KEEPING CO_2 WHERE IT BELONGS.
REQUIREMENTS FOR SEALING FUTURE AUTOMOTIVE CLIMATE CONTROL SYSTEMS.

ABSTRACT

This paper is intended as a review of the desirable characteristics for automotive climate control system couplings.

Past automotive climate control systems have relied on screwed couplings between the main components and the delivery pipes.

Recently, push fit couplings have been developed which are simpler to assemble. The couplings rely on elastomeric seals to contain the refrigerant. The long term performance of these seals is therefore very important. Sealing force may be lost due to stress relaxation and set (physical and chemical ageing). Over time, refrigerant will be absorbed and will permeate through the seal. The compatibility of the refrigerant and rate of diffusion through the elastomer are critical properties. In service, couplings will have heat and pressure cycles which, with vibration, may lead to leakage.

An accelerated ageing test has been developed which includes the effect of vehicle vibration and thermal cycles using a novel test rig which allows 12 couplings to be tested simultaneously. There is continuous monitoring of the amount of gas leaking past the coupling seals. A test sequence has been developed which includes periods at high temperature followed by periods at sub zero temperatures. In most cases leakage occurs during cooling, when the seals are most vulnerable. This enables different coupling designs and the performance of seal materials to be compared in the laboratory.

The proposed CFC and HFC replacement refrigerant gases are likely to be less efficient which means that the climate control systems will be working harder, putting the seals in the system under increased strain. This underlines the importance of life assessment tests and accelerated tests which will permit say 10 years service conditions to be compressed into a few months. In addition, some proposed refrigerant gases are absorbed so readily by certain elastomer types, that the pressure cycling due to normal operation of the climate control system may cause seal rupture due to explosive decompression. The additional complication of the fire hazard of hydrocarbon refrigerants is self evident. Verification of the life of the seal and coupling under realistic, but laboratory conditions, is of prime importance.

1.0 INTRODUCTION

Past automotive climate control (C/C) systems have relied on screwed couplings between the main components and the delivery pipes. These couplings rely on elastomeric seals to contain the refrigerant. The ideal design for a coupling would be 'no coupling at all', so that there are no leakage paths and no fasteners to come loose. However, in reality, couplings are needed to make assembly of the climate control system into the vehicle possible, and to allow for repair/servicing of the system. Steps must therefore be taken to avoid leakage and other forms of fluid loss.

As couplings cannot be avoided, the best compromise might be to use two perfectly flat non-porous parts (ie metal) firmly clamped in intimate contact. This would require expensive machining operations to achieve an adequate surface finish and, even so, on a molecular scale, would be likely to leave leakages paths across the mating faces large enough for significant fluid transport. Successful sealing is much more likely (and more cost effective) if normally manufactured metal parts are used with a conformal layer between the mating faces - in other words a elastomeric seal should be used. However, fluid transport around and through the elastomer then has to be considered which will be discussed below.

To simplify assembly, in recent years, push fit couplings have been developed which have the additional benefit of being tamperproof. The careful design and good long term performance of these elastomeric seals in their housings is therefore very important in preventing uncontained leakage of the refrigerant fluid into the environment - a wholly undesirable situation.

2.0 COUPLING DESIGN

There are really only two fundamental ways in which a seal functions - spigot or flange. By their elastic nature seals need be fitted with a degree of permanent compression to maintain sealing stress. This has a number of advantages. The seal is held firmly in place even when the pressurised fluid is not blowing ’it into position. The compression means that potential leakage paths both *past* the seal and any diffusion path *through* the seal are increased in length so that fluid escape will be reduced.

2.1.1 FLANGE TYPE COUPLING

Figure 1 shows a typical flange coupling with a seal. The gaps between the mating parts on either side of the seal are very small if not actually zero which will lower the rate of diffusion and the related phenomenon of permeation through the seal. In the past, these couplings have usually been bolted together which has some disadvantages. Bolting together all the couplings in a vehicle system will take a considerable time. Tools and space to operate the tools will be required. If not mechanised, repeated hand tool usage can lead to problems of carpel tunnel damage to the operator.

2.1.2 SPIGOT COUPLING

This is also shown in Figure 1. Here the design means that the cylindrical male and female mating parts slide concentrically inside each other, compressing the seals at the same time. These also have similar disadvantages to flange couplings, in that the coupling must be held together by a bolt, fastener or clip. Time and space will be required to assemble the coupling and tools may be needed. There must be a finite clearance between the parts to allow them to fit together which means that there will be a significant leakage path through the connector.

Figure 1 Schematic diagram of fluid couplings

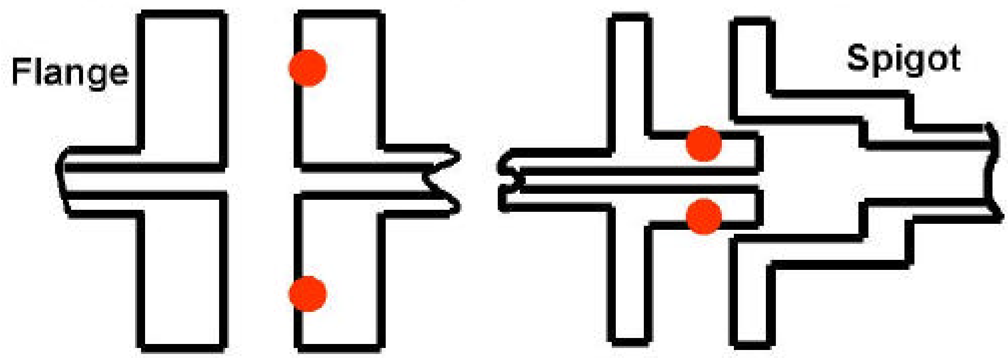
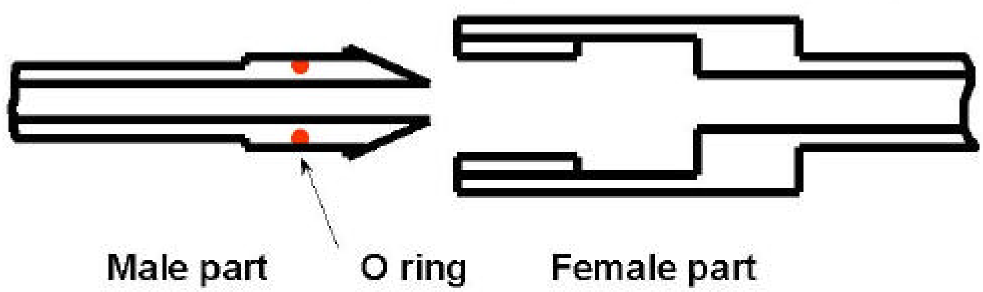


Figure 2 Diagram of 'push fit' fluid coupling



2.1.3 SNAP COUPLINGS

In recent years, snap together couplings have been developed from the spigot coupling which address some of the disadvantages of bolted couplings. A simple push mates the two parts of the coupling instantly, no tools are needed and appropriate design can make the coupling tamperproof.

2.1.4 GENERAL

All spigot type couplings will still have finite clearance between the mating parts which will allow fluid to permeate through the seal and, under extreme conditions, may allow extrusion of the seal through the gap. This gap can also allow a small amount of relative movement of the coupling parts which is undesirable in this application. This movement can relieve the stresses in the pipework from relative motion of say, the engine and body, but it can also prevent full adherence of the seal to the coupling and may cause fatigue of the elastomer. Any movement is likely cause premature seal failure.

The long term performance of these seals is of prime importance in preventing refrigerant escape.

2.2 MECHANICS OF SEAL OPERATION

A number of environmental factors influence the performance of seals :-

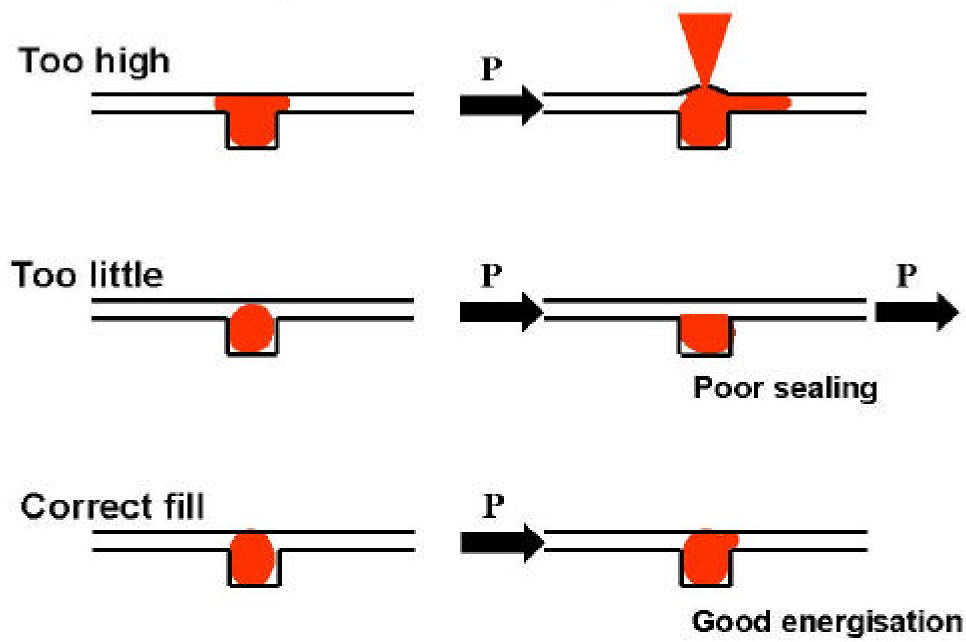
- Heat initially softens the seal enabling energisation but in the long term may cause chemical softening or hardening of the elastomer, depending on how cure continues. However, once the seal has located correctly at a high temperature, cold cycles causing thermal shrinkage can lead to leakage especially at temperatures below the glass transition temperature (Tg) of the material.

- Initial pressurisation by the fluid causes seal energisation by blowing 'the seal into the optimum position for sealing.

- Vibration may prevent the seal adhering to metal surfaces, if the coupling type permits relative movement between the coupling parts, making leakage past the seal more likely and may also cause fatigue of the elastomer. In extreme cases where there is actual movement of the seal over the surface of the coupling, wear of the seal may occur.

- The degree of fill of the seal groove is important as shown in Figure 3. Too much fill will mean that the coupling will be difficult to assemble, too little fill will obviously give poorer sealing due to inadequate sealing stress. Groove fill can be adjusted by changing the cross sectional shape of the seal. Generally, circular cross section seals (O rings) are used, but oval or square section rings can increase groove fill. Groove fill is greatly affected by swelling of the elastomer by the fluid, which will be discussed later, and by thermal contraction of the elastomer during temperature reductions which can result in a total loss of sealing.

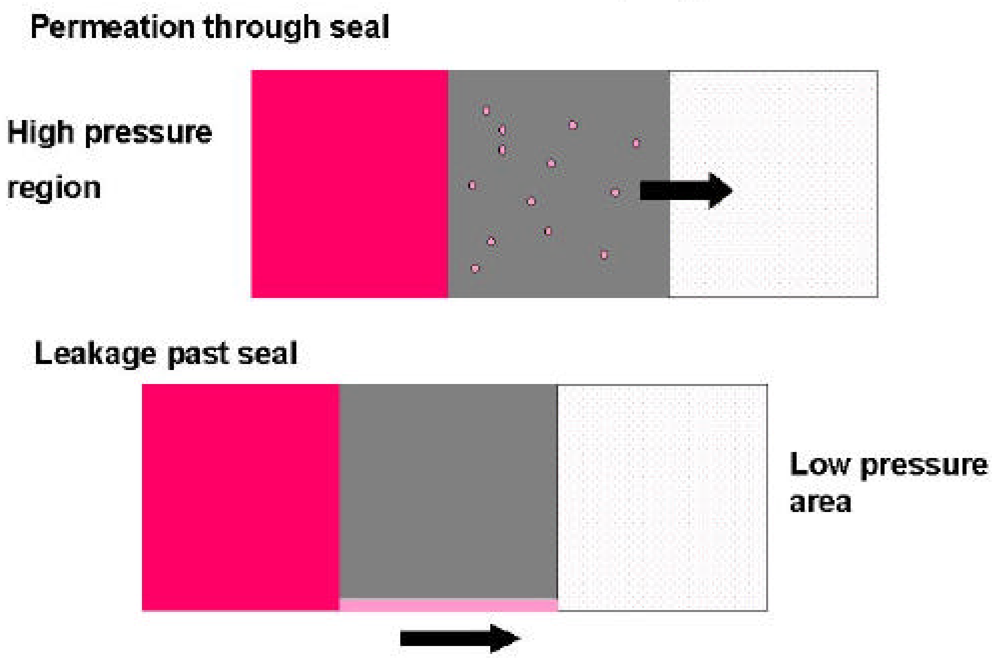
Figure 3 Fill of O ring groove



2.3 TYPES OF FLUID ESCAPE

The elastomer material, comprising long chain molecules cross linked at intervals, has a significant free volume (space between molecules) in the material which allows diffusion of fluid *into* or diffusion of fluid *through* the elastomer. This is a phenomenon which is always present at a low level and is called permeation and is shown in Figure 4 below.

Figure 4 Leakage types



Once stress relaxation and set have happened due to a long period of use at high temperature, leakage *past* the seal may occur. This is most likely to happen during cold cycles when thermal shrinkage exacerbates the effects of set. This leakage will result in an uncontained loss of the refrigerant fluid.

3.0 SEAL ELASTOMER and REFRIGERANT FLUID INTERACTIONS

Selecting the optimum elastomer material for the refrigerant fluid is of prime importance. This section looks at appropriate compatibility issues. Thermodynamic and physical data have been gathered from a number of sources to enable comparisons to be made.

Two physical processes are involved in fluid uptake by an elastomer. Liquids and gases adsorb onto the surface of the elastomer, and then penetrate further by diffusion. This uptake of liquid may result in volume and mass increases called swelling. If evaporation occurs at a remote surface we have the phenomenon of permeation.

3.1 GAS AND LIQUID TRANSPORT THROUGH ELASTOMER

For liquids, the degree of mass increase in the bulk of an elastomer (absorption) is largely independent of pressure.

For gases, molecules of gas at high pressure dissolves into the surface of an elastomeric membrane (adsorption) according to Henrys Law :-

$C = \mathbf{s} P$ where C is the concentration, **s** is the solubility coefficient and P is the applied (vapour) pressure which is actual pressure for gases

Although Henry's Law applies to liquids too, vapour pressure is largely independent of pressure.

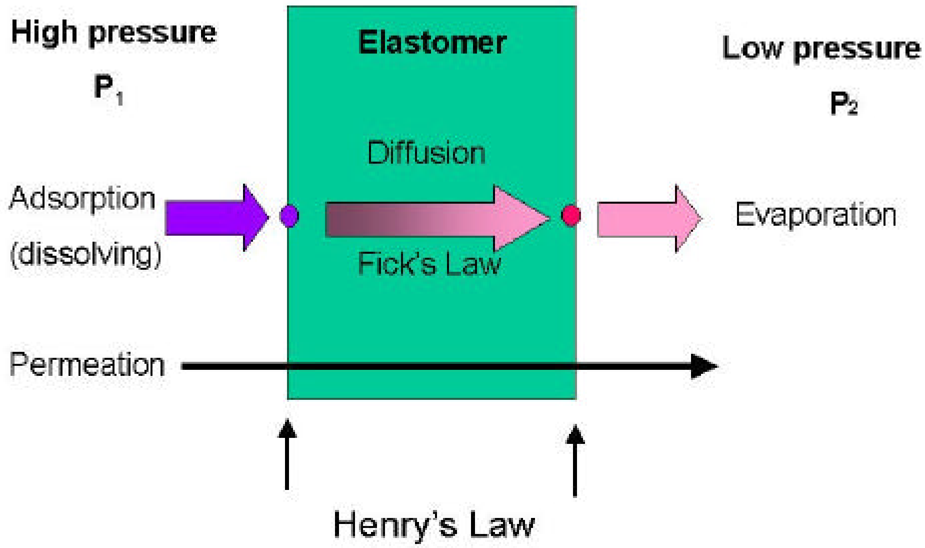
In both cases, the subsequent diffusion of the fluid through the body of the elastomer is governed by Fick's Laws of diffusion which must be solved for the particular boundary conditions for the fluid and elastomer of interest, and uses a proportionality term D, the diffusion coefficient. For a membrane :-

$(1 / A)(q / t) = D (C_1 - C_2) / h$ where q / t is the diffusion rate C_1, C_2 is the concentration difference across the membrane, A is the area,

For gas permeation, the gas then evaporates from the surface of the elastomer into the low pressure region, according to Henry's Law again.

Permeation is illustrated in Figure 5.

Figure 5 Gas transport mechanisms through elastomer



Combining Henry's and Fick's laws gives us the general gas permeation equation for permeation through a parallel faced membrane :-

$$q / t = Q A (P_1 - P_2) / h$$

where q / t is the gas permeation rate, P_1, P_2 are the high and low pressures, A is the area, h is the thickness and Q is the permeation coefficient. Clearly, gas permeation is controlled by the pressure difference across the thickness (h) of the elastomer. Q is also the product of D (the diffusion coefficient) and **s** (the solubility coefficient). These three coefficients are specific to an elastomer / fluid combination : permeation rate may be dependent on geometry and test conditions. D and Q can be measured separately during a permeation test, so **s** = Q / D is then obvious. Also, the gas concentration C at the high pressure side during permeation testing can then be obtained at any pressure which can give useful information when considering explosive decompression (discussed in section 3.4 below).

Illustrative values for some of these coefficients for carbon dioxide with a variety of elastomers are shown in Table 1 below.

Table 1 Gas Permeation and Related Data

elastomer	FEPM type i [2]	FKM type ii [2]	FKM type iii [2]	FEPM type ii [3]
Q permeation coefficient ($cm^2/s/atm \times 10^{-6}$)	6.4	7.0	4.5	3.11
D diffusion coefficient ($cm^2/s \times 10^{-6}$)	5.3	6.3	1.0	17
s solubility coefficient (atm^{-1})	1.2	1.1	4.4	0.31
elastomer	FEPM type i	FKM type ii	FKM type iii	FEPM type ii
conditions	100ºC 2500 psi			204ºC 2000 psi

It can be seen that there is a considerable variation in Q, **s** and D depending on the elastomer and temperature used. The most likely of these to suffer from explosive decompression damage is the FKM iii (shaded) and this is discussed in section 3.4.

Rates of liquid permeation are low because the general permeation equation here refers to the vapour pressure, not hydrostatic pressure. In an air conditioning system, the same refrigerant is present in different parts as a gas and a liquid, therefore it is probable that the vapour pressure in the coolest part will be the driving force throughout the system.

3.2 FLUID VISCOSITY

Viscosity of the refrigerant has a significant effect on solubility in a given elastomer. Low molecular weight, low viscosity fluids are likely to be the most soluble. Carbon dioxide and low molecular weight hydrocarbons as refrigerants are likely to increase fluid lost by permeation. The following table 2 gives molecular weights for some candidate refrigerants:-

Table 2 Molecular weights of refrigerants

Fluid	molecular weight (MW)	Fluid	molecular weight (MW)
Ammonia	17	R 11	136
Butane	58	R 12	120
CO2	44	R 13	104
Pentane	72	R134a [1]	102

3.3 LIQUID SWELLING OF THE ELASTOMER

From thermodynamic considerations, if a liquid swells an elastomer significantly by absorption, they will posses similar solubility parameters (δ). However, other considerations may over-ride swelling, such as high crosslink density or high filler content. Therefore, an elastomer may not always swell even if the liquid has a matching δ value. It should be borne in mind that, while a climate control system contains both liquid and gaseous refrigerant, swelling will not occur significantly in the presence of a liquid.

Table 3 lists solubility parameter data (δ) for a number of elastomers and liquids. At a moderate level, up to 20%, liquid swelling can be beneficial by improving groove fill and increasing the diffusion/permeation path length, but too much swell may extrude the elastomer out of the groove completely or may distort the metal parts. High levels of liquid uptake may eventually cause shrinkage of the elastomer due to the loss of constituents by leaching making the seals more prone to leakage. It should be noted that swelling may also cause a decrease in physical properties such as tear strength and modulus.

Table 3 Solubility parameter data (δ) [2]

Elastomer	δ range $(cal/cm^3)^{1/2}$	Liquid	δ $(cal/cm^3)^{1/2}$
EPDM	7.5 - 9.0	iso Octane	6.90
FEPM	8.5 - 10.0	n pentane	7.00
NBR (low ACN)	8.5 - 11.0	Hexane	7.33
NBR (high ACN)	9.0 - 12.0	Octane	7.60
HNBR	8.5 - 11.5	Decane	7.77
ECO	9.0 - 12.5	Toluene	8.97
FKM	9.0 - 12.5	Propanol	12.02
		Ethanol	12.97
		Methanol	14.52

As a simple example, it can be seen that toluene has a similar δ value to many elastomers, which is why it is often used to swell and remove rubber from metal substrates. also, EPDM swells in hydrocarbons but not in alcohols.

Similar data for R134a are not available.

Below their critical temperatures, gases can be liquefied by pressure. Pure CO_2 cannot be liquid above 31°C, therefore any swelling with a pure CO_2 based C/C system will be confined to the coldest parts of the system.

The lubricants contained in the refrigerant fluid may cause problems because the individual δ of the mixture will proportionate by volume fraction from the δ values for refrigerant and lubricant. Thus δ for the refrigerant alone may be well away from that of the proposed elastomer, but the addition of the lubricant will shift δ, potentially towards or even overlapping that of the elastomer, resulting in unacceptably high swelling.

3.4 EXPLOSIVE DECOMPRESSION (ED)

Large amounts of dissolved gas in the elastomer, caused by pressurisation, can cause rupture of the seal during subsequent rapid pressure decreases. The dissolved gas expands as the pressure falls and may collect at flaws in the elastomer. If the gas cannot diffuse out of the material quickly enough bubbles above a certain critical size may grow, crack and cause rupture of the seal. The diffusion of fluid into the elastomer and permeation of fluid through the elastomer are separate, different parameters. This effect is particularly likely when using carbon dioxide as it is very soluble in many elastomer types. The FKM seal shown in Figure 6 has been completely shattered by ED from extreme conditions, from the conditions likely in an air conditioning system, ED damage is likely to be no more than a few surface blisters.

ED will be minimised by good mechanical properties and tear strength, a low solubility coefficient, high diffusion coefficient. Looking at table 1, for the three elastomers at the same conditions, provided all has similar mechanical properties, the FKM iii (shaded) would expected to most prone to ED damage.

This variability emphasises the importance of measuring permeation, diffusion and solubility coefficients (Q, **s** and D) for every refrigerant fluid and elastomer combination being considered at representative conditions to eliminate those combinations with undesirable characteristics.

3.5 SELECTION OF AIR CONDITIONING FLUIDS

The Kyoto protocol of 1995 has banned the use of CFCs (like R 12)and is curtailing the use of HFCs (like R134a). Alternative fluids are therefore being sought including carbon dioxide and some hydrocarbons. All new refrigerant fluids are likely to be less effective than CFCs, so climate control systems will need to run at higher temperatures and pressures to provide the same cooling effect, which will have a efficiency penalty.

The critical temperature is the temperature above which the fluid cannot be a liquid, no matter what pressure is applied. The transition from liquid to gas and back again at sensible temperatures is the key process of C/C system.

Table 4 Critical temperature data for some refrigerants

	Tc Critical temperature °C (°F)	Pc Pressure at Tc Mpa (psi)
Ammonia	132 (270)	11.3 (1638)
Butane	152 (306)	4.3 (628)
CO_2	31 (88)	7.4 (1073)
Pentane	196 (386)	3.4 (489)
R11	198 (388)	4.4 (633)
R12	112 (234)	4.1 (590)
R13	29 (84)	3.9 (561)
R134a	101 (214)	4.0 (590)

This paper is intended to consider the physical aspects of sealing new refrigerants, rather than discussing detailed thermo-dynamic properties, but there are some points which should be highlighted.

3.5.1 Carbon Dioxide

CO_2 is a potential candidate for a refrigerant but to liquefy the gas, the system will need to be below 31°C, which may be a problem in hot climates. A pure CO_2 C/C system would be likely to run at pressures of around 1600 psi and at these high pressures, it is particularly soluble in many types of elastomer. This would not be so much of a concern if the pressure was constant but the pressure fluctuations expected during the use of an C/C system might give rise to explosive decompression. This is where the fluid dissolved in the elastomer, which was at high pressure, comes out of solution as the pressure falls. If the gas cannot diffuse out of the material quickly enough small bubbles may form, which may then grow causing seal rupture.

Despite being *the* green house gas, carbon dioxide has a much lower global warming potential (GWP) than R134a (1 : 1200) [1] and does not have serious toxicity problems. It could be argued that a leakage of a given mass of R134a has 1200 times the environmental impact than the same leakage of CO_2. R134a itself has one third of the halocarbon GWP of R 11 [1].

3.5.2 Hydrocarbons
Pentane has been used as a low temperature refrigerant and can be used down to -65ºC or -85ºF. As *total* hydrocarbon emissions from the entire vehicle (not just through the exhaust pipe) are now very tightly controlled, a leakage of a hydrocarbon refrigerant is undesirable. The flammability of hydrocarbon fluids is also a significant safety issue.

4.0 LABORATORY EVALUATION OF MATERIALS FOR SEALS

Determinations of the following parameters should be considered when choosing a seal material and are shown below. The first three require physical tests to be made :-

- Stress relaxation) over the full temperature range
- Compression set) likely to be encountered
- Diffusion, soloubility and permeation coefficient
- Solubility parameter for both the elestomer and refrigerant
- Explosive decompression

4.1 FINITE ELEMENT ANALYSIS
FEA can be used to determine the shape of the energised seal. In a coupling, it can be difficult to determine the area of seal exposed to the high pressure gas which makes it difficult to determine the permeation and diffusion coefficients. However, concentration contours can also be determined by FEA for the energised seal in the coupling which then allow the permeation and diffusion coefficients to be calculated.

5.0 VALIDATION BY ACCELERATED LIFE AND RELIABILITY TESTING

The above assessment process should enable a small number of potentially suitable coupling and elastomer combinations to be selected in combination with a particular refrigerant fluid. The next stage is to use sealing rings manufactured in these elastomers for final proof testing of the optimum new designs before vehicle tests. These will be under laboratory conditions and will establish comparative life time data for each coupling and elastomer combination.

These tests should replicate as many features of the vehicle installation as possible. The most important factors affecting performance of the seals in the couplings are temperature, internal fluid pressure, vibration level and the compatibility of refrigerant fluid and seal material. High temperature will age the sealing rings most rapidly and will accelerate compression set. However, high temperatures combined with high fluid pressures will give a high energising force to the sealing rings which will suppress leakage. Vibration is likely to promote leakage when the energising force on the seals is low. It is known that uncontained leakages are most likely when the system is at low temperature and pressure. Regular cold cycles where the temperature is reduced to -20ºC (-4ºF) or less will provoke leakage when the seals are sufficiently aged.

The test method is detailed in full in reference [4] but will be summarised here for completeness.

5.1 TEST RIG CONCEPT

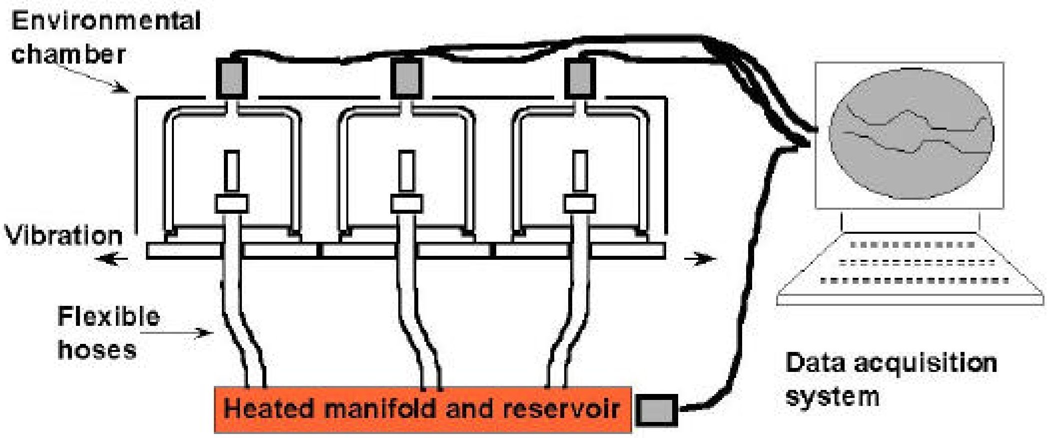
A novel test rig has been developed where up to 12 automotive climate control system refrigerant pipe couplings of different types can be tested simultaneously. A test duration of several months is used to represent many years of service conditions. Over 5 years to date, many thousand hours of testing have been completed, comparing the performance of different coupling designs and sealing materials for climate control systems.

5.2 RIG DESCRIPTION

The couplings to be tested are fitted inside gas collection cells which will collect any leaked gas. These cells are mounted on an sliding plate. All couplings are blanked off at one end and are internally pressurised with the refrigerant gas from beneath the vibrating table.

A motor mounted adjacent to the aluminium plate provides the vibrational excitation. The amplitude of vibration can be altered and the motor speed can be adjusted. Figure 7 shows a diagram of the rig.

Figure 7 Arrangement of gas collection cells and heated reservoir



The gas collection cells are contained in a close fitting chamber with heating and cooling facilities. The possible operating envelope of the rig is shown in table 5 below:-

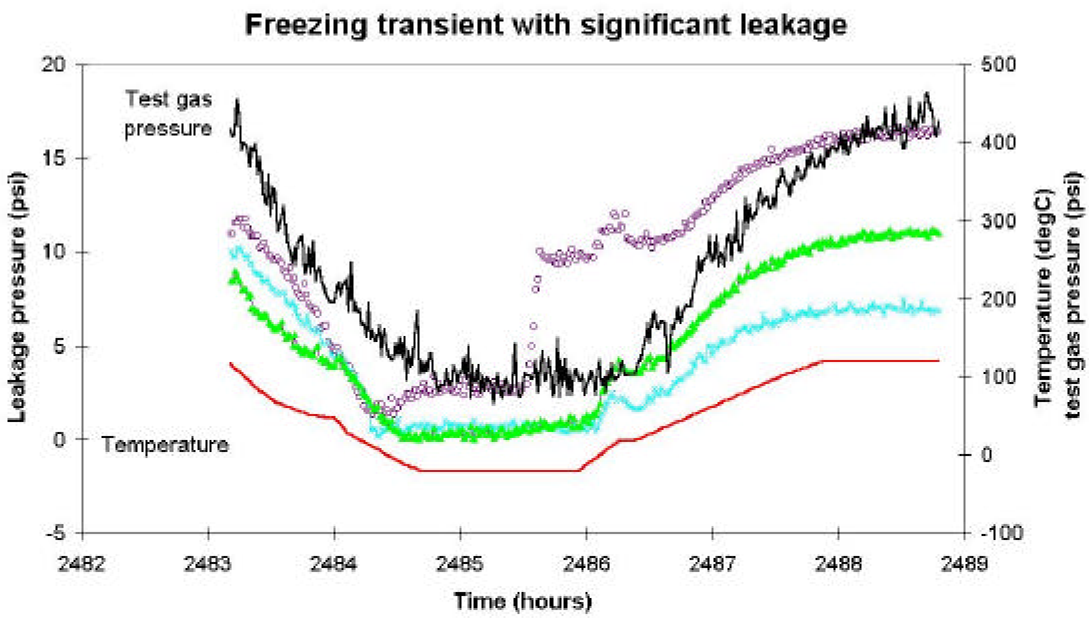
Table 5 Rig operating envelope

Maximum temperature	150	ºC
Minimum temperature	-20	ºC
Test gas pressure	800	psi
Leakage pressure	14	psi
Vibration	6	g
Speed	60	Hz
Amplitude	6	mm

Each gas collection cell consists of two parts, 1) the base which is attached to the vibrating table and in which the test fitting is mounted, and 2) a bell shaped cover which fits closely over the coupling and on which the pressure transducer is mounted. The signals from all these transducers are fed to a computer data acquisition system which displays all the data in real time.
Leakage often occurs during a freezing cycle after a considerable time of ageing at high temperature (at least 1000 hours) and detection of a leak is normally by inspection of the pressure fluctuations of the gas collection cells during a freezing cycle.

Tests can be tailored to the clients requirements but usually consist of steady state periods at high temperature and hence high test fluid pressure, interspersed by short cycles at temperatures as low as -40ºC which cause the test fluid pressure to decrease.   Continuously vibration is usually applied.

A typical chart showing leakage is shown as figure 8 below.



Examination of the sealing rings after several thousand hours of testing often shows considerable set.   This shows that sealing force, due to the natural resilience of the elastomer, has been lost.   Set can often reduced by adjustments of the elastomer compounding ingredients, to reduce age hardening and oxidation. resistance.

6.0 CONCLUSIONS

Many factors chemical, physical and environmental affect the long term performance of the seals in an automotive climate control system.

The successful long term performance of these seals relies on the careful selection of the elastomer to be fully compatible with the refrigerant fluid so that degradation due to ageing is avoided in the long term.

This can only be successfully proven after extensive laboratory tests of all candidate elastomers, followed by accelerated testing of complete coupling assemblies in a laboratory test rig under simulated vehicular conditions.

In the future, more stringent evaporative emission levels, which will include emissions due to permeation through seals and pipes, extend the significance of this approach to sealing systems and pipelines for fuels.

7.0 ACKNOWLEDGEMENTS

The sponsorship and technical assistance of FORD MOTOR COMPANY and VISTEON is gratefully acknowledged.

The permission of MERL to publish the data, and the particular assistance of Bob Campion, Des Deham and Glyn Morgan (among others) is also acknowledged.

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