Composition Changes in Refrigerant Blends for Automotive Air Conditioning

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ABSTRACT

Three refrigerant blends used to replace the chlorofluorocarbon R-12 in automotive air conditioners were evaluated for composition changes due to typical servicing and leakage. When recommended service procedures were followed, changes in blend compositions were relatively small. Small changes in blend compositions caused no significant changes in refrigeration capacities. However, when recommended procedures were not followed, changes in compositions were relatively large. The amount of change in composition and the resulting effect on performance varied among the three refrigerant blends that were tested. Of the three blends, a quaternary blend containing hydrochlorofluorocarbon R-22 had the greatest changes in composition, while a binary blend containing hydrofluorocarbon R-134a had the smallest changes in composition.

INTRODUCTION

Title VI of the 1990 Clean Air Act Amendments requires the U.S. Environmental Protection Agency (EPA) to regulate substitutes for ozone-depleting substances, including substitutes for chlorofluorocarbon R-12. The EPA implemented the Title VI requirements with the Significant New Alternatives Policy (SNAP) Program that began in 1994. Under the SNAP Program, the EPA evaluates substitutes for effects on human health or the environment including toxicity, flammability, ozone depletion, and global warming. As of June 3, 1997, ten substitutes for R-12 in motor vehicle air conditioning were listed as "acceptable subject to use conditions." Use conditions include a requirement for unique fittings to prevent cross-contamination, a requirement for labeling to identify refrigerants in each vehicle, a prohibition against topping off one refrigerant with another, and a prohibition against the recycling of refrigerant blends. Additionally, refrigerant blends containing hydrochlorofluorocarbon R-22 require the use of barrier hoses to reduce permeation.

Of the ten currently acceptable substitutes, hydrofluorocarbon R-134a is the only single-component refrigerant and the only refrigerant that has been widely endorsed by the automotive original equipment manufacturers (OEMs). The other nine substitutes are refrigerant blends that can change composition due to fractionation during servicing or leakage. A recent study has indicated potential problems caused by fractionation (Atkinson 1997). To evaluate changes in blend composition and resulting changes in air-conditioning system performance, testing was conducted by the EPA.

DESCRIPTION OF TESTING

Three representative refrigerant blends were selected for study and compositions are shown in Table 1. A binary, a ternary, and a quaternary blend were selected.

Refrigerant blends were mixed in the laboratory to the compositions specified in Table 1 using an electronic balance with an accuracy of ±0.007 oz (±0.2 g). No attempt was made to verify composition of refrigerant blends available from manufacturers. Gas chromatography was used to measure the changes in blend composition after typical service procedures and after refrigerant leakage from an automotive air-conditioning system. Refrigerant blend samples of known composition were tested in parallel with samples of unknown composition to ensure the accuracy of the results.

System performance with compositions of various blends was evaluated with an instrumented, OEM, automotive air-conditioning system designed for use with R-12 and mineral

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TABLE 1
Refrigerant Composition (Weight Percent)

Name	R-22	R-124	R-142b	R-134a	Butane (R-600)	Isobutane (R-600a)
Quaternary Refrigerant Blend	51	28.5	16.5			4
Binary Refrigerant Blend			20	80		
Ternary Refrigerant Blend		39		59	2	

oil lubricant. This 1993 passenger car system had an orifice tube expansion device and a suction line accumulator. The evaporator and housing were located inside an insulated calorimeter chamber. Refrigeration capacity was determined by measuring the power input to electric heaters, heater fans, and evaporator fans inside the chamber. Refrigeration capacity was determined with an uncertainty of approximately ±340 Btu/h (±100 W) and a repeatability of ±100 Btu/h (±30 W). Refrigerant blend manufacturer recommendations on lubricants were followed. The quaternary refrigerant blend was tested with the mineral oil specified for the OEM system. The ternary and binary blends were tested with 3 oz (89 cm^3) of POE (polyolester) lubricant added to the existing mineral oil. The POE lubricant had a viscosity reported by the manufacturer to be 134 cSt at 104°F (40°C) and 25 cSt at 212°F (100°C).

Conditions for the two performance tests are shown in Table 2. Evaporator air inlet temperatures were set high enough to provide sufficient load to prevent cycling of the compressor. Steady-state operation enabled accurate measurement of refrigeration capacity. Data were collected for a two-hour period for each steady-state test. A significant part of the refrigeration load on an air-conditioning system can result from moisture condensing on the surface of the evaporator. In the test system, air inside the evaporator chamber was not humidified to avoid added complexity. Relative humidity was maintained at a low level during testing to prevent any condensation of water vapor. Electrical potential applied to the evaporator fan motor was regulated and maintained at 10.6VDC, and the rotational speed of the evaporator fan was measured to ensure consistent airflow through the evaporator. Evaporator air outlet temperatures were not measured.

LIMITATIONS OF TESTING

Test results reported here contribute to the information available on refrigerant blends for automotive air conditioning. However, any conclusions based on these results should be carefully considered because of the following limitations of the testing:

- One automotive air-conditioning system was used for testing. Results may vary with different vehicle air-conditioning systems.
- Two performance tests were conducted for each refrigerant blend composition. Automotive air conditioners operate over a range of conditions greater than those represented by the test conditions, and performance may vary under different operating conditions.
- Steady-state conditions were used for performance tests. Automotive air conditioners usually operate under dynamic conditions with changing rotational speed, changing load conditions, changing capacity, or on/off cycling of the compressor. Performance may vary under dynamic conditions.
- Tests were performed to evaluate changes in refrigerant blend compositions and resulting changes in air-conditioning system performance. Other important factors involved in refrigerant evaluation include permeation, materials compatibility, and long-term system durability. Extensive laboratory and field testing is required to adequately evaluate these factors. Changes in refrigerant blend compositions can also affect safety and flammability, but these issues were not investigated in this work

TABLE 2
Performance Test Conditions

	1	2
Compressor Rotational Speed (rpm)	1000	3000
Evaporator Air Inlet Temperature, °F (°C)	100 (37.8)	120 (48.9)
Condenser Air Inlet Temperature, °F (°C)	115 (46.1)	95 (35.0)
Condenser Air Inlet Velocity, ft/min (m/s)	200 (1.02)	350 (1.78)
Compressor Ambient Temperature, °F (°C)	130 (54.4)	130 (54.4)

DISCUSSION OF RESULTS FOR QUATERNARY REFRIGERANT BLEND

Of the three blends that were tested, the quaternary refrigerant blend had the greatest changes in composition due to the relatively large differences in the vapor pressures of the blend components. Table 1 shows the composition specified by the manufacturer and listed by the EPA SNAP Program. Table 3 shows the composition variation in weight percent deviation from the specified composition. For example, in row 1 the "+ 14" indicates that the sample contained 14% more R-22 than the specified composition (the sample contained 65% R-22 compared to the specified composition with 51% R-22).

A cylinder was prepared with the specified composition for the quaternary blend with liquid occupying approximately 80% of the cylinder volume. A vapor sample was removed from the vapor space at the top of the cylinder, and the sample was analyzed using gas chromatography. The vapor composition was 14% higher in R-22 than the specified composition, as shown in row 1 of Table 3. After removal of 90% of the refrigerant from the cylinder as a liquid, a sample of the remaining liquid was analyzed. The sample contained 2% less R-22 than the specified composition, as shown in row 2 of the table. Another cylinder was prepared with the correct composition specified for the quaternary blend. Refrigerant vapor was removed from the cylinder and samples of the remaining liquid were analyzed. Rows 3 and 4 show the changes in composition after 40% and 80% of the refrigerant were removed from the cylinder. As shown in row 4, the composition changed considerably after 80% of the refrigerant was removed as a vapor, with 32% less R-22 than the specified composition. These results show the importance of properly charging the blend from a cylinder as a liquid.

Composition changes for the quaternary blend were evaluated after typical service procedures. The automotive air-conditioning system was charged with the specified composition for the blend and was operated for over four hours. Refrigerant was then recovered from the system following the Society of Automotive Engineers (SAE) recommended service procedures (SAE J1989, SAE J2211 1989) for R-12 and R-134a. According to the SAE procedures, the recovery process should be continued until the system pressure has been reduced to a minimum vacuum level of 4 in. (102 mm) of mercury below atmospheric pressure, followed by a five-minute waiting period with the recovery unit off. If the system pressure rises above atmospheric pressure, additional recovery is required to remove the remaining refrigerant until the system vacuum level remains stable for two minutes. When the SAE procedures were followed, 93% of the charge was recovered and the change in composition of the recovered refrigerant was small, as shown in row 5 of Table 3. Refrigerant remaining in the system after recovery was captured by applying a deep vacuum through a cryogenic vacuum trap filled with liquid nitrogen. An additional 5% of the original charge was captured and the blend composition was analyzed. Results are shown in row 6 of Table 3. This residual refrigerant would typically be removed by evacuation during service, but the blend composition of the residual refrigerant was measured to evaluate the composition changes during service. The results show that due to the relatively high vapor pressure of R-22, the blend removed during the beginning of the recovery process contained an excess of R-22, and the blend removed during the end of the recovery process had a deficit of R-22.

If recommended procedures for recovery and recycling are not followed, a technician may improperly end the recovery process when a system vacuum level of 4 in. (102 mm) of mercury below atmospheric pressure is reached and not wait to check the system pressure after five minutes nor continue to remove any remaining refrigerant. When this improper procedure was followed, only 60% of the original charge was recovered, and the blend composition of the recovered refrigerant changed significantly, as shown in row 7 of Table 3. This result shows the importance of following recommended service

TABLE 3
Composition Variation for Quaternary Refrigerant Blend (Weight Percent Deviation from Specified Composition)

	Description	R-22	R-124	R-142b	Isobutane
1	Vapor in cylinder	+14	−7	−8	+1
2	Liquid remaining in cylinder after 90% liquid removed	−2	+1	+1	0
3	Liquid remaining in cylinder after 40% vapor removed	−11	+7	+5	−0.3
4	Liquid remaining in cylinder after 80% vapor removed	−32	+18	+15	−1
5	Properly recovered refrigerant (93% of charge)	+0.3	0	−0.3	0
6	Residual refrigerant in system after proper recovery	−29	+12	+15	+1
7	Improperly recovered refrigerant (60% of charge)	+9	−5	−4	−0.2
8	Recovered refrigerant after 40% vapor leakage	−7	+4	+3	0
9	Residual refrigerant in system after vapor leakage and recovery	−21	+8	+11	+2

procedures to avoid large changes in composition.

Composition change for the quaternary blend was evaluated following leakage from the air-conditioning system. The system was charged with the correct composition and was operated for over four hours. With the system off and at room temperature, vapor was leaked from the system through a metering valve at a rate of less than 2% of the original charge per hour until 40% of the original charge was removed. The remaining refrigerant was recovered following the SAE recommended service procedures. After recovery of 53% of the original charge, the composition of the recovered refrigerant was measured and is shown in row 8 of Table 3. Refrigerant remaining in the system after recovery was captured with the vacuum trap. After 5% of the original charge was captured, the composition of the captured refrigerant was measured and is shown in row 9 of Table 3.

Refrigeration capacity for the quaternary blend was evaluated with three blend compositions. Results are shown in Figure 1. The pair of bars at the top of the chart shows capacities at the two test conditions with the specified composition. The second pair of bars shows capacities after 40% of the original charge was lost due to a vapor leak and the charge was topped off with refrigerant with the specified blend composition. No significant change in performance was measured after leakage and top-off. The third pair of bars shows capacities when the system was charged with an incorrect blend composition containing 35% less R-22 than the specified composition. This incorrect composition (16% R-22, 48% R-124, 33% R-142b, 3% isobutane) could be obtained if refrigerant is improperly removed from a cylinder as a vapor and the system is charged from the cylinder containing less than 20% of the original refrigerant weight. Refrigeration capacity decreased by 13% at the 1000 rpm test condition and decreased by 9% at the 3000 rpm test condition.

DISCUSSION OF RESULTS FOR TERNARY REFRIGERANT BLEND

The ternary refrigerant blend was tested following the same procedures as described for the quaternary blend. Composition variation results are shown in Table 4. Generally, composition variation for the ternary blend was less than the variation for the quaternary blend due to the smaller differences in the vapor pressures of the ternary blend components. However, in some cases, the composition variation for the ternary blend was nearly the same as for the quaternary blend. It is likely that the composition variation for the ternary blend was also affected by the relatively large differences in lubricant miscibility of the blend components.

A cylinder was prepared with the specified ternary blend composition with liquid occupying approximately 80% of the cylinder volume. A vapor sample contained 8% more R-134a than the specified composition, as shown in row 1 of Table 4. When 90% of the refrigerant was removed from the cylinder as a liquid, the composition of the remaining liquid changed by only 1%, as shown in row 2. When refrigerant was removed from a cylinder as a vapor, the changes in blend composition were more significant, as shown in rows 3 and 4. After 80% of the refrigerant was removed as a vapor, the remaining liquid had 15% less R-134a than the specified composition, as shown

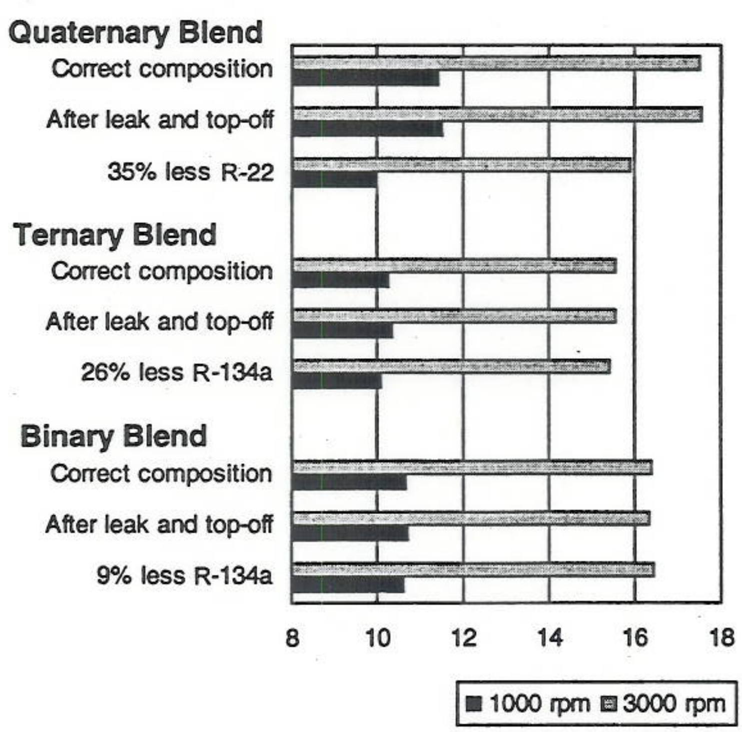

Figure 1 Refrigeration capacity (× 1000 Btu/h).

TABLE 4
Composition Variation for Ternary Refrigerant Blend (Weight Percent Deviation from Specified Composition)

	Description	R-134a	R-124	Butane R-600
1	Vapor in cylinder	+8	−9	+1
2	Liquid remaining in cylinder after 90% liquid removed	−1	+1	0
3	Liquid remaining in cylinder after 40% vapor removed	−4	+5	−0.4
4	Liquid remaining in cylinder after 80% vapor removed	−15	+16	−0.7
5	Properly recovered refrigerant (96% of charge)	+1	−1	−0.1
6	Residual refrigerant in system after proper recovery	−32	+29	+3
7	Improperly recovered refrigerant (60% of charge)	+7	−7	0
8	Recovered refrigerant after 37% vapor leakage	−3	+3	−0.1
9	Residual refrigerant in system after vapor leakage and recovery	−27	+26	+2

in row 4. These results show the importance of properly charging the ternary blend from a cylinder as a liquid.

When SAE-recommended service procedures for recovering refrigerant were followed, 96% of the original charge was recovered and the blend composition changed by only 1%, as shown in row 5 of Table 4. An additional 4% of the original charge was captured with the vacuum trap following recovery, and the captured refrigerant contained 32% less R-134a than the specified composition, as shown in row 6. The results show that due to the relatively high vapor pressure and relatively low lubricant miscibility of R-134a, the blend removed during the beginning of the recovery process contained an excess of R-134a, and the blend removed during the end of the recovery process had a deficit of R-134a.

When the recovery process was improperly terminated after reaching a system pressure of 4 in. (102 mm) of mercury below atmospheric pressure, the results were similar to those for the quaternary blend. Only 60% of the original charge was recovered, and the recovered blend contained 7% more R-134a than the specified composition, as shown in row 7 of Table 4. This result shows the importance of following proper recovery procedures for the ternary blend.

Composition change was evaluated for the ternary blend following leakage of refrigerant from the system. After 37% of the original charge was leaked as a vapor, the remaining refrigerant was recovered following recommended service procedures. The composition of the recovered refrigerant is shown in row 8 of Table 4, and the composition of the residual refrigerant remaining in the system after recovery is shown in row 9.

Refrigeration capacities for the ternary blend, evaluated at three blend compositions, are shown in Figure 1. No significant change in capacity was measured after 37% of the charge was lost due to a vapor leak and the system was topped off with the specified blend composition. When the system was charged with a blend containing 26% less R-134a than the specified composition, the refrigeration capacity decreased only slightly. This composition (33% R-134a, 66% R-124, 1% butane) could be obtained if refrigerant is improperly charged from a cylinder as a vapor and the system is charged from the cylinder containing less than 20% of the original refrigerant weight.

DISCUSSION OF RESULTS FOR BINARY REFRIGERANT BLEND

The binary refrigerant blend was tested following the same procedures as described for the quaternary and ternary blends. Composition variation results are shown in Table 5. Generally, composition variation for the binary blend was less than the variation for the other two blends.

A cylinder was prepared with the specified binary blend composition with liquid occupying approximately 80% of the cylinder volume. A vapor sample contained 5% more R-134a than the specified composition, as shown in row 1 of Table 5. When 90% of the refrigerant was removed from the cylinder as a liquid, the composition of the remaining liquid changed by only 0.4%, as shown in row 2. When refrigerant was removed from a cylinder as a vapor, the changes in blend composition were greater, as shown in rows 3 and 4. After 80% of the refrigerant was removed as a vapor, the remaining liquid contained 9% less R-134a than the specified composition, as shown in row 4. These results show the importance of properly charging the binary blend from a cylinder as a liquid.

When SAE-recommended service procedures for recovering refrigerant were followed, 96% of the original charge was recovered and there was no significant change in the refrigerant blend composition, as shown in row 5 of Table 5. The composition of refrigerant remaining in the system after recovery is shown in row 6. An additional 3% of the original charge was captured with the vacuum trap, and the captured refrigerant contained 24% less R-134a than the specified composition. When the recovery process was improperly terminated after reaching a system pressure of 4 in. (102 mm) of mercury below atmospheric pressure, only 54% of the original charge was recovered, and the recovered refrigerant contained 3% more R-134a than the specified composition, as shown in row 7 of Table 5.

TABLE 5
Composition Variation for Binary Refrigerant Blend (Weight Percent Deviation from Specified Composition)

	Description	R-134a	R-142b
1	Vapor in cylinder	+5	−5
2	Liquid remaining in cylinder after 90% liquid removed	−0.4	+ 0.4
3	Liquid remaining in cylinder after 40% vapor removed	−3	+3
4	Liquid remaining in cylinder after 80% vapor removed	−9	+9
5	Properly recovered refrigerant (96% of charge)	+ 0.1	−0.1
6	Residual refrigerant in system after proper recovery	−24	+24
7	Improperly recovered refrigerant (54% of charge)	+3	−3
8	Recovered refrigerant after 41% vapor leakage	−2	+2
9	Residual refrigerant in system after vapor leakage and recovery	−12	+12

Composition change was evaluated for the binary blend following leakage of refrigerant from the system. After 41% of the original charge was leaked as a vapor, the remaining refrigerant was recovered following recommended service procedures. The composition of the recovered refrigerant is shown in row 8 of Table 5, and the composition of the residual refrigerant remaining in the system after recovery is shown in row 9.

Refrigeration capacities for the binary blend, evaluated at three blend compositions, are shown in Figure 1. No significant change in capacity was measured after 41% of the charge was lost due to a vapor leak and the system was topped off with the specified blend composition. The bottom pair of bars in the figure shows that there was no significant change in refrigeration capacity when the system was charged with an incorrect blend composition containing 9% less R-134a than the specified composition. This composition (71% R-134a, 29% R-142b) could be obtained if refrigerant is improperly removed from a cylinder as a vapor and the system is charged from the cylinder containing approximately 20% of the original refrigerant weight.

CONCLUSIONS

Due to the limitations of the testing described above, any conclusions based on the test results should be carefully considered, but some general conclusions can be drawn from the results of the tests with the three refrigerant blends. When recommended service procedures were followed, changes in blend compositions were relatively small. Small changes in blend compositions resulting from typical leakage and service caused no significant changes in refrigeration capacities. However, when recommended procedures were not followed, changes in compositions were relatively large. The amount of change in composition and the resulting effect on performance varied among the three refrigerant blends that were tested. Of the three blends, the R-22-containing quaternary blend had the greatest changes in composition, while the R-134a-containing binary blend had the smallest changes in composition.

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