New Refrigerant Fluids to Meet Demanding Environmental Criteria

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ABSTRACT

The growing awareness that climate change is a man-made phenomenon has focused the attention of regulators on the question of Green House Gases (GHGs). The chemical industry has been working to develop safe refrigerant fluids with low GWPs. This paper describes the development and testing of a leading LOW GWP candidate to replace R-134a in automotive air-conditioning systems.

INTRODUCTION

The issue of climate change (global warming) is becoming ever more important as the scientific evidence, that the earth's climate is warming at an alarming rate, becomes more unequivocal. In addition to measures to curb emissions of CO_2, emissions of other green house gases (GHGs) are being brought into effect, both voluntarily and through legislative pressures. HFC refrigerant working fluids have been introduced over the last decade to replace ozone depleting substances (ODSs) regulated through Montreal Protocol related legislation, and their use has led to a significant reduction in the impact on the climate of direct emissions of GHGs from refrigeration and air-conditioning systems. HFCs however are, in themselves, potent GHGs and the chemical industry has been researching potential substitutes for HFCs, which would have acceptable toxicity and overall safety characteristics similar to HFCs in commercial use today. This R&D effort was intensified when the European Union introduced legislation (Directive 2006/40/EC) to ban the use of high GWP refrigerant working fluids in new car air-conditioning systems in a phased manner starting in 2011. This legislation sets an upper limit on the GWP of permitted fluids for use in new automotive systems (from the year 2011) of 150. (The current standard refrigerant used in car air-conditioning systems, R-134a, has a GWP of 1300). Subsequently other regulators (notably the California Air Resources Board) have announced that they are considering similar legislation.

Until recently, the leading candidate to replace R134a has been carbon dioxide (GWP = 1). However, CO_2 has several drawbacks including significantly higher pressure and low thermodynamic efficiency. These properties necessitate significant design changes to systems to enable them to use CO_2 and would result in higher equipment and other transition costs.

A new refrigerant fluid, DP-1, was recently identified as a potential low GWP alternative to R-134a for automotive air-conditioning systems, easily meeting the EU GWP requirement. DP-1 has vapor pressures and other properties similar to R134a, and has a GWP of approximately 40. It also has zero ozone depletion potential, thus meeting current stringent environmental requirements. Operating performance results in conventional (R-134a) automobile air conditioning systems show this product to be an attractive candidate to replace R-134a in these systems.

DP-1 has already undergone substantial physical, chemical compatibility and toxicity evaluations, and acceptance testing in mobile air-conditioning systems. All the results to-date have been very encouraging. These test results are summarised below.

1 TOXICITY

DP-1 is a mixture of two components: one a commercial refrigerant which has been fully characterized from a toxicological standpoint; the second (the major component) is a new compound which requires a complete toxicity assessment.
Acute toxicity testing for the new compound has been completed and toxicity is comparable to R134a and its predecessor in automotive air conditioning, CFC-12. Acute toxicity tests completed include Ames, Chromosome AB, LC-50, cardiac sensitization, and in vivo micronucleus as shown in Table 1.
Chronic tests are in progress including longer term inhalation tests (28 and 90 day), developmental and a first generation reproductive test (1-Gen). All tests are conducted following OECD guidelines.

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Table 1: Toxicity Test Summary

Test	Type	New Compound	R134a	R12
Ames	Acute Genetic - Mutagenic	Passed	Passed	Passed
Chrome AB	Acute Genetic - Chromosomal	Passed	Passed	Passed
LC-50 (Rat)	Acute 4 hour inhalation to 50% lethality	>750,000 ppm	>359,300 ppm	>800,000 ppm
Cardiac Sensitization	No Effect Level	25,000 ppm	50,000 ppm	40,000 ppm
Cardiac Sensitization	Threshold Level	50,000 ppm	75,000 ppm	50,000 ppm
In Vivo Micronucleus	Genetic	Passed	Passed	Passed
Full Developmental	Developmental	In progress	Passed	Passed
1-Gen	Reproductive	In progress	Passed	Passed
28-Day, 90- Day	Inhalation	In progress	90 Day No effect level 49,500 ppm	Reported 90 Day No effect level 810 ppm, 10,000 ppm

2 ENVIRONMENTAL AND SAFETY

DP-1 has an estimated 100 year GWP of 40 based on rigorous atmospheric modeling. Results are being confirmed experimentally. DP-1 also has zero ozone depletion potential. Flammability has been measured using ASTM 681-04 (2004) and DP-1 was found to be non-flammable based on composition and leak scenarios specified in ANSI/ASHRAE Standard 34 (2004).

3 THERMAL STABILITY

DP-1 has been evaluated for thermal stability using the methodology defined in ASHRAE Standard 97-99 (1999). Three test sequences were conducted: refrigerant only, refrigerant with uncapped dry polyalkylene glycol (PAG) or polyol ester (POE) lubricant; and refrigerant/lubricant contaminated with

1000 ppm water. Refrigerant and lubricant were placed in sealed glass tubes containing aluminum, copper and carbon steel coupons and held at 175°C for two weeks. Results indicate DP-1 is thermally stable with no significant corrosion to the metals observed. Another test sequence was conducted under more severe conditions with two additional PAG lubricants, a single end-capped and double end-capped PAG at 200°C with 30,000 ppm moisture. Again, no significant corrosion was observed.

4 MATERIALS COMPATIBILITY

DP-1 was evaluated for compatibility with typical plastics and elastomers used in automotive air conditioning systems. Sealed tubes were prepared containing DP-1 and uncapped PAG lubricant and held at 100°C for two weeks. Plastics were then inspected for weight change after 24 hours and physical appearance. Elastomers were evaluated for linear swell, weight gain and hardness using a durometer. The specific plastic and elastomers tested with their results are shown in Tables 2 and 3. DP-1 has very similar behavior with plastics and elastomers to R134a, indicating that many materials in use in current air conditioning systems should be compatible with DP-1. The following ratings were used to assess changes to plastics: Rating = 0 if weight gain is less than 1% and there is no physical change. Rating = 1 if weight gain is between 1 and 10% and physical change = 2.
For elastomers, Rating = 0 if for < 10% weight gain, < 10% linear swell and < 10% hardness change. Rating = 1 for > 10% weight gain or > 10% linear swell or >10% hardness change.

Table 2: Plastics Compatibility

Refrigerant	Plastics	Rating	24 h Post Weight Chg. %	Physical Change
DP-1	Polyester	1	3.6	0
"	Nylon	0	-1.1	0
"	Epoxy	0	0.7	0
"	Polyethylene terephthalate	1	2.8	0 -- 1
"	Polyimide	0	0.6	0

Refrigerant	Plastics	Rating	24 h Post Weight Chg. %	Physical Change
R134a	Polyester	1	4.5	0
"	Nylon	0	-1.2	0
"	Epoxy	0	0.0	0
"	Polyethylene terephthalate	1	4.2	0 -- 1
"	Polyimide	0	0.4	0

Table 3: Elastomers Compatibility

Refrigerant	Elastomers	Rating	24 h Post Linear Swell %	24 h Post Weight Gain %	24 h Post Delta Hardness
DP-1	Neoprene	0	-4.4	-2.6	3
"	HNBR	0	5.8	6.9	-5
"	NBR	0	-5.7	-1.4	3
"	EPDM	0	-3.5	-1.8	1.5
"	Silicone	0	5.4	3.8	-10
"	Butyl rubber	0	-2.3	-0.1	-1.5
Refrigerant	**Elastomers**		**24 h Post Linear Swell %**	**24 h Post Weight Gain %**	**24 h Post Delta Hardness**
R134a	Neoprene	0	-3.8	-2.4	2
"	HNBR	0 -- 1	8.6	9.8	-11.5
"	NBR	0	-1.4	1.3	-1.5
"	EPDM	0	-3.3	-1.3	0
"	Silicone	0 -- 1	1.7	2.3	-10.5
"	Butyl rubber	0	-3.1	-1.1	-2

5 LUBRICANT MISCIBILITY

DP-1 was also evaluated for miscibility with several PAG lubricants and a POE lubricant. In all cases, miscibility was very similar to R134a. Miscibility data for a single end-capped PAG and a double end-capped PAG versus R134a are given in Figures 1 and 2. For the POE lubricant tested there was complete miscibility with DP-1 from –40 to +65°C.

Figure 1: Single End -Capped PAG

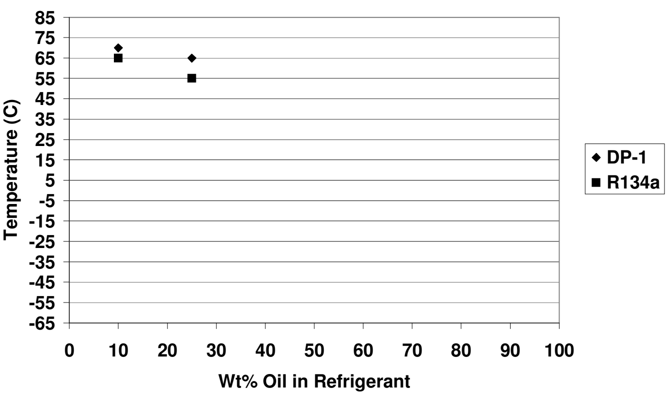
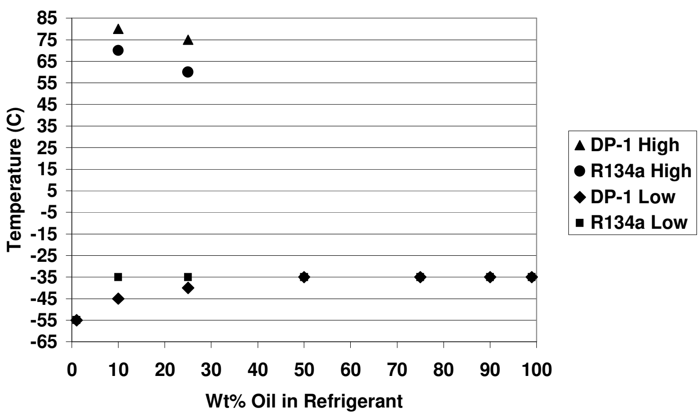


Figure 2: Double End-Capped PAG



6 REFRIGERATION PERFORMANCE TESTS
(Laboratory Calorimeter and MAC System)

Calorimeter tests were conducted for DP-1 using a reciprocating domestic refrigeration compressor. Three evaporator temperatures were tested: -25°C, -20°C and –10°C. Results showed on average that the cooling capacity of DP-1 was 5% lower than R134a and the energy efficiency equivalent to R134a.

DP-1 was also evaluated in a direct substitution vehicle test where R134a was removed from the air conditioning system and DP-1 charged with no other system modifications being made (no adjustment was made to the thermal expansion device (TXV)). Driving tests were conducted on a roll bench at 35°C and 40°C ambient conditions using the NEDC drive cycle. The vehicle was monitored for cooling capacity and fuel consumption. Results showed once again that DP-1 had about 5% lower cooling capacity than R134a with equivalent fuel consumption. DP-1 was also tested in another system which was soft-optimized by adjusting the thermal expansion device. Capacity results at two compressor speeds, 1000 and 2000 rpm are shown in Figure 3. COP results are shown in Figure 4. Results shown cooling capacity average deficit is 5.6% and COP average increase is 9.4%.

Figure 3: Cooling Capacity in System Test – Optimized TXV

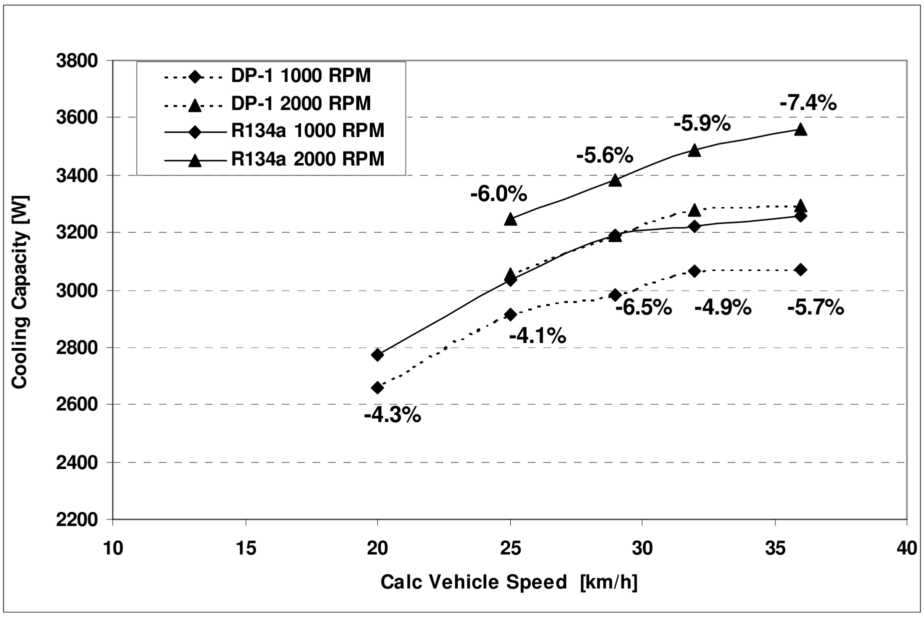
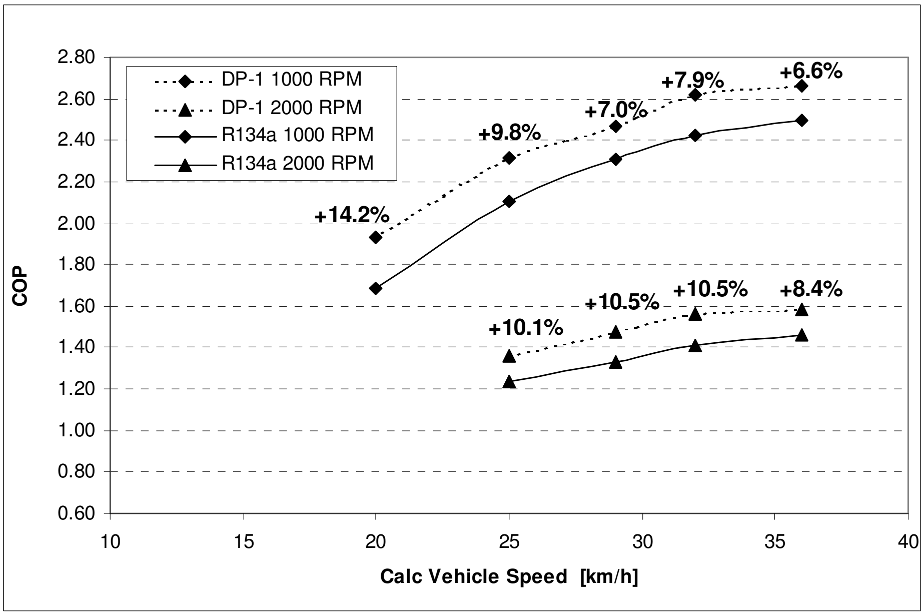


Figure 4: COP in System Test – Optimized TXV



7 CONCLUSIONS

The data presented in this paper indicate that DP-1 has strong potential to be a viable alternative to R134a or CO_2 in mobile air conditioning. DP-1 has excellent environmental properties with no ODP and GWP of approximately 40. DP-1 is thermally stable and compatible with existing materials used in mobile air conditioning. It also has pressures similar to R134a. DP-1 should not, therefore, require the significant air-conditioning system design modifications and changes to the automotive aftermarket service structure that would be necessary with CO_2. DP-1 is currently undergoing acceptance testing by several automobile OEMs and their first tier suppliers.

REFERENCES

ASTM E681-04, 2004 "Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases)," American Society for Testing and Materials (ASTM), West Conshohocken, PA.

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