Refrigeration Oils for Natural Refrigerants

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Refrigeration Oils for Natural Refrigerants

Content

• General requirements

• Key characteristics – miscibility and viscosity

• RENISO refrigeration oils for Natural refrigerants (NH₃) Hydrocarbons (e.g. propane, propylene) Carbon Dioxide (CO₂)

• Summary / outlook
Requirements for refrigeration oils

- Reliable lubrication properties (viscosity, antiwear performance)
- Good miscibility with refrigerants (oil transport, heat transfer)
- High chemical and thermal stability (in combination with refrigerant)
- Good compatibility with components (metals, plastics, elastomers)
- Reliable isolation properties (in hermetic compressors)
- Low water content
Oil-refrigerant mixtures: „poor miscibility“
What does that mean?

Poor miscibility = phase separation into oil phase + refrigerant phase

Refrigeration oil with refrigerant → milky turbid emulsion

Refrigeration oil (with poor miscibility)

Refrigerant → completely separated

Poor miscibility:
→ Negative impact on oil transport: Oil gets collected in the system → compressor is running dry
→ Negative impact on heat transfer: Insulating/blocking oil film → decrease in performance
Viscosity temperature diagram: Viscosity index (VI)

Viscosity temperature diagram or viscosity index (VI) describes:

- 100% oil (without refrigerant)
  - ✓ viscosity decreases with increasing temp.
  - ✓ depending on the base oil type

Ideal: viscosity should …
- not increase at lower temp.
- not decrease at higher temp.

→ flat line / high VI (> 100)

Kinematic viscosity in mm²/s

Temperature in °C

40 °C reference temperature

Synthetic oil (PAO): VI = 130

Mineral oil (naphthenic): VI = 40
The PVT diagram shows

Viscosity (V) of the mixture =
Oil with dissolved refrigerant under operating conditions (p, T)

✓ Viscosity decreases with increasing content of refrigerant.
✓ The higher the pressure and the lower the temperature, the higher the refrigerant content.

Example diagram: RENISO C 55 E/CO₂
(concentration data in mass-% oil in CO₂)
RENISO refrigeration oils for
Ammonia (NH₃, R717)
Refrigeration oils for ammonia (NH$_3$)

Refrigeration oils based on mineral oils

„Classic“ refrigeration oils for ammonia: Naphthenic mineral oils

- ... good low temperature properties:
  Based on naphthenic mineral oil

- ... world-wide available:
  Long-term availability is secured

- ... compatibility and miscibility with all other NH$_3$ oils (except PAGs):
  In every proportion

- ... very good compatibility with elastomers:
  No problems with HNBR, NBR, CR elastomers
  → Proven seal compatibility with commonly used elastomers

RENISO KM 32
RENISO KS 46
RENISO KC 68
RENISO KES 100
RENISO KW 150
Refrigeration oils for ammonia (NH₃)

Refrigeration oils based on PAOs…

…like:

RENISO UltraCool 68
RENISO Synth 68

… surpass mineral oils with regard to:

- Low temperature flowability → for lower evaporation temperatures
- Evaporation loss → for less oil consumption
- Thermal stability → for less deposits in compressors / filters
- Lifetime → for longer oil change intervals
Refrigeration oils for ammonia (NH₃)
Refrigeration oil stability in contact with ammonia (DIN 51538)*

Appearance of oil + tubes after test:

- **Mineral oil RENISO KC 68**: no deposits, slight discoloration
- **PAO R.UltraCool 68**: no deposits, no discoloration
- **PAO RENISO SYNTTH 68**: no deposits, no discoloration
- **Mineral oil (average)**: deposits, dark coloration

*oil ageing procedure acc. DIN 51538: 120 °C / 7d / NH₃ + air / steel coupons
Refrigeration oils for ammonia (NH₃)  
Evaporation loss (→ oil carry over)  

Evaporation loss acc. to ASTM D 972  
150 °C / 22 h / air flow rate 2 l/min  

Synthetic PAO refrigeration oils have lower evaporation losses than refrigeration oils based on mineral oil  
→ less oil refilling quantities in the compressor
Refrigeration oils for ammonia (NH₃) Sealing compatibility

Sealing material: Chloroprene (CR). Storage in oil: 7 days at 100 °C

Moderate swelling of 5 – 15% means:
No problems with oil leakage at the seal

→ PAO without seal conditioner may perhaps cause problems with CR

→ Suitable are mineral oils and PAO with seal conditioner:
  RENISO UltraCool 68 and UltraCool 100
Refrigeration oils for ammonia (NH₃) based on synthetic PAO

<table>
<thead>
<tr>
<th>ISO VG</th>
<th>Basis naphthenic mineral oil</th>
<th>Basis synthetic oil PAO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RENISO K</td>
<td>RENISO UltraCool</td>
</tr>
<tr>
<td></td>
<td>Kin. visc. at 40 °C [mm²/s]</td>
<td>Kin. visc. at 100 °C [mm²/s]</td>
</tr>
<tr>
<td>68</td>
<td>RENISO KC 68</td>
<td>68</td>
</tr>
<tr>
<td>100</td>
<td>RENISO KES 100</td>
<td>100</td>
</tr>
<tr>
<td>150</td>
<td>RENISO KW 150</td>
<td>150</td>
</tr>
<tr>
<td>220</td>
<td>RENISO KX 220</td>
<td>220</td>
</tr>
</tbody>
</table>

**Synthetic PAO refrigeration oils provide high lubricating film thickness: also at high temperatures reliable lubrication (“High VI effect”)**

→ Suitable especially for heat pumps
Refrigeration oils for ammonia (NH₃) 
Miscibility at higher temperatures (!)

Fig. 4 Miscibility behavior in the system Reniso KC 68 – R717

Fig. 2 Miscibility behavior in the system Reniso Synth 68 – R717

at 80 °C: up to 6.5% NH₃ are miscible with refrigeration oil
Refrigeration oils for ammonia (NH\textsubscript{3})

Maximum NH\textsubscript{3} concentration

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Maximum NH\textsubscript{3} concentration in the oil/NH\textsubscript{3} mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mineral oil RENISO KC 68</td>
</tr>
<tr>
<td>&lt; 0 °C</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>40 °C</td>
<td>2.2%</td>
</tr>
<tr>
<td>60 °C</td>
<td>4.1%</td>
</tr>
<tr>
<td>80 °C</td>
<td>6.4%</td>
</tr>
</tbody>
</table>

→ Also in „non-miscible“ NH\textsubscript{3} oils there can be a homogeneous mixture with ammonia at elevated temperatures.

→ Synthetic oils: less NH\textsubscript{3} is solved → less impact on viscosity
Refrigeration oils for ammonia (NH₃)
Miscibility and viscosity

How big is the influence of miscibility on the viscosity?

Please see here:

Forschungsrat Kältetechnik Project

FKT 208/17 Effect of the ammonia solubility on the viscosity of different refrigeration oil types

Examined oils:
- Mineral oil based
- PAO based (both in ISO VG 68)

Result:
→ Mixture viscosity of PAO oils is in general higher compared to mineral oils
RENISO refrigeration oils for Hydrocarbons (Propane, Propylene, Isobutane etc.)
Refrigeration oils for hydrocarbons
Miscibility with R290

R290 shows good miscibility with refrigeration oils based on mineral oil, PAO or POE.
Refrigeration oils for hydrocarbons
Miscibility with R290

PAG: Miscibility depends on the chemical basic structure:
Relation ethylene oxide / propylene oxide in the molecule

- For PAG 11-Typ (EO:PO = 1:1), miscibility is indicated at certain concentration levels for a given temperature range.
- For PAG 01-Typ (EO:PO = 0:1), miscibility is indicated at different concentration levels for another temperature range.

Oils in ISO VG 68
Refrigeration oils for hydrocarbons: R290 solubility and viscosity

<table>
<thead>
<tr>
<th></th>
<th>Base oil</th>
<th>Without R290 40 °C</th>
<th>With R290 5 bar / 40 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>RENISO</td>
<td></td>
<td>kv [mm²/s]</td>
<td>Conc. [m% R290]</td>
</tr>
<tr>
<td>KC 68</td>
<td>MO</td>
<td>68</td>
<td>8.0</td>
</tr>
<tr>
<td>SYNTH 68</td>
<td>PAO</td>
<td>68</td>
<td>9.0</td>
</tr>
<tr>
<td>SEZ 68</td>
<td>POE</td>
<td>68</td>
<td>6.5</td>
</tr>
<tr>
<td>PG 68</td>
<td>PAG</td>
<td>68</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Different oil types show different degrees of solubility:

PAG and POE: Lower solubility and higher mixture viscosity
Mineral oil and PAO: Higher solubility / lower mixture viscosity (esp. MO)

→ PAG / POE best choice for hydrocarbons with regard to wear protection
PAG also have high VI (>200): additional benefits at high temperatures

kV = kinematic viscosity

PAG also have high VI (>200): additional benefits at high temperatures
RENISO refrigeration oils for
Carbon Dioxide (CO$_2$, R744)
Refrigeration oils for CO$_2$
R744 / CO$_2$ cooling applications

Stationary applications (cooling / refrigeration / heat pump):

➢ Supermarket cooling
   (cascade and transcritical systems)
➢ Ship cooling
➢ Heat pumps (industrial and domestic use)

Mobile applications (A/C): mainly projects

➢ Passenger cars (Daimler, VW)
➢ Coaches
➢ Trains
Refrigeration oils for CO\(_2\)

CO\(_2\) miscibility of the refrigeration oil

- Polyalphaolefins (PAO) oils are not miscible with liquid CO\(_2\).
- Polyalkylene glycol (PAG) show a limited miscibility: used in compact systems (car a/c, heat pumps etc.).
- CO\(_2\) refrigeration oils based on polyol esters (POE): are the most important group because of the very good miscibility with CO\(_2\).
Refrigeration oils for CO$_2$
RENISO C: CO$_2$ refrigeration oils based on POE

**Excellent miscibility of RENISO C with CO$_2$**

- High flowability at low temperatures
- No negative impact on the heat transfer in the evaporator
- Safe oil transport back to the compressor also in large tubing systems (supermarket)
- No oil separator necessary
Refrigeration oils for CO₂
CO₂: Established technology in supermarkets in Central / Northern Europe

Installed in more than 1600 supermarkets

POE with special additive system for

• Good CO₂ miscibility (oil return, heat transfer)
• High thermal stability (transcritical)
• Reliable lubricating properties (high pressure)
Refrigeration oils for CO₂
RENISO ACC 68: CO₂ refrigeration oil based on PAG (double end-capped)

- Significant miscibility gap
- Use in compact cooling systems
- Lower dilution under CO₂ atmosphere: higher lubricant film thickness

➔ Very good practical experience in heat pump and air conditioning applications
Refrigeration oils for CO$_2$

For carbon dioxide (CO$_2$, R744)

RENISO C: Based on POE
Special anti-wear additivation guarantees excellent lubricating properties

- **RENISO C 55 E:** subcritical, e.g. supermarket cooling
- **RENISO C 85 E:** subcritical / transcritical, e.g. supermarket cooling
- **RENISO C 170 E:** mainly in subcrit. screw compressors e.g. ship cooling

RENISO C oils are used in nearly all relevant CO$_2$ compressors in all regions

RENISO ACC: Based on double end-capped PAG incl. special anti-wear (AW) additives

- **RENISO ACC series:**
  
  For heat pumps and A/C applications (passenger car A/C e.g. Daimler, VW)

> 15 years of experience
Why using anti-wear (AW) additives in CO\textsubscript{2} refrigeration oils?

Anti-Wear (AW) additives are “activated” under mixed friction conditions:

→ Lubricating film tears off, no hydro-dynamics
→ No separating oil: contact of roughness peaks of the metal surfaces

*Danger of wear!*

Mixed friction is more often present with CO\textsubscript{2}:
High oil dilution with CO\textsubscript{2}
High loads in the bearing
High temperature in lubricating gap
Low sliding speed (start-up)

AW additives form **protective reaction layer on the surface**
→ Protection against wear
Refrigeration oils for CO₂
Additional reactant carbonic acid

Carbonic acid: carbon dioxide and water

\[ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \]  carbonic acid

Possible consequences:  Decomposition of the lubricant
Attack of seals and metal
surfaces  corrosion, copper
plating
Refrigeration oils for CO\textsubscript{2}

Copper plating

Example: polyol ester oil (POE) with a water content of 300 ppm in CO\textsubscript{2} cascade system

Copper in polyol ester oil shows green colour (in some cases)

Copper plating main bearing of crank shaft
Summary / Outlook

• The number of applications using natural refrigerants is increasing

• New challenges for refrigeration oils – very specific & related to the refrigerant

• Lubricant solution do already exist and work

• But – there is still a lot more to learn and sometimes to improve
„Keep cool…it‘s all natural!“

Thank you for your attention!
eurammon is always available as a sparring partner for questions on refrigeration with natural refrigerants

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