



00 COMMONWEALTH DRIVE, WARRENDALE, PA 15096-0001 U.S.A.

HFC-134a Lubricant Compatibility



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**HFC-134a LUBRICANT
COMPATIBILITY**

**SAE COOPERATIVE
RESEARCH PROJECT**

FOREWORD

This report evaluates the chemical compatibility of mixtures of twelve (12) lubricants which were chosen by ten (10) major compressor manufacturers for use with HFC-134a in mobile air conditioning (MAC) systems.

The purpose of this work was to assist in developing the technology to recycle HFC-134a used in MAC systems. HFC-134a is a refrigerant that will be phased in as a replacement for CFC-12 in MAC systems as early as the fall of 1991. In order to have confidence in the use of recycled HFC-134a refrigerant, the trace amounts of MAC compressor lubricants remaining in the recycled refrigerant must be evaluated for their ability to cause MAC system damage. Since only trace amounts of lubricant (< 500 ppm by weight - see SAE J2210) are expected to be present in the recycled refrigerant, the only likely effect resulting therefrom might be chemical reactions between the lubricants and/or refrigerant. As a result, this work is limited to evaluating the chemical compatibility of lubricant mixtures with HFC-134a.

The following lubricants were tested:

ZK-10	SK-20 (PAG)
SUN PAG 56	ND-OIL8
Daphne Hermetic FD-1 (M)	K10
DGLF-118	ICI DGLF-196
S-20	GM9985752
Daphne Hermetic PR	APG1

Results of testing show that no chemical reactions occur as a result of intermixing these lubricants in the presence of HFC-134a. This testing provides a basis for confidence (for the above lubricants) that HFC-134a can be recycled without fear of MAC system damage due to trace amounts of compressor lubricants that might remain in the recycled refrigerant.

SAE will maintain the list of lubricants tested. If your organization plans to use a different lubricant(s) for production and would like to have this additional lubricant(s) tested and included on the list, please contact the SAE Cooperative Research Department by phoning Gary W. Pollak, Manager, or Marilyn Kennedy, Research Coordinator, (412-776-4841) for further details.



**HFC-134a LUBRICANT COMPATIBILITY
SAE COOPERATIVE RESEARCH PROJECT**

Final Report

**By: Hans O. Spauschus
Spauschus Associates, Inc.**

**Reviewed: SAE Office
Troy, Michigan
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HFC-134a LUBRICANT COMPATIBILITY PROJECT FOR SAE

INTRODUCTION

Mobile air conditioner manufacturers are on an accelerated schedule to phase out CFC-12 refrigerant to meet environmental requirements regarding ozone depletion. The alternative refrigerant, HFC-134a, requires use of a different class of lubricants than the mineral oils previously used with CFC-12. Each air conditioner manufacturer has carried out extensive test programs to approve one or several lubricants to meet the requirements of their equipment. The manufacturers requested SAE to develop and coordinate this investigation to assess concerns resulting from inadvertent trace mixing of lubricants during recycling or service operations and to assure compliance with J2099, Standard Of Purity For Recycled HFC-134a and J2210, HFC-134a For Recycled Equipment For Reliable A/C Systems.

The SAE Lubricants Compatibility Project was formulated under the leadership of an industry monitoring committee and managed by SAE. Spauschus Associates, Inc. was selected as contractor. Ten mobile air conditioner compressor manufacturers submitted a total of twelve lubricant samples for evaluation. Samples were submitted to SAE by the participating manufacturers, coded to eliminate their identity and forwarded to Spauschus Associates, Inc. for evaluation. A sealed tube test method, ANSI/ASHRAE 97-1989 was followed for preparing tubes containing 50/50 mixtures of all combinations of the twelve submitted lubricants. Each tube contained, in addition to the lubricant, an equal volume of HFC-134a and a metal catalyst comprised of steel, aluminum and copper. Each set of tubes was prepared in triplicate. The total number of sealed tubes required for the project was 234.

The sealed tubes were aged for 14 days at 347F (175C) and after aging, tube contents were carefully inspected for visual changes. To aid in tube inspection for color changes in the HFC-134a/lubricants mixtures, a series of color standards were prepared using iodine/methanol mixtures of different concentrations. Two tubes from each triplicate set were analyzed for fluoride ion content using a selective ion electrode method developed by Spauschus Associates, Inc. Fluoride ion provides a quantitative measure of HFC-134a reaction. The combination of visual observations and fluoride analyses provide the basis for mixture compatibility assessment in this report.

In response to urgency, the project was conducted on a fast-track basis and completed in a period of 3 1/2 months from time of receipt of the first lubricant samples.

HFC-134a LUBRICANT COMPATIBILITY

SUMMARY

A total of 12 candidate motor vehicle air conditioning lubricants from 10 compressor manufacturers have been evaluated for chemical stability with HFC-134a and metals. As well as the neat lubricants, 50/50 volume mixtures of all combinations of the lubricants were studied. The objective of this project is to determine whether inadvertent lubricant mixing during servicing will jeopardize system reliability.

The ANSI/ASHRAE test method 97-1989 was followed in preparation of sealed tubes containing the lubricant samples, HFC-134a and metal specimens. Accelerated aging was at 347F (175C) for 14 days. After aging, the tube contents were inspected for liquid color change, particulate formation, change in appearance of metals and copper plating. Contents of the tubes were then analyzed for fluoride ion as a quantitative measure of refrigerant/lubricant reaction.

Based on both visual examination and chemical analysis for fluoride ion, it is concluded that mixing of the lubricants will not deteriorate the chemical stability of the working fluids. It is noted that:

- the stability of HFC-134a/synthetic lubricants is much superior to that of the present CFC-12/mineral oil fluids
- differences in chemical stability of one lubricant to another, among those included in this project, are insignificant

Particulate formation during aging was observed for a number of the lubricants that were evaluated. The amount formed under the conditions of test was small. The practical significance of this observation is unknown. The mechanism is believed to be related to thermal stability limitations of synthetic base fluids and/or additives rather than lubricant/refrigerant reaction chemistry.

Miscibility with HFC-134a is an important property that differentiates one synthetic lubricant from another. General experience, outside of the work related to the present project, has shown that large differences in liquid phase separation temperatures can exist for different lubricants. Since no experience is available regarding the effect of mixing lubricants on miscibility with HFC-134a, it is recommended that the project be continued to determine this important property for the lubricants under consideration.

Compatibility with elastomers and polymers, in our judgement, should not be significantly different from one lubricant to another provided they represent the same chemical family. Therefore mixed lubricant polymer compatibility is not anticipated as a potential problem.

EXPERIMENT DESIGN, MATERIALS AND PROCEDURES

EXPERIMENT DESIGN

The work statement for this project called for sealed tube stability tests on the neat lubricants and 50/50 lubricant mixtures with HFC-134a and metals. A total of twelve lubricants were submitted which resulted in a test matrix consisting of 66 mixtures and 12 neat lubricant samples, as shown in Figure 1. Since triplicate tubes were prepared for each lubricant sample or mixture, a total of $78 \times 3 = 234$ sealed tubes were prepared for aging and analysis.

MATERIALS

One liter lubricant samples were submitted to SAE by the participating companies in clean glass bottles provided for these tests. Samples identification was coded by SAE and blind, coded samples were shipped to Spauschus Associates, Inc. for evaluation. Sample identification, for purposes of this report, is as follows:

Spauschus / SAE Sample Code

A = CL-0010
B = CL-0020
C = CL-0030
D = CL-0040
E = CL-0060
F = CL-0070
G = CL-0080
H = CL-0090
I = CL-0100
J = CL-0110
K = CL-0050
L = CL-0120

Special precautions were observed regarding storage and sampling for analysis to avoid contamination of the lubricant samples.

A new thirty pound cylinder of HFC-134a was obtained and reserved for this project. Vapor phase and liquid phase samples were analyzed by gas chromatography. Purity of the vapor was determined to be above 99% (V/V basis), while the liquid phase purity was 99.4% (V/V). Liquid sample HFC-134a was used in preparation of all of the sealed tubes. Details of the gas chromatographic procedure and results are provided in the Appendix to this report.

Standard metal specimens consisting of 1/8 inch by 3/4 inch coupons of steel and copper, separated by aluminum shims, were used as catalysts for the sealed tube experiments. Changes in appearance of the metals after aging provide visual evidence of corrosion, film formation and copper plating.

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FIGURE 1. EXPERIMENTAL DESIGN

SAMPLE	NEAT	MIXTURES											TOTAL #
#1	A	AB	AC	AD	AE	AF	AG	AH	AI	AJ	AK	AL	12
#2	B	BC	BD	BE	BF	BG	BH	BI	BJ	BK	BL		11
#3	C	CD	CE	CF	CG	CH	CI	CJ	CK	CL			10
#4	D	DE	DF	DG	DH	DI	DJ	DK	DL				9
#5	E	EF	EG	EH	EI	EJ	EK	EL					8
#6	F	FG	FH	FI	FJ	FK	FL						7
#7	G	GH	GI	GJ	GK	GL							6
#8	H	HI	HJ	HK	HL								5
#9	I	IJ	IK	IL									4
#10	J	JK	JL										3
#11	K	KL											2
#12	L												1
Grand Total Samples													78
Grand Total Tubes													234

PROCEDURES: SEALED TUBE PREPARATION AND AGING

Heavy-wall sealed tubes were prepared according to ASHRAE/ANSI 97-1989. The metal catalysts, described above, were carefully prepared for uniformity of size and cleanliness of surface. The coupons were introduced into clean tubes which were constricted near the top. One milliliter of lubricant was introduced below the constriction by means of a syringe; for the lubricant mixtures, 0.5 ml of each lubricant was introduced. The tube and contents were then evacuated on a gas handling system of calibrated volume. HFC-134a was introduced into the system and 1.21 grams of the refrigerant was condensed into the sample tube using liquid nitrogen as cooling medium. The tube was then sealed off at the constriction and was ready for oven aging.

The sealed glass tubes were aged in aluminum blocks which served as heat sink and contain glass in the event of an explosion. After aging 14 days at 347F (175C), tube contents were inspected for visual changes in appearance of liquid and metals. After recording visual results, two tubes of each set were analyzed for fluoride using a specific ion electrode method, as described in the Appendix to this report. Percent refrigerant reaction, calculated from the fluoride ion concentration, provides a quantitative measure of stability of the HFC-134a/lubricant combination, as discussed in the next section of this report.

RESULTS: VISUAL INSPECTION

Results of visual inspection of the sealed tubes after aging are provided in the next thirteen pages; one page for the neat lubricants and twelve pages for the mixtures. There is redundancy in the mixture data in that, for example, lubricant mixture AB is also reported as BA. This arrangement facilitates comparisons of all mixtures containing lubricant A with all mixtures containing lubricant B, etc. It will also provide SAE with a simple means of distributing results without disclosing company proprietary information.

Colors of the lubricant/HFC-134a mixtures before and after aging were determined by side-by-side visual comparison with a set of liquid color standards prepared by sequential 50% dilutions of an iodine methanol solution. Appearance of the color standard ranges from colorless (1.0) to tan/yellow (5.0) to dark brown (11.0). Color differences from standard 1.0 to 2.0 are barely discernable, so some judgement is involved in the ratings provided on each of the data sheets.

In addition to color change, observation were made for clarity of the liquid phase, particulate formation, color or brightness change of metal surfaces and for copper transfer to the steel surface, which gives an indication of the potential for copper plating in compressors or systems which use copper as a structural material

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VISUAL CHANGE ON AGING 14 DAYS AT 175C (347F)*

NEAT LUBRICANTS WITH HFC-134a AND METALS

Lube.	A	B	C	D	E	F	G	H	I	J	K	L
Before Aging	1.0	1.5	1.0	1.0	1.0	1.0	2.0	2.5	2.0	1.5	1.0	1.0
After Aging	2.0	2.0	1.0	1.5	1.0	1.0	3.0	3.0	2.0	1.5	3.0	1.0
	2.0	2.0	1.0	1.5	1.0	1.0	3.0	3.0	2.0	1.5	3.0	1.0
	2.0	2.0	1.0	1.5	2.0	1.0	3.0	3.0	2.0	1.5	3.0	1.0
Color Change	1.0	0.5	0	0.5	0**	0	1.0	0.5	0	0	2.0	0

* Color change with iodine reference tubes for comparison

** Color change in one of three replicate tubes

ADDITIONAL COMMENTS BASED ON VISUAL OBSERVATIONS

- For tubes A1-3, B1-3, C1-3, F1-3, G1-3, H1-3, I1-3 and L1-3
Lubricant clear
Copper bright pink
No corrosion of steel
No visible copper transfer
No particulates in liquid
- For tube E-3
Darkening of steel
Darkening of lubricant
For tubes E-1, E-2
No change on aging
- For tubes D1-3, J1-3
Lubricant translucent blue
Few small soap-like particulates
- For tubes K1-3
Small and few large brown-white particulates; tan deposit on bottom of tubes

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VISUAL CHANGE ON AGING 14 DAYS AT 175C*
LUBRICANT A MIXTURES WITH HFC-134a AND METALS

Lube.	A	AB	AC	AD	AE	AF	AG	AH	AI	AJ	AK	AL
Before Aging	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
After Aging	2.0	2.0	1.0	2.0	2.0	2.0	2.0	3.0	4.0	2.0	3.5	3.0
	2.0	2.0	1.0	2.0	2.0	2.0	2.0	3.0	4.0	2.0	3.5	3.0
	2.0	2.0	1.0	2.0	2.0	2.0	2.0	3.0	4.0	2.0	3.5	3.0
Color Change	1.0	1.0	0	1.0	1.0	1.0	1.0	2.0	3.0	1.0	2.5	2.0

* Color change with iodine reference tubes for comparison

ADDITIONAL COMMENTS BASED ON VISUAL OBSERVATIONS

- For tubes A1-3, AD1-3, AE1-3, AF1-3, AH1-3, AJ1-3, AK1-3, and AL1-3:
Lubricant clear
Copper bright pink
No corrosion of steel
No visible copper transfer
No particulates in liquid
- For remaining tubes, only difference was formation of dispersed particulates:
AB1-3 and AI1-3 Many small white particulates
AG1-3 Few small white particulates
AC1-3 Few small brown particulates

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VISUAL CHANGE ON AGING 14 DAYS AT 175C*
LUBRICANT B MIXTURES WITH HFC-134a AND METALS

Lube.	B	BA	BC	BD	BE	BF	BG	BH	BI	BJ	BK	BL
Before Aging	1.5	1.0	1.0	1.0	1.0	1.0	2.0	2.0	2.0	1.5	1.0	1.0
After Aging	2.0	2.0	1.0	1.5	1.5	1.5	2.0	2.5	3.0	2.0	3.0	2.5
	2.0	2.0	1.0	1.5	1.5	1.5	2.0	2.5	3.0	2.0	3.0	2.5
	2.0	2.0	1.0	1.5	1.5	1.5	2.0	2.5	3.0	2.0	3.0	2.5
Color Change	0.5	1.0	0	0.5	0.5	0.5	1.0	0.5	1.0	0.5	2.0	1.5

* Color change with iodine reference tubes for comparison

ADDITIONAL COMMENTS BASED ON VISUAL OBSERVATIONS

- For tubes B1-3, BE1-3, BG1-3 and BH1-3:
Lubricant clear
Copper bright pink
No corrosion of steel
No visible copper transfer
No particulates in liquid
- For remaining tubes, only difference was formation of dispersed particulates:
BA1-3, BC1-3, BD1-3 Many small white particulates
BF1-3 Few large brown/white particulates
BI1-3 Clear gel deposit on tube bottom
BJ1-3 Cloudy; many small white particulates
BK1-3 Many small to large brown particulates
BL1-3 Very few large gray particulates