Influence of Residues From Aluminum Brazing Processes on Refrigerating Systems Involving R-134A and PAG Lubricants

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ABSTRACT

Aluminum is recognized as a construction material for refrigeration systems. The choice of joining techniques is receiving significant interest in that respect. Each brazing or soldering process produces residues like soot oxides or flux.

The Nocolok® flux brazing process is widely used for the production of automotive heat exchangers. The flux that is used for that process (general formula: $K_{1\text{-}3}AlF_{4\text{-}6}$) remains on the surface of the joined parts after production. A test rig has been erected to examine possible interactions between the flux residues and the refrigeration system, involving the refrigerant, the lubricant and also the incorporated components. The stability of R-134a in presence of Nocolok flux residues and the influences of these residues on the refrigeration cycle are described.

As a result of a detailed literature search, the paper will also give a general overview on the role of different contaminants in refrigeration cycles.

INTRODUCTION

Aluminum brazing is now the preferred process for the production of automotive heat exchangers. Due to the nature of the Nocolok flux brazing process, flux residues remain on the brazed parts after production as a very thin adherent film with a thickness in the range of 1-2 μm. For certain techniques of fluxing small amounts of this residue may be present on the internal surfaces of the heat exchanger and by that means in contact with the media flowing through the heat exchanger. When joining tube to tube connections by Nocolok flame brazing, the presence of flux residues on the inside of tube cannot be avoided .The layer of flux residue is non-hygroscopic, non-corrosive and insoluble in aqueous media.

The refrigerant/oil mixture which circulates through an automotive air conditioning unit is complex. The combination of R-134a and a polyglycol lubricant, which can be regarded as a standard for automotive air conditioning, is a fairly strong solvent due to the polarity of the two substances. The composition of the refrigerant/oil mixture varies within the refrigeration cycle and can not be predicted exactly. Further contaminants are to be expected within the cycle such as water and wear from the compressor. When brazing heat exchanger cores in a continuous furnace, it is possible that some flux residues will be in contact with the refrigerant. However it is more likely that the refrigerant will be in contact with flux residues from flame brazing operations.

Regarding this complicated system, it appears to be appropriate to establish a scientific proof of the stability of the refrigerant/oil system with the flux residues. The research program that is outlined in figure 1 has been started to deliver such a proof. Starting from the open literature various known influences and reactions caused by impurities have been evaluated and summarized. The results have been used to design a test rig for the stability analysis. Regarding the fact that moisture and acidity have great influence on possible reactions in the system, their content was gradually increased within the carried out tests. If during a worst case scenario as generated in **Test 4** no notable influence of Nocolok Flux residues on the system is detected, a sufficient proof of the compatibility of this joining technology for the refrigeration industry is given.

LITERATURE RESEARCH

In the following, the effects of impurities in general are described on the basis of literature research. This chapter represents a summary of a detailed literature research given by **König /1/.** Impurities include: production-related residues, residues from solder and screwed joints, products of oil reactions after water absorption as well as aging as a result of thermal stress and abrasion.

Refrigerant/oil reactions were already studied in the early 60s, though always in connection with the refrigerants R-11, R-12, R-22 and others. These earlier examinations already ascertained the tendency that

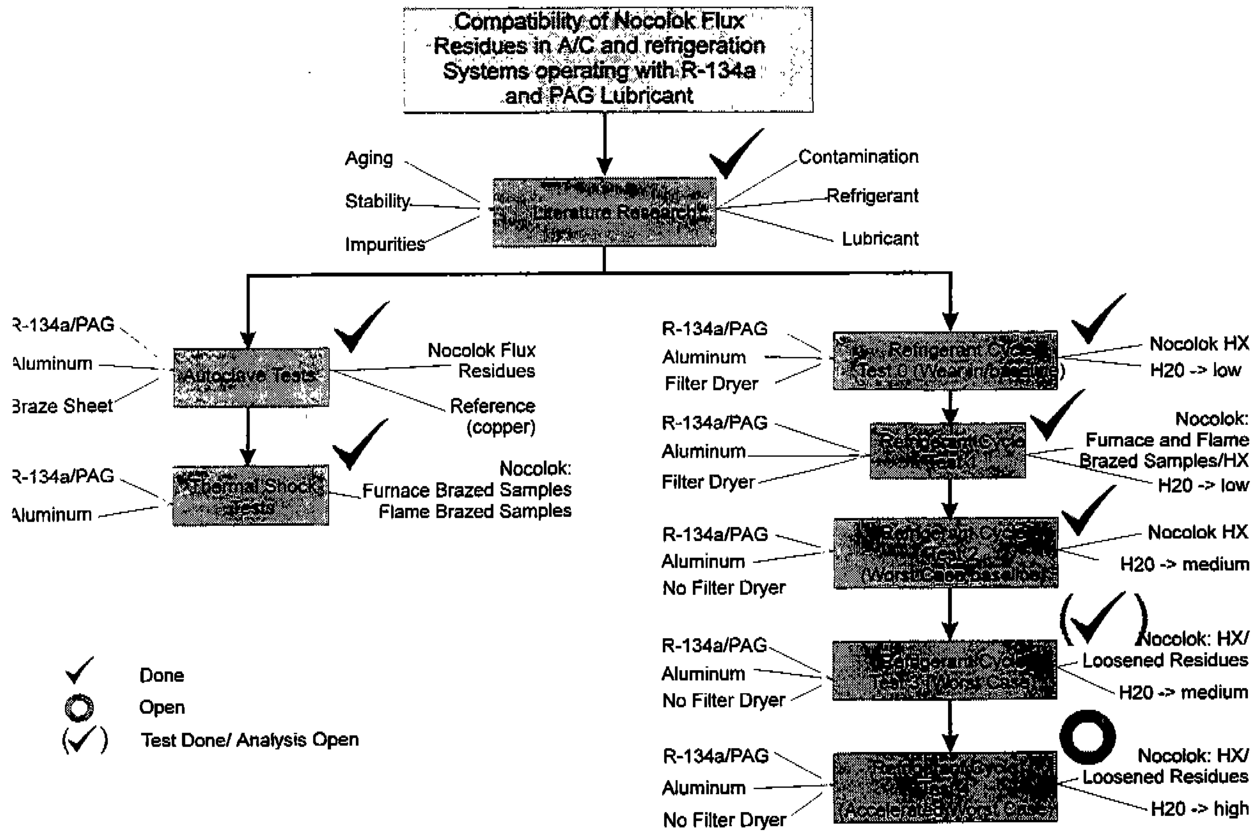

Figure 1: **Research Program: Compatibility of Nocolok Flux in A/C and refrig. systems operating on R-134a and PAG**

the stability of oil/refrigerants is invariably enhanced when the fluorine content in the refrigerants is increased. **(ASHRAE 1965 /2/)**.

Parallel to the development of a reaction test between refrigerator oils and refrigerants, the aging of oil was described by **Hypko /4/** 1977 as a function of extinction, i.e. of the absorption spectrum. Also examined was the effect of copper and iron. While no larger deviations were established among the examined oils — based on polyethylene, polyalkylbenzene and mineral oil - in connection with copper, the aging of the examined mineral oil was found to intensify considerably with iron. An inhibiting effect was detected in the case of CU/polyethylene oils. Aluminum was excluded in this connection since reactions are to be regarded as being less critical than those with copper or iron. In his work, Hypko already described oil as being the "dustbin" of the refrigeration system.

Further examinations to ascertain the suitability of aluminum and the stability of refrigerants were carried out in 1978 by **Häntzschel et al. /5/**. A detailed examination of Al99.5 and AlMg3 in connection with R-12 was carried out in this study. The effect of the passivation of aluminum was compared on the basis of various oxidation processes. In particular the $AlCl_3$ reactions possible in connection with R-12 under high thermal loading of the refrigerant circuit up to temperatures of 150 °C are described. In this connection, transformations of R-12 into R-22 (2-3% transformation rate) known as the Spauschus Reaction and the oil aging, i.e. the color of the oil, are taken into consideration as indicators of thermal overloading. The results, based on reaction tests, are that chemical aging caused by aluminium and copper is less than with iron alloys. According to these tests, however, pitting corrosion can occur if there are chloride ions in the circulation.

The decomposition temperature of refrigerants and oils decreases in connection with metals. In contrast, **Pielke /6/** describes neutral behavior when aluminum is used.

The corrosion studies carried out by **Davies** (1984) **/7/** on Al 99.9 to determine the effect of sodium fluoride (NaF) in water and refrigerants (100ppm) showed that - as opposed to the occurrence of pitting corrosion in the event of free Cl ions - the presence of fluorine leads to a passivation of aluminum.

Fluorinated refrigerants require new polyester oils. **Synek /8/** reports that the tendency towards copper plating is only slight in the case of these oils and that loose metal content in the form of dusts and fine particles are to be regarded as significantly more problematic. The abrasion tests undertaken in this study did not produce results of any significance.

The influence of Nocolok flux residue on the stability of R-12/mineral oil, R-22/mineral oil and R-134a/mineral oil has been investigated by **Sitko et al. /9/** but at a time, when oils miscible with R-134a were not available. There was however no measurable effect of the flux on the stability of the tested refrigerant lubricant pairs. The report recommended further research as soon as miscible lubricants were widely available.

Tseregounis et al. /10/ examined the effect of more than 40 PAG additives on various friction pairings and also on aluminum. In comparison to the characteristics of the basic oil which was used, no improvement was found when additives were used on aluminum friction pairs.

The known results concerning the use of aluminum with ammonia as a refrigerant have only been of an inadequate nature up to the present. **Kauffeld/Burke/König /11/** provided an overview in this respect. It is currently unclear as to which effect oil and the water released therein have on aluminum in connection with NH_3.

The stability of the POE/R-134a combination with respect to insulating materials for hermetic engines was studied by **Kujak /12/**. He concluded that the same proportion of moisture in POE/R-134a has less effect than mineral oil/R22 combinations on various insulating materials.

The possibility of acids forming in the refrigerant circuit in the case of the new hygroscopic oils was discussed by **Blom /13/** for substitute and transitional refrigerants. The requirements on modern drying materials are described to the effect that, besides the water absorption, athe absorption of acids is also necessary. The formation of acids calls for the presence of free water in the circulation. Acids develop as a result of the decomposition of the oil and also invariably when the refrigerant is decomposed as a result of high thermal loading.

The effect of thermal loading on refrigerant/oil mixtures (PAG/R-134a) in bearings is described in great detail by **Ishida et al. /14/**. Very high levels of thermal loading were attained on a four ball tester; these enabled the decomposition — due to strong friction forces — of the refrigerator oil to carboxylic acid salts and also a local decomposition of R-134a at temperatures above 250 °C. The high circumferential speeds and the concentrated loading of the test pieces result to a certain extent in extremely high temperatures. Under these conditions, metal fluorides formed on the catalytically functioning rubbing surfaces.

Fahl and **Synek /15/** examined aluminum as a structural material in connection with POE oils. They established the occurrence of chemical reactions which take place subject to the presence of high water contents and lead to "corrosion-like damage" to aluminum parts due the tendency of the POE oils to form acids by hydrolysis. However, in comparison with mineral oils, the POE oils generally display significantly superior lubricating properties as well as high levels of thermal and chemical stability. The formation of copper plating occurs less frequently and only in connection with high water contents. Neither silver nor zinc alloys should be used as solder. As opposed to PAG oils, cast aluminum and wrought alloys in connection with POE oils require wear improvers.

Field and **Henderson /16/** examined the corrosion behavior of various metals in contact with R-134a and POE lubricant at various moisture and organic acid levels. The examined ferrous metals (cast iron and steel) showed significant weight loss at elevated moisture and acid concentrations which was confirmed to be the result of corrosion. Aluminum and also copper in contrast showed no or only negligible interaction with the lubricant, the refrigerant or the contaminants.

Summarizing this literature research it can be stated that aluminum is a good option as a construction material for refrigeration systems regarding stability and compatibility with refrigerants and oils. The complexity of the influencing parameters to be examined leave little room for interpretation with respect to HFC refrigerants since only a few fundamental examinations have been carried out until now. Practically oriented tests are called for in this respect.

AUTOCLAVE TESTS

In order to exclude interactions of braze sheet alloys and Nocolok Flux with pure R-134a at elevated temperatures, autoclave tests with various material combinations where carried out. Apart from Aluminum (AA3003), Braze Sheet (AA4343) and Nocolok Flux Residues, regular copper was also analyzed for comparison. The methods of analysis included weight (table 1) and visual analysis of the test coupons, continuos monitoring of the pressure in the autoclaves and GC analysis of the refrigerant before and after the test (table 2). The vessels where heated to 300 °C in steps of 10 K. The pvT behavior of the refrigerant as monitored with a pressure manometer showed normal behavior.

Table 1: Weight Analysis of autoclave test coupons

Sample	Weight before test (g)	Weight after test (g)	Variation (%)
copper	11,6996	11,699	-0,005
AA3003	0,8349	0,8348	-0,012
AA3003 + Nocolok	0,8730	0,8730	0
AA3003 + AA4343 + Nocolok	0,5921	0,5923	0,034

Table 2: Gaschromatographic Analysis of R-134a before and after the Autoclave tests

Product	R-134a	R-134	R-143a
	(%)	(%)	(%)
R-134a (before the test)	99,97	0,018	0,0026
R-134a	99,98	0,024	-
R-134a + AA3003	99,98	0,019	0,0027
R-134a + AA3003 + Nocolok	99,97	0,026	-
R-134a + AA3003 + Nocolok + AA4343	99,97	0,026	-
R-134a + Cu	99,98	0,025	-

As a result it is stated that no interaction of AA3003, AA4343 and Nocolok Flux residues with R-134a was detected.

TEST APPARATUS

The design of the apparatus had to meet various requirements. In the first place the test rig had to resemble an automotive AC unit as closely as possible. On the other hand it was essential to choose components that can be disassembled in order to analyze and understand the processes inside the system. It was also necessary to minimize the amount of materials influence parameters in order to be able to detect possible sources of problems. This minimization on the other hand moves the system away from an authentic automotive AC unit. Finally it was essential to create an apparatus that is capable of handling different refrigerants in order to obtain comparative results with the measurements that are scheduled for the future. The test rig that was finally erected represents a good compromise of the above mentioned points.

A detailed description of the test rig is given by **Meurer, Lauzon and König /17/.**

RESULTS TEST 0 AND TEST 1

The wear in period and baseline test was chosen to be 500 hours which was in accordance with the compressor manufacturer. Compared to the virgin samples no significant differences with respect to the oil or refrigerant analysis were detected.

The length of the test period (test 1) was chosen to be 1000 hours with a condensation temperature of 75 °C (p_c = 24 bar) and an evaporation temperature of 2 °C. A GCMS analysis of the refrigerant after the test cycle showed that the composition remained unchanged. There were no additional peaks nor deletion of peaks in the spectrogram. The results of the analysis for the main compounds are shown in the Table 3.

The analysis of the refrigerant oil was carried out by the producer. Samples were taken after the wear in period and after the test cycle. The analysis of the virgin oil is also included. In addition to looking at viscosity, acidity and moisture content, other elements were analyzed as shown in Table 4. A number of other elements were analyzed for, but not detected in the virgin oil, after the wear in and after the test cycle, including: Pb, Fe, Zn, Al, Cu, Cr, Sn, Ag, Mg, Ni, Mo, Na, Ca, Ba, B, Mn, Ti and Li. Only minor change in color was detected and classified as normal among the 3 oil samples.

After the test cycle, the angle on coupon test specimens were carefully degreased. The weight loss or weight gain was determined for each of the 40 samples in the vessel of the liquid line and was identified to be negligible. The flame brazed tube to tube joints showed a slight weight loss which is suspected to origin from metal loss from the tube ends during coupling and uncoupling. All tube to tube joints were also longitudinally sectioned to examine the internal surfaces of the brazed joint area after the test period. There was no difference in the pre-test and post-test appearance of the internal surfaces.

Table 3: Refrigerant Analysis

Compound	Weight % Virgin	Weight % After Test 1
R-134a	**99,93**	**99,93**
R-143a	0,01	0,02
R-125	0,02	0,02
unsaturated comp.	0,04	0,03

Table 4: Lubricant Analysis

	Unit	Virgin	After wear in (500 h)	After test 1 (1072 h)
Viscosity (40°C)	mm^2/s	41	41	41
Acidity	mgKOH/g	0.11	0.12	0.10
H_20	mg/kg	2000	1900	210
Si	mg/kg	0	42	12
P	mg/kg	n.d.	832	850
K	mg/kg	n.d.	10	5
Cl	mg/kg	n.d.	n.d.	27

n.d. = not detected

Via X-ray diffraction traces of Al, K and F where found in the residues of the filters that where incorporated behind the test section. An identification of Nocolok Flux in the residues of the filter however was not possible. A detailed discription of statistical, spectroscopical and optical results of test 0 and test 1 is given in **/17/.**

RESULTS TEST 2 AND TEST 3

As quoted within the literature research, modern filter dryers not only remove moisture from the system but are also capable of extracting acids. The removal of the filter dryer during test 2 and test 3 and the operation of the test rig over 500h created far more aggressive conditions. In order to further accelerate possible interactions of the flux, R-134a and the lubricant, flux residues were mechanically scratched of test specimens and then injected into the refrigeration cycle (test 3). The test was also conducted without the residues (test 2) to record baseline conditions. The analysis of test 3 is currently carried out but the preliminary results give good reason to believe that also within these worst case conditions Nocolok flux did not contribute to any kind of interaction with the other materials in the refrigeration cycle. A detailed discussion of the results from test 2 and test 3 will be given in a further publication. We are also confident to be able to present this data at the conference in Purdue in July 98.

DISCUSSION OF TEST RESULTS (TEST 0 AND TEST 1)

Impurities in a refrigeration cycle are usually present from the manufacturing of the refrigeration components and generated from the operation of the refrigeration cycle. Impurities in a refrigeration cycle are usually trapped by such components as filters and dryers and to some extent by the oil itself.

The analysis of the refrigerant and the lubricant gave no reason to assume any interaction of the flux residues. There were minor changes in the concentration of the impurities of the refrigerant, but these are considered to be within the accuracy of the GC and therefore insignificant. There were in fact no changes in viscosity and acidity of the oil in this investigation. There was a significant drop in the moisture content because the filter dryer was present. Otherwise, no change in the oil performance was detected.

The negligible overall weight change and visual inspection of the brazed coupons give no reason to assume any interaction between the flux residue and the refrigerant / oil mixture.

The compressor analysis gave no indication of unusual behavior during operation. The wear of the parts due to friction can be identified as normal. The aluminum parts of the compressor showed no reaction or change whatsoever. A detailed discussion of the test results is given in **/17/.**

CONCLUSION

The stability of the mixture of R-134a and polyglycol lubricant as it is found in automotive air conditioners in the presence of flux residue as it is generated by continuous furnace brazing process was sufficiently proven by this work. Interactions were detected neither on the test coupons nor in the refrigerant or lubricant. All these components remained virtually unchanged during the test period. The operation of the test cycle was normal for the whole test period.

The fact that a comparably high amount of flux residue was exposed to the mixture of refrigerant and oil gives a good reason to believe that flame brazed tube to tube joints are also compatible with the mixture of R-134a and polyglycol lubricant.

OUTLOOK

Further work still has to be done to demonstrate the compatibility of flame brazed tube to tube connections under worst case conditions within refrigeration cycles. As shown in figure 1 the results however show that this is a promising technique that might make way for a broad use of aluminum in refrigeration and air conditioning industry. SOLVAY will continue its work on the analysis of the compatibility of Nocolok Flux with refrigerants and refrigerant oil systems respectively as illustrated in figure 1.

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