

AN ASSESSMENT OF CAPPED POLYALKYLENE GLYCOL TECHNOLOGY FOR CO₂ REFRIGERATION.

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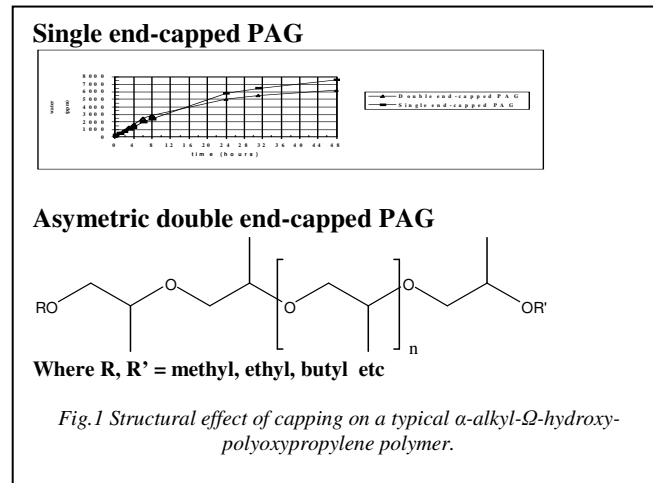
Introduction

The refrigeration industry has recently realised a number of significant changes due to problems associated with ozone depletion. Until relatively recently the main refrigerants in use were ozone depleting types such as R12, R22 and R502. The use of these refrigerants, with the exception of R22, is now prohibited in developed countries, plans are also developing to phase out R22 as a result of the ozone depletion potential, albeit small, which is also associated with this gas. A number of significant alternative refrigerants have been established, including HFCs such as R134a, R407c, R404a and R410a, which though not impacting directly on ozone depletion have an indirect contribution to global warming. Halogen-free refrigerants offer significant possibilities as long-term refrigerants, with single substances including NH₃ (R717), propane (R290), iso-butane (R600a) and carbon dioxide (R744) also being considered as refrigerants with minimal impact on global warming.

Carbon dioxide has no ozone depleting potential (ODP), is non-flammable and chemically very stable. It is only harmful to health in very high concentrations and is inexpensive, hence eliminating any need for recovery and disposal. These safety characteristics were the main reason for the widespread use of CO₂ until the introduction of the "Safety Refrigerants" caused a decrease in the popularity of CO₂. Carbon dioxide offers unfavourable characteristics for usual refrigeration applications, with a very high discharge pressure and a very low critical temperature of 31°C (74 bar). This requires sub and supercritical operating conditions in single stage systems with discharge pressure above 100 bars, and in addition the energy efficiency is lower compared to the traditional vapour compression process. However, in applications with potentially high leakage rates and where flammable refrigerants cannot be accepted for safety reasons, there exist opportunities for CO₂. A number of development projects, primarily in the area of vehicle air-conditioning are underway, and an additional potential application is in heat pumps for sanitary water heating. Initial work indicates that CO₂ systems for automotive air-conditioning and heat pumps show improved efficiency over traditional R134a technology. For larger commercial and industrial refrigeration units, CO₂ may be used as a secondary fluid in a cascade system and developments are also underway in this field⁽¹⁾.

There are a range of issues affect the selection of lubricant for CO₂ refrigeration, these include lubricity, refrigerant miscibility, chemical / thermal stability and hygroscopicity. Performance advantages in these areas have been associated with the use of "capped" polyalkylene glycol technology, wherein the polyalkylene glycol polymer chain has chemically inactive groups at both ends of the molecule (double end-capped) rather than the terminating hydroxyl functionality found commonly in polyalkylene glycol polymer chains.

Additionally, it has been identified that performance attributes useful for HFC and CO₂ refrigeration may be enhanced by the selection of specific terminating functionalities, achieved by capping of a single terminating hydroxyl rather than by end-capping both ends simultaneously.



Miscibility

Polyalkylene glycols typically demonstrate partial miscibility with CO₂⁽²⁾, compared with PAO, AB and mineral oils which all show immiscibility. POE typically demonstrates good CO₂ miscibility. Miscibility of double end-capped polyalkylene glycols may be enhanced by correct choice of the terminating functionality:

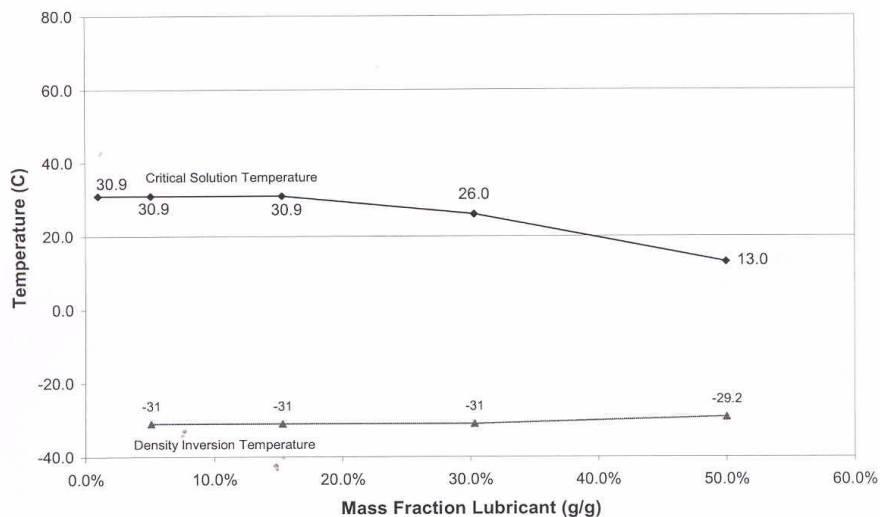


Figure 2 – Example of double end-capped PAG (ISO 46) miscibility with CO₂

The density inversion temperature is attributable to the high variation in CO₂ density with temperature, and hence a temperature is observed at which the density of CO₂ and lubricant is reversed. Whilst this point is observable in laboratory studies, the existence of a single phase without separation of

lubricant and refrigerant is observed both above and below the “density inversion temperature” for particular double end-capped PAG structures.

Improved miscibility of lubricant and refrigerant is expected to result in a reduction in viscosity of the mixture, particularly with CO₂ due to the low Elizabeth Dixon

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viscosity of liquid CO₂. Whilst CO₂ miscibility of a double end-capped capped PAG may be enhanced above that of a standard PAG by correct selection of capping functionality, the viscosity reduction is less than that observed for a POE⁽³⁾ and that which is commonly observed for a less miscible PAG.

	Viscosity (cSt) @ 80bar, 30% CO ₂	Viscosity (cSt) @ 30bar, 10% CO ₂
POE	1.50	11.1
Double end-capped PAG	1.91	14.2
Double end-capped PAG (CO ₂ specific)	2.43	19.2

Table 1 – Example of viscosity reductions under CO₂ dilution observable for ISO 46 lubricants.

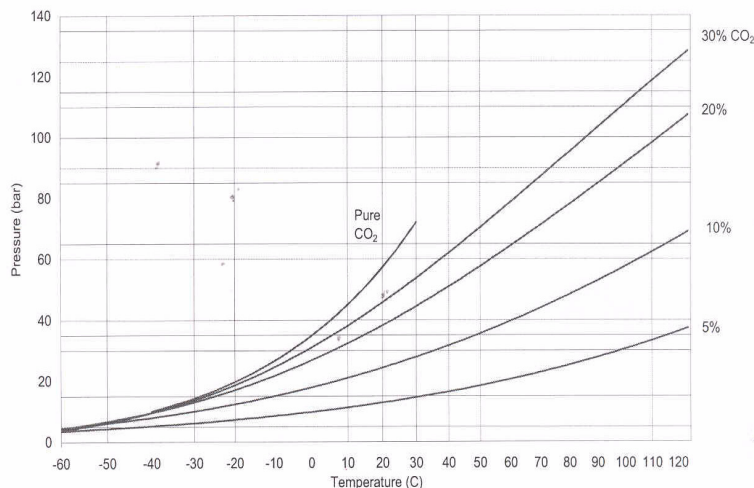
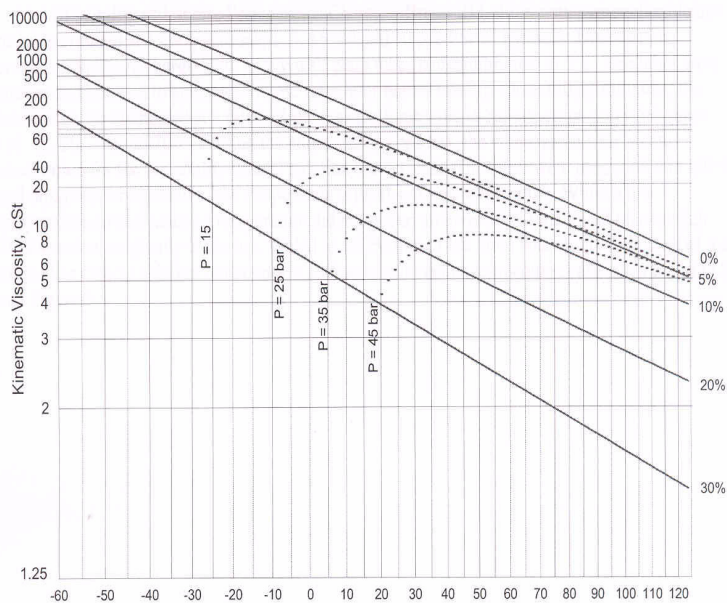


Fig 3 – Pressure-Viscosity-temperature profile of a CO₂ specific double end-capped PAG

Lubricity

The development of trans-critical CO₂ systems requires speciality lubricants due to the higher pressures and subsequently higher loading on bearings. The extreme pressure and anti-wear properties of PAGs are superior to POEs, and where higher ISO viscosity grade selection can be necessary with POEs due to the viscosity reduction under CO₂ dilution, this is not the case with PAGs, where lubricating properties and viscometrics are better retained under high levels of CO₂ dilution. Capped PAG technology in particular provides efficient lubrication for CO₂ refrigeration units, with improved lubricating properties being achieved as a result of the capping technology:

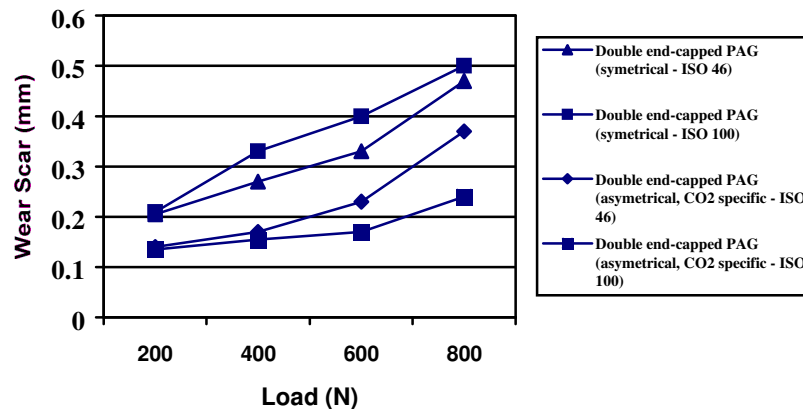


Figure 4 – Wear property of Capped PAGs by Falex pin & v-block⁽⁴⁾ (atmospheric CO₂, 100°C) (ISO 46 & 100)

The load carrying property is also observed to be partly a function of the terminating groups of the double end-capped PAG:

	Falex Block-on ring Failure Load (lb)
Asymmetrically double end-capped PAG (specific design for CO ₂ systems)	380
Symmetrically double end-capped PAG (methyl terminations)	230

Table 2 – EP property of capped PAGs by Falex block-on-ring⁽⁵⁾ (10 bar CO₂, >90°C) (ISO 46)

Chemical Stability

Polyalkylene glycols are very hygroscopic and may absorb several thousand ppm of water when exposed to humid conditions. Despite this, PAGs will not hydrolyse under such conditions and therefore do not pose any concerns regarding chemical stability. The tendency of double end-capped PAGs to absorb water is reduced as a result of the replacement of the hydroxyl termination, and they also cannot react with any carbonic acid formed as a result of the reaction of CO₂ with water. The hydrolysis of POEs remains a

cause for concern in CO₂ systems, as in HFC systems, and copper corrosion inhibitors are necessary where copper plating is a concern.

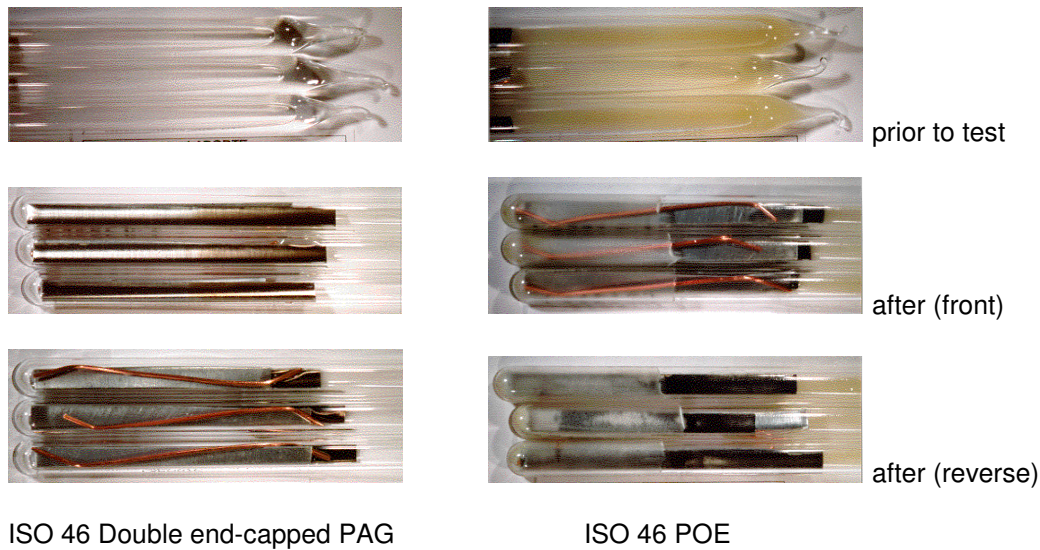


Fig 5 - ASHRAE 97 test (14 days, R134a, 175°C, 1.0wt% H₂O) comparing POE and double end-capped PAG

Sample	TAN (unreacted) MgKOH/g	TAN reacted MgKOH/g
R134a		
Asymmetrical double end-capped PAG	0.04	0.02
Asymmetrical double end-capped Pag + 1.0wt% H ₂ O	-	0.03
POE	0.22	0.37
POE + 1.0wt% H ₂ O	-	26.0
CO₂		
Asymmetrical double end-capped PAG (CO ₂ specific)	0.12	0.01
Asymmetrical double end-capped PAG (CO ₂ specific) + 0.1wt% H ₂ O	0.12	0.01

Table 3 – Chemical stability by TAN comparison of capped PAGs and POE by ASHRAE 97 Sealed Glass Tube Test.

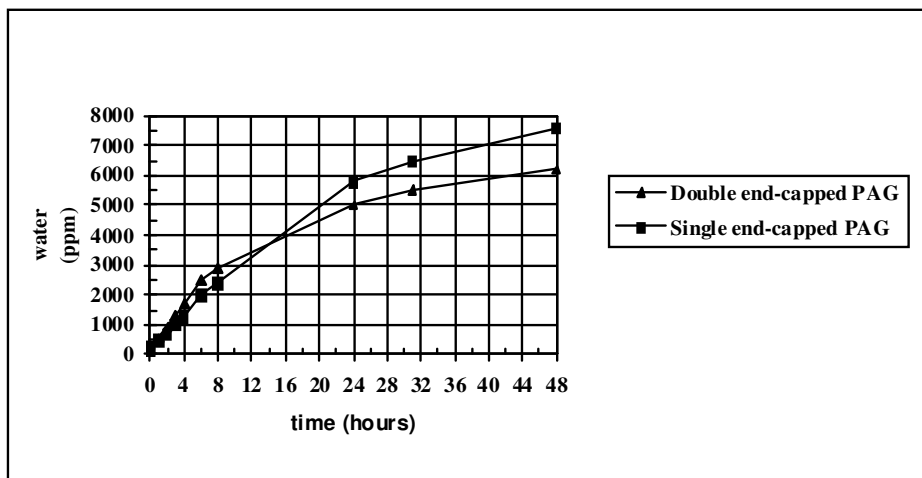


Fig 6 – Water absorption comparison of single and double end-capped PAGs
Note: (1) sample stirring speed: 500 rpm, (2) temp: 20 °C,
 (3) initial sample size: 30 g, (4) surface area: 3.1 cm² (5) Relative Humidity 52%

In addition to PAGs being chemically stable, any water absorbed by a PAG is bound by hydrogen bonding to the PAG ether linkages, and as a result the water is not "free" within the system and problems typically associated with free water such as corrosion and capillary ice formation are prevented. The presence of free moisture in POEs remains a problem for CO₂ systems and requires handling procedures to ensure low levels of free water within the system.

Conclusions

A range of lubricant technologies are available for CO₂ compressor systems, with synthetic fluids such as PAGs and POEs demonstrating advantages. Double end-capped PAGs show particular performance advantages and may be designed to specifically enhance performance attributes such as CO₂ miscibility and improved lubricity in high pressure systems.

References

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