Compatibility of Refrigerant R134a and PAG Oil in the Presence of Post-Braze Flux Residue from Cesium-Containing Fluxes (NOCOLOK® Cs Flux)

Martin Schwiegel, Christoph Meurer, Hans-Walter Swidersky
Solvay Fluor und Derivate GmbH & Co. KG, Hanover (Germany)
Daniel C. Lauzon, Solvay Fluorides, Inc., St. Louis, MO (USA)

ABSTRACT
This paper summarizes and evaluates compatibility tests of the refrigerant Solkane® 134a and polyalkylene glycol lubricant (PAG oil) with post-braze flux residue from cesium-containing non-corrosive fluxes (NOCOLOK® Cs Flux).

NOCOLOK® Cs Flux contains 2% cesium. It can be used for all aluminum brazing applications (e.g., controlled atmosphere or furnace brazing [CAB], flame brazing, and induction brazing). The cesium-containing flux allows to braze aluminum alloys with a slightly higher magnesium content (i.e., up to 0.6 – 0.8%).

Several tests were performed to research possible interactions between cesium-containing flux residue and other substances present in a common residential A/C system. The work focused on potential interactions of flux residue with R134a refrigerant and the lubricant (PAG oil for R134a units). Main objectives were to exclude flux residue as a potential source for malfunctions of automotive A/C systems operating on R134a, and to establish scientific evidence for the stability of the refrigerant/lubricant system in the presence of cesium flux residue.

The equipment design for these tests resembled an automotive A/C unit with a CAB-brazed aluminum heat exchanger. Each of the tests ran for approximately 500 h, followed by a detailed analysis of all system components.

This work adequately proved the stability of mixtures containing R134a and PAG oil in the presence of flux residue from cesium-containing flux. It was also confirmed that cesium-flux residue generated by flame brazing processes shows no effect on the lubricant and the refrigerant.

1. INTRODUCTION
Since NOCOLOK® Flux brazed heat exchangers are in use with R134a/ PAG oil, questions of system stability and potential chemical interactions are of concern. Most of these heat exchangers are used in automotive A/C systems. Over the last few years, Solvay carried out a research project to identify any adverse interactions between the flux, the refrigerant and the lubricant [1] – [5].

This research program was the basis for further tests: a) stability of R407C with POE lubricant in presence of standard NOCOLOK® Flux [6], and b) stability of R134a with PAG lubricant in presence of NOCOLOK® Cs Flux [this paper].
2. SCOPE

The test program described in figure 1 was carried out to study interactions of NOCOLOK® Cs Flux residue in refrigeration and A/C systems operating with R134a and PAG oil.

All experiments were realized in a test rig that was previously used for the above mentioned stability tests of the couples R134a/ PAG oil and R407C/ POE lubricant in the presence of post-braze flux residue from standard NOCOLOK® Flux. The program consisted of four test cycles (test 0 – test 3) with gradually deteriorating operating conditions, up to the point in which a much higher amount of moisture was intentionally added to the system than normally accepted.

Sufficient proof for the compatibility of NOCOLOK® Cs Flux with the R134a refrigerant and PAG oil is established, when during the worst case scenario (test 3), no notable influence of NOCOLOK® Cs Flux residue on the system is detected, particularly not on the refrigerant/ lubricant mixture.

Based on the positive results of the referenced tests, it was decided to shorten the scope and to start with test 2.
3. EXPERIMENTS

3.1. TEST APPARATUS

A flow chart of the test rig is illustrated in figure 2:

![Flow chart of the test rig](image)

Figure 2: Schematic illustration of the system used for post-braze flux residue compatibility tests

Only a limited range of materials was selected for constructing the test rig. Besides sealing materials (mostly Teflon™ and paper sealing of the compressor), the entire system only consisted of Stainless Steel for the pipes, and aluminum for the evaporator as well as the condenser. These choices of component materials minimized the parameters potentially influencing the test results and thus reduced possible sources of problems.

The test section consisting of the filter and a sample vessel (see figure 2) was located in the liquid line. A combination of wire mesh- and dry powdered Stainless Steel was used as filter element. After the test, the filters were analyzed as indicators of chemical reactions or corrosion effects caused by the refrigerant/ lubricant/ NOCOLOK® Cs Flux mixtures.

In front and behind of the sample vessel, a series of filters – consisting each of one 40 micron filter followed by three parallel 15 micron filters – was placed sequential with the refrigerant flow. A new set of filter elements was build into this section for each test – to ensure comparable conditions.
Cleaning Procedure:
Prior to all experiments, the complete installation was thoroughly cleaned for two days by rinsing with propane 2-ol using a standardized procedure as described in [2].

3.2. ANALYTICAL METHODS

Refrigerant Analysis
Gas chromatography (GC) was used for the refrigerant analysis.

Lubricant Analysis
All lubricant samples were analyzed by the manufacturer [7]. PAG oil with a viscosity class of 46 was used for the tests.

The following parameters were characterized:

- Viscosity at 40°C – in [mm²/ s]
- Water content (by Karl-Fischer-Analysis) – in [mg/ kg]
- Acidity – in [mg KOH/ g]
- Trace impurities (by ICP) – in [mg/ kg]

Gravimetrical Analysis
The angle-on-coupon samples (see chapter 3.3), which were introduced in the sample vessel (figure 2) during test 2 and 3, were weighed before and after the tests (each coupon three times) to determine erosion or corrosion potentially initiated by exposure to the refrigerant/ lubricant mixture. The scale precision was ± 0.1 mg.

REM/ WDX – XRD Analysis
Before each test, the eight filter elements (see chapter 3.1) before and after the sample vessel, and the filter behind the compressor (in the high pressure part of the installation), were replaced with fresh units. These filter elements and the furnace-brazed samples, as well as some selected components (e.g. tubes) of the test rig were analyzed by scanning electron microscopy in connection with a wave dispersive x-ray scan (REM/WDX). Through this method, chemical elements on the sample surfaces can be characterized to identify potential corrosion effects.

Optical Analysis
To further determine corrosion or other chemical reactions of the installation, all tubes, vessels and parts of the compressor were visually examined. Photographic documentation of the internal tube surfaces was performed before and after the tests, using a macro lens with endoscopes.

Light microscope photos were also taken of the valve plate in the compressor.
3.3. SAMPLE PREPARATION

Angle-on-coupon Samples:

For tests 2 and 3, each 45 aluminum angle-to-coupon specimens were prepared as samples with NOCOLOK® Cs Flux. Brazing took place in a laboratory glass tube furnace – to generate joints similar to those in the standard manufacturing process for aluminum heat exchangers. A schematic illustration of the aluminum angle-to-coupons is shown in figure 3.

![Figure 3: Angle-on-coupon samples (top view and side view)](image)

Dimensions and materials for the angle-on-coupon samples were as follows:

- Aluminum coupon: Size: 25 x 25 x 0.4 mm
- Base material: AA 3003
- Clad material: 10% AA 4343 (7.5% Si)
- Angle: Size: 40 x 5 x 0.5 mm, with 45° angle
- Material: 99.5% Al
- Flux coating: 5 g/ m²
- Heating rate: 30°C/ min
- Brazing: 600°C

40 of the 45 coupons were introduced in the sample vessel on different levels. The remaining five coupons were used as a reference after the tests. The preparation of the angles-on-coupon samples is described in detail in [3].

Mechanically detached NOCOLOK® Cs Flux residue

Additional NOCOLOK® Cs Flux residue powder from a flame brazing experiment was obtained for the stability tests 2 and 3 – by mechanical removal from the joint areas after brazing. This residue was then incorporated into the sample vessel together with the coupons.

The following materials were used to prepare NOCOLOK® Cs Flux residue powder:

- Aluminum sheet - base material AA 3003
- Thickness: 1.5 mm
- Clad material: 10% AA 4343 (7.5% Si)
- Flux coating: > 10 g/ m²
- Brazing: 600°C for 2 minutes
This additional NOCOLOK® Cs Flux residue powder should maximize any potential interactions between the flux and the refrigerant and/or the lubricant. The presence of powder in the system increased the residue surface area in direct contact with the refrigerant/lubricant mixture. The quantity of NOCOLOK® Cs Flux residue powder placed into the sample vessel was about 0.5 g – each, for test 2 and 3.

3.4. TEST CYCLES

Worst case test (no. 2)

Based to the program as outlined in figure 1, a worst-case-test was performed for 500 h. Before the test, the installation was cleaned with propane 2-ol (see point 3.1 and [2]). 40 angle-on-coupon specimens were placed with 0.5 g NOCOLOK® Cs Flux residue into the sample vessel on different levels (see point 3.3). The sample vessel was located in the liquid line of the A/C cycle (figure 2).

Before and after the test, all coupons were cleaned in a propane-2-ol-ultrasonic-bath and weighed (see point 3.2: gravimetric analysis). The mean value of the total weight of all angle-on-coupons placed into the sample vessel was 38.2531 g.

After the test, no signs of corrosion could be found in the filter elements. Only a few loose NOCOLOK® Cs Flux residue grains were located in the pores.

The mean value of the total weight of all angle-on-coupons of test 2 (after cleaning) was 38.274 g – an increase of + 0.0209 g. No further optical surface analysis of the coupons was carried out after the test.

The lubricant exhibited a slightly higher neutralization number and water content. However, all values were still within acceptable ranges.

Accelerated worst case test (no. 3):

The conditions of the last test were comparable with test no. 2, except for some distilled water that was injected into the cycle. The injected quantity represented a water content of 500 ppm in correlation with the combined weight of refrigerant and lubricant. 0.5 g of NOCOLOK® Cs Flux residue and 40 angle-on-coupons were placed in the sample vessel of the liquid line. The experiment then ran for 500 h.

The mean value of the total weight of all angle-on-coupons added to the vessel in test 3 was 38,1403 g.

After this period, neither on the filter elements nor in the tubes or on the compressor valve plate any corrosion was observed.

The refrigerant analysis revealed no degradation. GC-analysis of the refrigerant sample showed a small but negligible increase of the impurities R143a and R125, when compared with the analysis of the original material.

A lubricant sample was analyzed by ICP for trace element contaminations (Pb, Fe, Zn, Si, Al, Cu, Cr, Sn, Ag, Mg, Ni, Mo, Na, Ca, P, Ba, B, Mn, Ti, and Li). No impuri-
ties were found. Consequently, it could be concluded that the compressor revealed no signs of abrasion during this test cycle.

The infrared (IR) spectra of the lubricant indicated some contamination with water (as could be expected) and minimal ester traces. For this lubricant sample no tests for viscosity-at-40°C, neutralization-number, and water-content were performed.

The optical analysis of the angle-on-coupon surfaces showed an unchanged top (i.e. surface with flux residue and brazed angle) when compared to the reference coupons (figure 4). The coupon bottom was rougher when compared with the reference (figure 5). The mean value of the total weight of all angle-on-coupons of test 3 was 38.1534 g – an increase of + 0.0131 g.

All other components of the test rig showed no changes.

3.5. TEST CYCLES – ANALYTICAL RESULTS

Lubricant analysis of test 2 and 3:

Both lubricant samples of test 2 and 3 showed no significant impurities. The water content and the neutralization number of test 2 are slightly higher but still within acceptable ranges. Viscosity at 40°C, water content and the neutralization number of test 3 were not analyzed (see chapter 3.4: Accelerated worst case test – no. 3).

Table 1: Oil-analysis realized by the lubricant manufacturer:

<table>
<thead>
<tr>
<th>Units</th>
<th>Test 2:</th>
<th>Test 3:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 40°C</td>
<td>mm²/ s</td>
<td>58.78 not analyzed</td>
</tr>
<tr>
<td>Acidity</td>
<td>mg KOH/ g</td>
<td>0.11 not analyzed</td>
</tr>
<tr>
<td>H₂O (Karl Fischer)</td>
<td>mg/ kg</td>
<td>285 not analyzed</td>
</tr>
<tr>
<td>ICP-Elements</td>
<td>mg/ kg</td>
<td>not detectable not detectable</td>
</tr>
</tbody>
</table>

Weight analysis of the angle-on-coupon samples of test 2 and 3:

Table 2: Weight analysis of angle-on-coupon samples:

<table>
<thead>
<tr>
<th>Total – before test [g]:</th>
<th>Total – after test [g]:</th>
<th>Difference [g]:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 2:</td>
<td>38.2531</td>
<td>38.2740</td>
</tr>
<tr>
<td>Test 3:</td>
<td>38.1403</td>
<td>38.1534</td>
</tr>
</tbody>
</table>

The measuring precision of the balance was ± 0.0001 g. After test 2, the average weight difference for one coupon was about + 0.0005 g. After test 3, just as in test 2, a slight coupon weight increase was detected. The average weight difference for one coupon in test 3 was about + 0.0003 g.

GC-analysis of the refrigerant samples after each test:

Results for the GC-analysis of test 2 and 3 can be found in table 3. All samples were taken from the liquid line after the installation was switched off.
Table 3: GC-Analysis of R134a from test 2 and 3 – in [%] by weight:

<table>
<thead>
<tr>
<th></th>
<th>Air</th>
<th>R143a</th>
<th>R125</th>
<th>R134a</th>
<th>Impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original material</td>
<td>0.0027</td>
<td>0.0145</td>
<td>0.048</td>
<td>99.9053</td>
<td>0.0304</td>
</tr>
<tr>
<td>R134a – test 2</td>
<td>0.0769</td>
<td>-</td>
<td>0.0151</td>
<td>99.7313</td>
<td>0.1766</td>
</tr>
<tr>
<td>R134a – test 3</td>
<td>0.0997</td>
<td>0.027</td>
<td>0.1268</td>
<td>99.725</td>
<td>0.0216</td>
</tr>
</tbody>
</table>

The refrigerant analysis by GC revealed no significant degradation or decomposition of R134a for both tests.

**Optical analysis of the angle-on-coupon samples and the filter elements:**

The electron microscope pictures of the angle-on-coupon samples from test 3 indicated no substantial changes in the surface structures of the top sides (with flux residue). Figure 4 A shows the electron microscope picture of an angle-on-coupon after test 3, and figure 4 B shows a reference coupon from the same series.

![Figure 4: A: Angle-on-coupon surface after test 3 – top side (with flux residue) – coupon no. 36 (magnification 2000)
B: Reference angle-on-coupon surface – top side (with flux residue) – coupon no. 42 (magnification 2000)](image)

In figures 5 A and B, pictures of the coupon bottom surfaces are shown – with a slightly rougher appearance of the sample from test 3 compared to the reference.

![Figure 5: A: Angle-on-coupon surface after test 3 – bottom coupon no. 35 (magnification 2000)
B: Reference angle-on-coupon surface – bottom coupon no. 44 (magnification 2000)](image)
Figures 6 A and B depict a wire mesh filter element from the filter located after the sample vessel (see figure 2) – in the condition after test 3.

Figure 6:  
A: Filter element F3 (wire mesh Stainless Steel) after test 3 (magnification 100)  
B: Filter element F3 (wire mesh Stainless Steel) after test 3 (magnification 1000)

When comparing these images with that of a new filter element (see figure 7 A), there is no significant variation in the surface structure detectable.

By direct comparison of figures 6 A and B with the picture of a filter element from earlier tests (see figure 7 B), which shows corrosion by an acid [4], signs of surface deteriorations on the filter elements from test 3 can be excluded.

Figure 7:  
A: New filter element (wire mesh Stainless Steel) (magnification 442)  
B: Corroded filter element (wire mesh Stainless Steel) from an earlier tests [4] (magnification 442)

3.6. DISCUSSION OF RESULTS

Based on results from refrigerant and lubricant analysis, as well as gravimetrical examination of the angle-on-coupons and optical analysis of the filters it can be concluded that there are no interactions between post-braze flux residue from NOCOLOK® Cs Flux and the refrigerant 134a/ PAG oil system in a standard A/C unit.

The presence of flux residue does not cause or accelerate corrosive effects.
No indication for refrigerant decay was found; neither under worst case conditions nor under accelerated worst case conditions.

Under accelerated worst case conditions, the water content of the lubricant was slightly increased. However, the lubricant manufacturer confirmed the quality of the used lubricant was still comparable with the original PAG oil.

4. CONCLUSIONS

- The presence of post-braze flux residue from NOCOLOK® Cs Flux has no negative influence on the apparent running conditions and the stability of a refrigeration system – operating on R134a and PAG oil – even under worst conditions (such as the absence of a filter dryer, and with an artificially high moisture content).

- There is no evidence suggesting that the post-braze flux residue from NOCOLOK® Cs Flux accelerates, contributes to, or catalyzes the decomposition of the refrigerant and lubricant, or damages any other components of the system even under worst case conditions.

5. REFERENCES


[2] Schwiegel, M.; Untersuchung und Bewertung des Stabilitätsverhaltens von Flussmitteln für Aluminiumhartlötverbindungen mit Kältemitteln; Studienarbeit bei Prof. Dr.-Ing. S. Kabelac (Institut für Thermodynamik, Universität Hannover), in cooperation with SFD; 1998


[7] PAG Oil: Reniso PAG 46 – Fuchs Petrolub (Germany)