and desiccant by ion chromatography (IC).⁷ After aging the desiccant, the solid phase from one tube was separated from the liquid and vapor phases. The desiccant (solid phase) was washed with toluene. This toluene wash was added to the liquid phase from the tube, which was then extracted in deionized water for 24 hours. The washed desiccant was also extracted in deionized water. The aqueous phases from these two extractions were then analyzed by IC for fluoride

ion, chloride ion, organic anions (such as acetate, butyrate, formate) and inorganic ions (such as nitrate, sulfate).

In the development of this method, acidic and basic aqueous solutions were studied as extractants. Both caused degradation of some of the lubricants, producing the same organic ions which were formed during the test exposures. Methanol was also tried as an extractant, but excluded because it caused severe interference in the IC chromatogram. Water was determined to be a satisfactory extractant through secondary studies with test solutions of hexanoic acid (a weak acid).

Table VI: Summary of data obtained from the sealed-tube compatibility testing of several desiccant materials with CFC-12/mineral oil.

desiccant type	color	change in crush strength	TAN (mg KOH)	F in liquid	F on desiccant	organic acid on desiccant
Molecular Sieve (4A)	2.5 4.5	-23%	<0.1	4	670	2600
Molecular Sieve (3A)	2.5 4.5	-10%	1.3	41	1600	1900
Alumina	2.5 3.0	-20%	<0.1	3	10	1546
Silica	2.5 2.5	-33%	<0.1	8	335	10

- color values listed at 14 and 28 days

7.3.3.5 desiccant crush strength: Desiccant crush strength was determined first on freshly activated material, and then on material that had been aged. The change in crush strength was the data of most interest. For bead-type materials, the crush strength was determined for at least ten individual beads, with the average and the standard deviation reported. For core type desiccants, the average crush strength was determined from the few available samples. The method uses a digital force

gauge which displayed the peak force achieved while the specimen was slowly pressed between two parallel plates.

7.3.4 reporting

The experimental data is contained in tables. These included all of the measured data including visual observations, crush strength, percent refrigerant reacted, total acid number and ion concentrations from both the liquid phase and the desiccant. Photographs or videotape of the sealed tubes can be used to record their appearance after aging. An example of the type of data which should be obtained is included in Table VI.

7.4 References

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COMPLIANCE WITH AGREEMENT

There were no deviations from the work required for this report.

PRINCIPAL INVESTIGATOR EFFORT

The principal investigator (Michael Hawley) completed his responsibilities with respect to this project.