Criteria to be met for the commercial introduction of a new refrigerant

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Key references

ISO 817.5, Ashrae 34

Refrigerants – Designation and safety classification

EN 378

Refrigerating systems and heat pumps – Safety and environmental requirements

SAE J 639

Safety standards for motor vehicle refrigerant vapor compressions systems

ISO 17 584

Refrigerant properties

Environmental Impacts

Zero ODP (Ozone Depleting Potential)

Substances are defined in Annexes of the Montreal Protocol

Kyoto Protocol and EU regulation

European regulation,

- Directive 2006/40/CE and Regulation 842/2006
- The Directive forbids the use of refrigerants with a GWP > 150 as of January 1, 2011 in new types and as of January 1, 2017 in all vehicles.

Designation

An identifying number of 2 to 4 digits is assigned to each refrigerant (after the prefix R-)

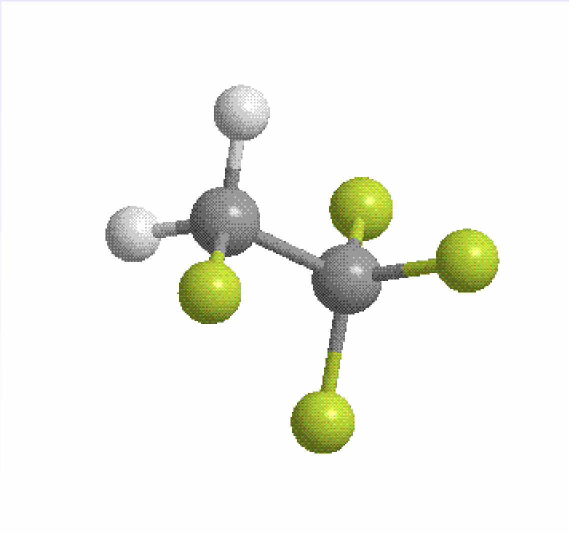
The chemical composition of the compound can be explicitly determined from the refrigerant number

Numbering rules ex: R-134a

The 400 series for the zeotropic blends

The 500 series for the azeotropic ones

The 700 series for inorganic compounds ex: R-744



Toxicity

2 classes (A and B) are assigned based on TLV-TWA (Threshold Limit Value-Time Weighted Average)

- Class A (lower chronic toxicity) toxicity **not** identified at concentration < 400 ppm/v

- Class B toxicity identified at concentration < 400 ppm/v
  Chronic toxicity refers to repeated exposure on a long period of time

  - tests for several months exposure up to 15 000 ppm
  - genotoxicity: study of mutagenic effects
  - teratogenicity
  - ecotoxicity

Toxicity (cont'd)

RCL is determined based on ATEL and ODL

- RCL (refrigerant charge limit)
- ATEL (acute toxicity exposure limit)
- ODL (oxygen deprivation limit) : minimum C 18%

ATEL based on determination of the lowest of the 4 TCFs (toxic concentration factors)

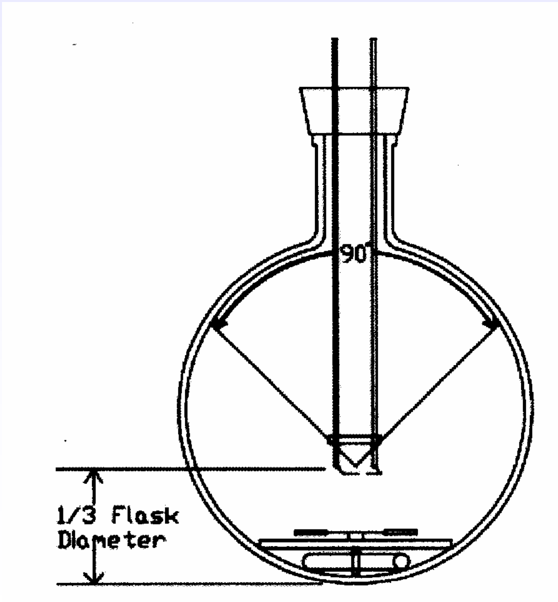
- ALC (approximative lethal concentration),
- CS (cardiac sensitisation),
- CNSE (central nervous system effect),
- OEIS (other escape impairing symptoms)

Flammability

ASHRAE 34, ISO 817.5, and EN-378 define three classes

- Class 1: no flame propagation
- Class 2: LFL > 3.5% v/v and HOC < 19 MJ/kg
- Class 3: LFL $\leq$ 3.5% v/v and HOC $\geq$ 19 MJ/kg

The lower flammability (LFL) is determined according to ASTM E681-01 tests.



Safety group classification

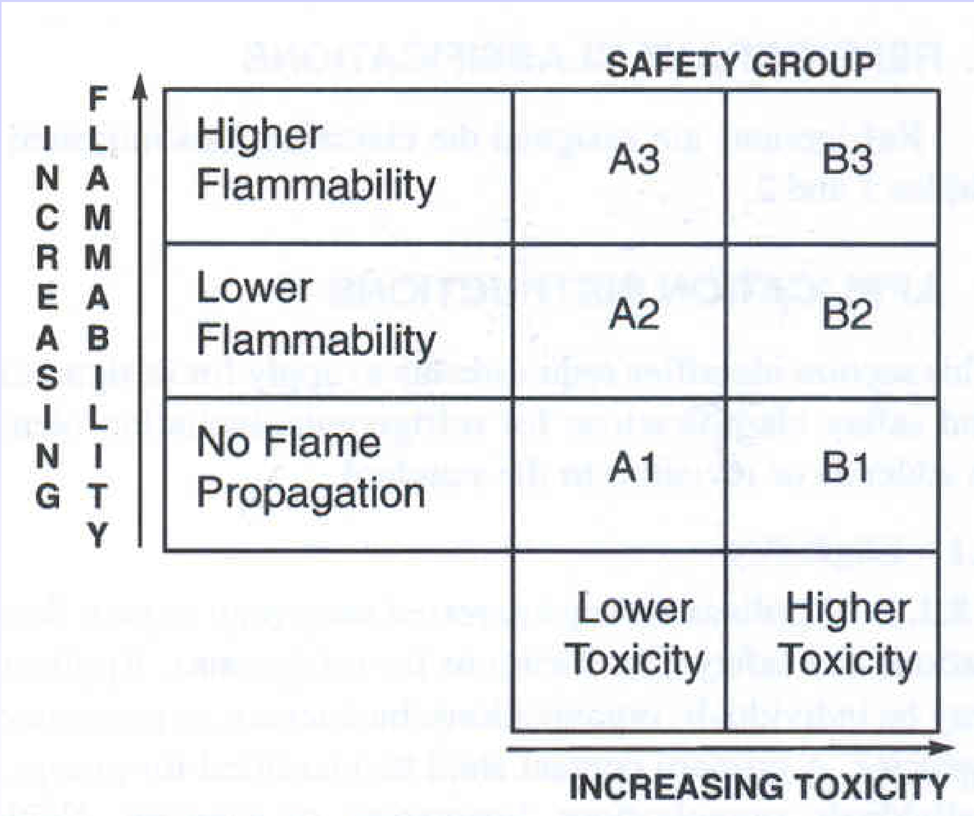
WCF (Worst Case Formulation)

WCFF (Worst Case Fractionated Formulation)

WCF & WCFF are determined both by simulation (using for example the Refleak Software developed by NIST) and by tests.

Tests for toxicity and flammability are performed for WCF and WCFF with the highest compostion of the most toxic or flammable component.

Safety group classification



Refrigerant concentration limit (RCL)

The RCL assumes full vaporization and uniform mixing of the refrigerant in the atmosphere.

The RCL is the lowest concentration value of:

- ATEL (acute toxicity exposure limit)
- ODL, minimum value of 18%
- FCL (flammable concentration limit) being 20% of the LFL.

Thermodynamic and thermophysical properties

The following properties are described in the standard:

density, pressure, internal energy, enthalpy, entropy, heat capacity, speed of sound in single phase state and along the liquid-vapor saturation boundary.

ISO 17584 presents equations of state that can be used to calculate a list of refrigerants. Among them are R-134a and R-744.

Energy performances

Cooling capacity should be identical for the same surface areas of condenser and evaporator.

Two options are possible

- Keep the same range of volumetric capacity (soft optimization): R-12, R-134a, blend H, and DP-1
- Change the range of volumetric capacity and consequently of pressures (R-744)

Energy performances (cont'd)

The most significant criteria are

- cooling capacity both for de-soaking and steady state
- COP linked to pressure ratio, viscosity, thermal conductivity, and evaporating and condensing pressures

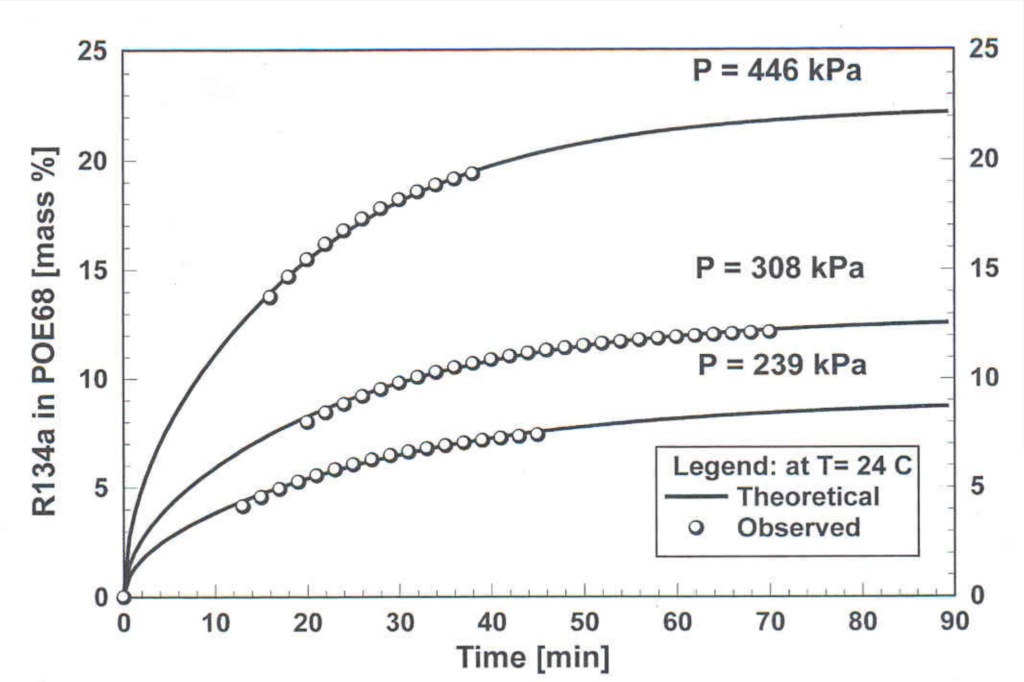
By design, the MAC system will be either soft optimized by integration of the detailed thermophysical properties or designed anew when thermophysical properties are significantly different.

Solubility of refrigerant in oil

Solubility:

refrigerant gas dissolving in the oil (P and T dependence).

Solubility of refrigerant in oil is highly important for the standstill period in order to know what quantity of refrigerant will be outgassing at the start of the compressor.



By courtesy of A. Yokozeki

Miscibility of oil in refrigerant

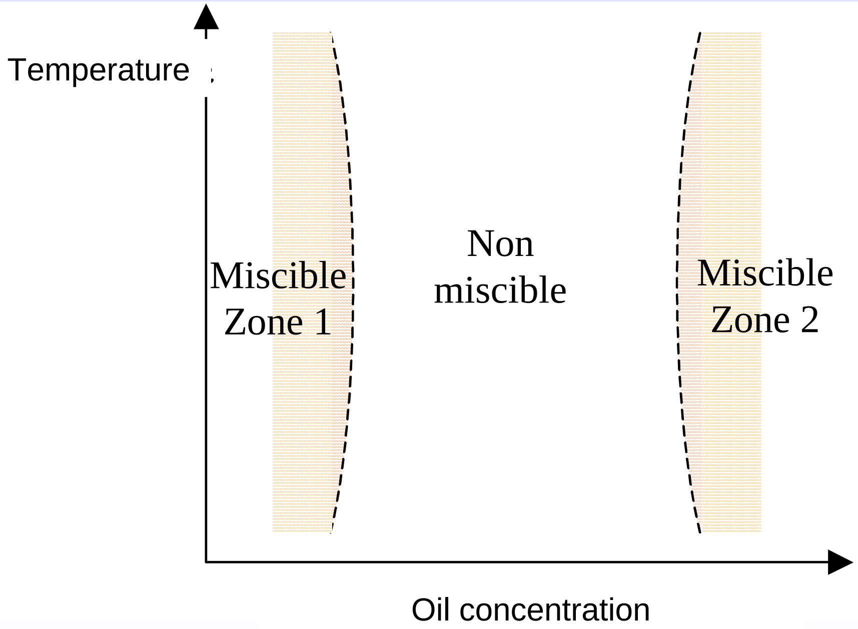
Miscibility:

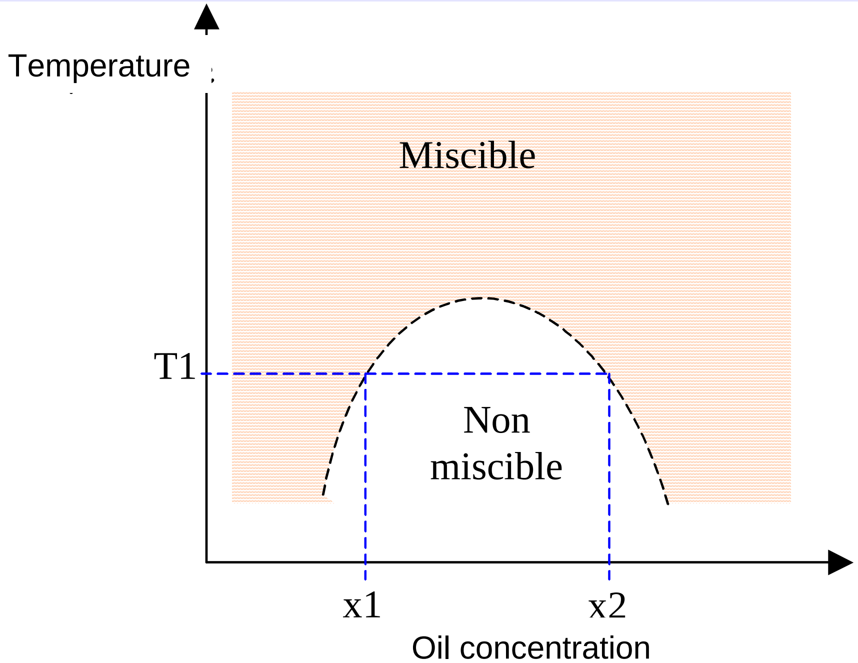
concentration of oil in liquid refrigerant.

Miscibility of oil in refrigerant determines the oil circulation in the MAC system and so the oil hold up in the system (out of the compressor) and the oil circulating ratio.

Miscibility of oil in refrigerant

By courtesy of Autofrost





Thermal stability

Highest pressures and temperatures are met at the discharge port of the compressor.

Tests are performed both in sealed tubes and on test benches in real operation conditions.

Possible decomposition of molecules occurs if the molecule bonds are weak or if active chemistry occurs (small water content).

Compatibility with materials and elastomers

Sealed glass tube containing all types of materials (aluminum, copper, steel) are blend with refrigerant and oil mixture and are heated up during long period of time (15 days) in order to verify possible reactions (Ashrae standard 97-99).

For elastomers tests are done at different temperatures to verify swelling or shrinkage, even reaction between the oil-refrigerant mixture and the elastomer material.

Diffusivity and solubility in elastomers

Characterization of the permeability of refrigerant gas through polymers used in hoses is necessary to verify the leak flow rate associated with elastomer permeability.

The leak flow rate is a function of the saturating pressure of the refrigerant, which varies with the square of the pressure. It has been one of the main drivers to keep the range of evaporating pressure identical when replacing R-12 by R-134a.

Dielectric properties
(for electric driven compressors EDC)

For hermetic electrical compressors refrigerant comes in direct contact with the motor. So electrical properties of refrigerant impact on performance and reliability.

Electrical properties include mainly breakdown voltage and dielectric constant.

The dilectric strength of a medium (refrigerant) is the breakdown voltage divided by the distance between the electrodes at breakdown.

The dielectric constant is the ability of a material to shield a charge from surrounding charges.

Dielectric properties (for electric compressors)

Measurements are done using ASTM D150 and ASTM D924.

Dielectric constant of

- R-134a: 1.064
- R-12 saturated vapor: 1.02

R-134a time frame introduction
Lessons learnt from the past

1978 Manufacturing process of 1,1,1,2-tetrafluoroethane (R-134a) disclosed in US patent 875,934.

1988 Implementation of AFEAS (alternative fluorocarbons environmental acceptability study) is set up by the main chemical manufacturers in order to study toxicity of several HFCs, and specially HFC-134a.

1989 Several patents for different manufacturing routes of R-134a.

First technical tests in systems.

1992 Early introduction in first MAC systems.

1994 Industrialization of MAC systems using R-134a.

Conclusions

Safety properties, toxicity and flammability lead to go / no-go development if the RCL is considered too low.

Environmental impacts, ODP and GWP, have now defined limits in Europe for refrigerants used in mobile air conditioning systems:

- ODP = 0
- GWP < 150

Thermodynamic properties imply limited or significant modifications of the current technology developed for R-134a.

Conclusions (cont'd)

Energy efficiency and cooling capacity are constrained by the physical dimensions of heat exchangers. At the introduction of a new refrigerant, energy performances should be in the same range as the replaced refrigerant.

Complementary technical properties: solubility of refrigerant in oil, miscibility of oil in refrigerant, thermal stability, and compatibility with elastomers lead also to complementary development, adaptation or changes.

The introduction of a new refrigerant, independently of manufacturing issues, is a process that takes about three years. The chronic toxicity studies require at least two years.