#### **Refrigeration Oils for Natural Refrigerants**

FUCHS Schmierstoffe GmbH, Christian Puhl

eurammon symposium, Klostergut Paradies, June 28, 2019

# eurammon

refrigerants delivered by mother nature



#### **Refrigeration Oils for Natural Refrigerants Content**



- General requirements
- Key characteristics miscibility and viscosity
- RENISO refrigeration oils for Natural refrigerants (NH<sub>3</sub>) Hydrocarbons (e.g. propane, propylene) Carbon Dioxide (CO<sub>2</sub>)
- Summary / outlook

#### **Requirements for refrigeration oils**



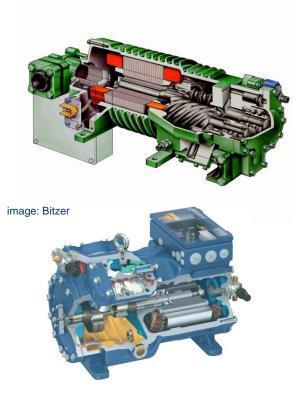


image: GEA Bock

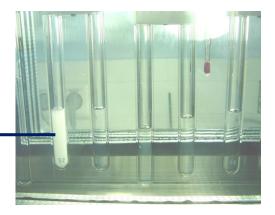
- Reliable lubrication properties (viscosity, antiwear performance)
- Good miscibility with refrigerants (oil transport, heat transfer)
- High chemical and thermal stability (in combination with refrigerant)
- Good compatibility with components (metals, plastics, elastomers)
- Reliable isolation properties (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:
- → Negative impact on heat transfer:

Oil gets collected in the system  $\rightarrow$  compressor is running dry Insulating/blocking oil film  $\rightarrow$  decrease in performance

## Viscosity temperature diagram: Viscosity index (VI)

Kinematic viscosity in mm<sup>2</sup>/s

1000

100

68

10

0



Viscosity temperature diagram or viscosity index (VI) describes: 100% oil (without refrigerant) viscosity decreases  $\checkmark$ with increasing temp. Synthetic oil (PAO): VI = 130  $\checkmark$ depending on the base oil type (naphthenic): VI = 40Ideal: viscosity should ... - not increase at lower temp. - not decrease at higher temp.  $\rightarrow$  flat line / high VI (> 100) 80 100 120 Temperature in °C

40 °C reference temperature

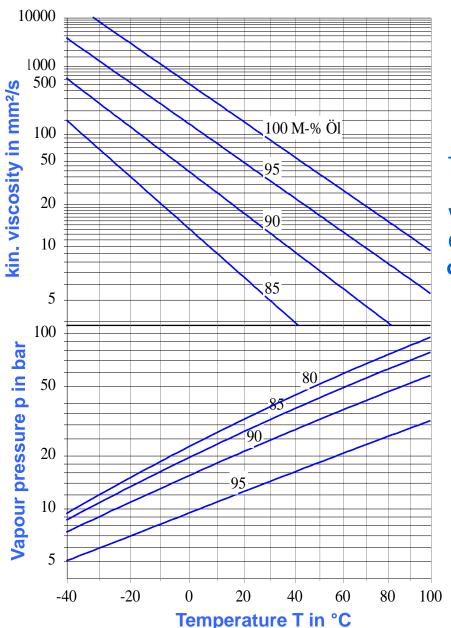
40

20

Mineral oil

60

#### PVT diagram (Pressure-Viscosity-Temperature)



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#### 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/CO<sub>2</sub> (concentration data in mass-% oil in CO<sub>2</sub>)





# RENISO refrigeration oils for Ammonia (NH<sub>3</sub>, R717)

#### **Refrigeration oils for ammonia (NH<sub>3</sub>)** 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

RENISO KM 32 RENISO KS 46 RENISO KC 68 RENISO KES 100 RENISO KW 150

- ... compatibility and miscibility with all other NH<sub>3</sub> 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

**Refrigeration oils for ammonia (NH<sub>3</sub>)** Refrigeration oils based on PAOs...



...like:

RENISO UltraCool 68 RENISO Synth 68

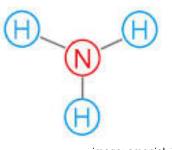


image: amoniak.info



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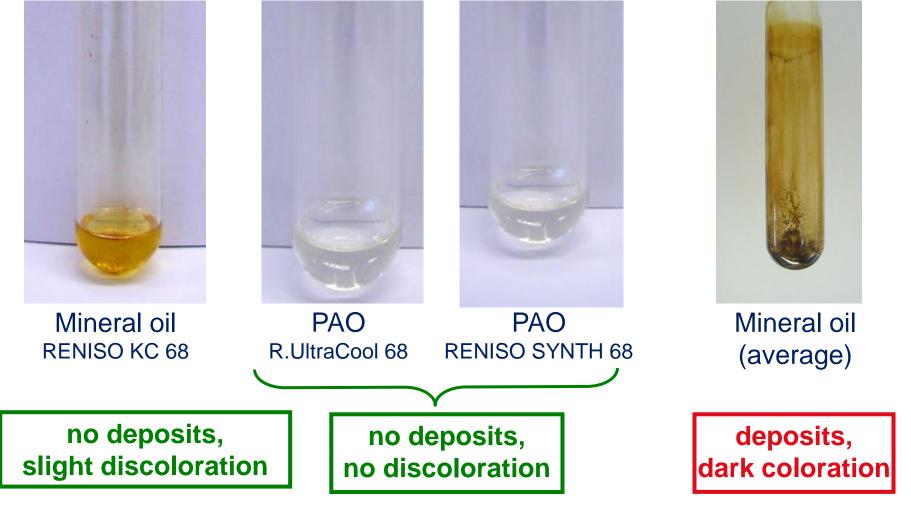
- Low temperature flowability  $\rightarrow$  for lower evaporation temperatures
- Evaporation loss  $\rightarrow$  for less oil consumption
- Thermal stability → for less deposits in compressors / filters
- Lifetime → for longer oil change intervals

... surpass mineral oils with regard to:

# **Refrigeration oils for ammonia (NH<sub>3</sub>)**

\*oil ageing procedure acc. DIN 51538: 120 °C / 7d /  $NH_3$  + air / steel coupons

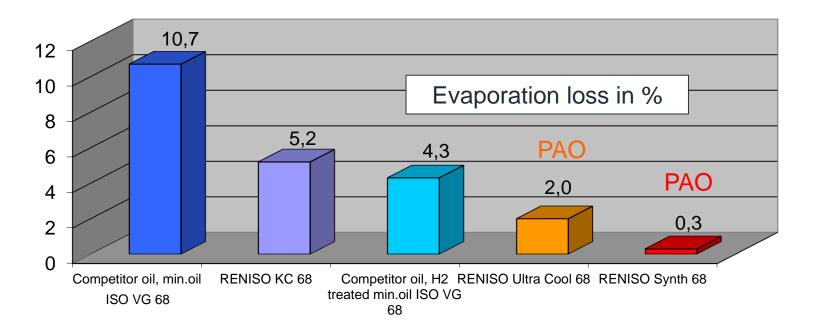
#### Appearance of oil + tubes after test:



#### Refrigeration oils for ammonia (NH<sub>3</sub>) Evaporation loss ( $\rightarrow$ oil carry over)



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



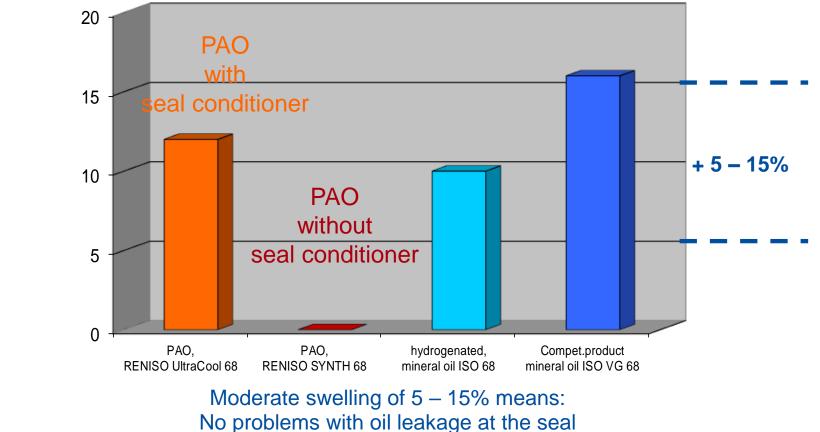
Synthetic PAO refrigeration oils have lower evaporation losses than refrigeration oils based on mineral oil → less oil refilling quantities in the compressor

# Refrigeration oils for ammonia (NH<sub>3</sub>) Sealing compatibility

Change of volume / %



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



 $\rightarrow$  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 (NH<sub>3</sub>) based on synthetic PAO**



| ISO<br>VG | Basis naphthenic mineral oil<br>RENISO K |                                   |                                    |    | Basis synthetic oil PAO<br>RENISO UltraCool |                                   |                                    |     |
|-----------|--|-----------------------------------|------------------------------------|----|---|-----------------------------------|------------------------------------|-----|
|           |  | Kin. visc.<br>at 40 °C<br>[mm²/s] | Kin. visc.<br>at 100 °C<br>[mm²/s] | VI |   | Kin. visc.<br>at 40 °C<br>[mm²/s] | Kin. visc.<br>at 100 °C<br>[mm²/s] | VI  |
| 68        | RENISO<br>KC 68                          | 68                                | 7.4                                | 58 | RENISO<br>UltraCool 68                      | 62                                | 9.1                                | 124 |
| 100       | RENISO<br>KES 100                        | 100                               | 8.4                                | 20 | RENISO<br>UltraCool 100                     | 108                               | 14.4                               | 136 |
| 150       | RENISO<br>KW 150                         | 150                               | 10.9                               | 27 |   |                                   | $\widehat{\mathbf{A}}$             |     |
| 220       | RENISO<br>KX 220                         | 220                               | 13.6                               | 25 | <b></b>                                     |                                   |                                    |     |

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 (NH<sub>3</sub>) Miscibility at higher temperatures (!)



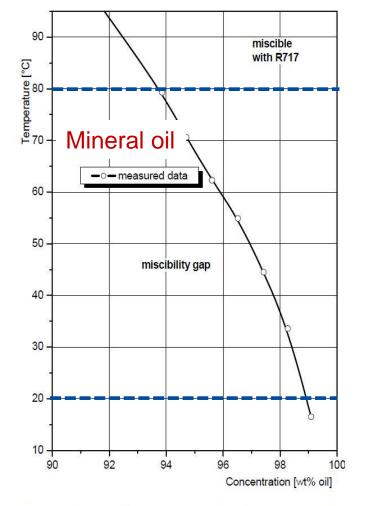


Fig. 4 Miscibility behavior in the system Reniso KC 68 – R717

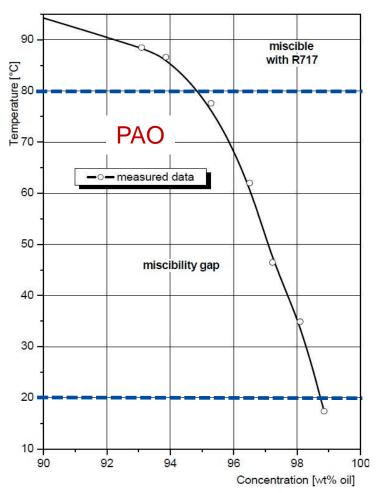


Fig. 2 Miscibility behavior in the system Reniso Synth 68 – R717

#### at 80 °C: up to 6.5% NH<sub>3</sub> are miscible with refrigeration oil

#### Refrigeration oils for ammonia (NH<sub>3</sub>) Maximum NH<sub>3</sub> concentration



|             | Fig. 4 Miscibility behavior in the system Reniso $KC  68 - R717$            | Fig. 2 Miscibility behavior in the system Reniso Synth 68 – R717 |  |
|-------------|---|--|--|
| Temperature | Maximum NH <sub>3</sub> concentration<br>in the oil/NH <sub>3</sub> mixture |  |  |
|             | Mineral oil<br>RENISO KC 68   | PAO<br>RENISO SYNTH 68   |  |
| < 0 °C      | < 1%  | < 1%   |  |
| 40 °C       | 2.2%  | 2.2%   |  |
| 60 °C       | 4.1%  | 3.4%   |  |
| 80 °C       | 6.4%  | 5.4%   |  |

Also in "non-miscible" NH<sub>3</sub> oils there can be a homogeneous mixture with ammonia at elevated temperatures.
 → Synthetic oils: less NH<sub>3</sub> is solved → less impact on viscosity

#### Refrigeration oils for ammonia (NH<sub>3</sub>) 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

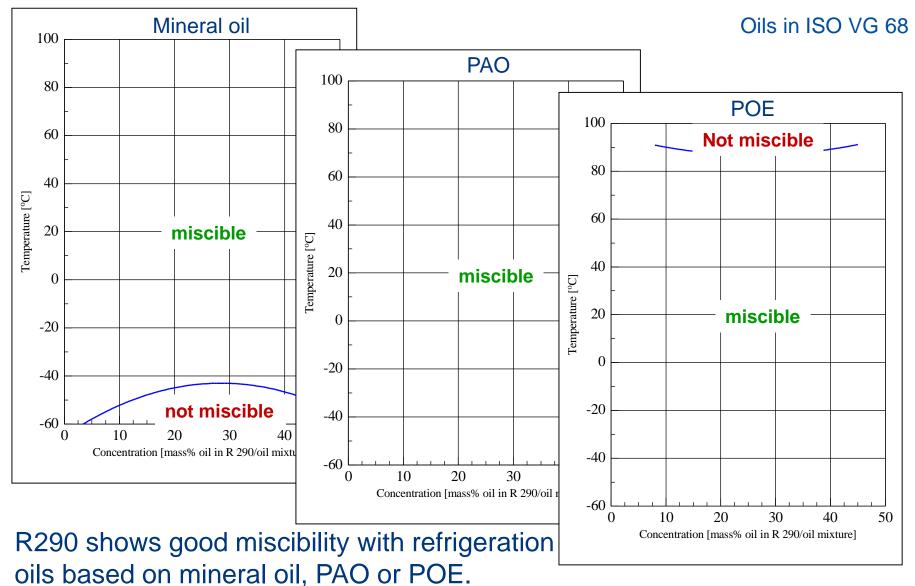




#### RENISO refrigeration oils for Hydrocarbons (Propane, Propylene, Isobutane etc.)

### **Refrigeration oils for hydrocarbons Miscibility with R290**



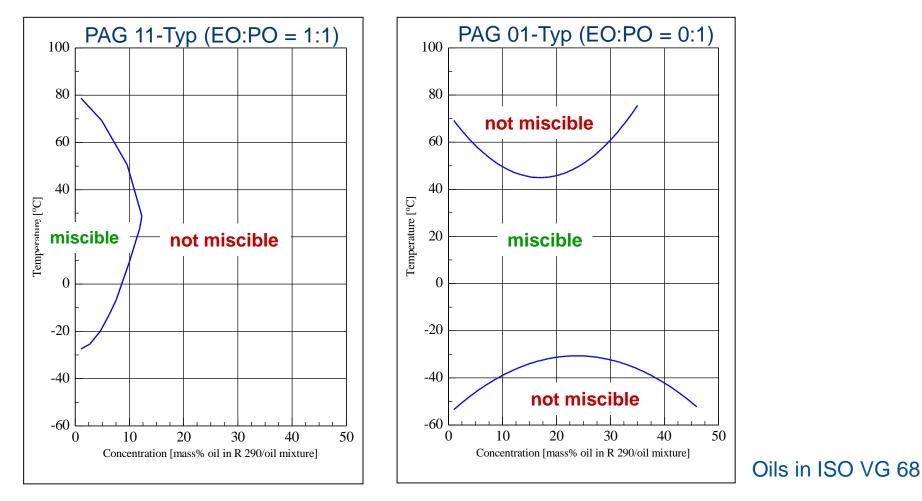


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## **Refrigeration oils for hydrocarbons Miscibility with R290**



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



### **Refrigeration oils for hydrocarbons: R290 solubility and viscosity**



|          |          | Without<br>R290<br>40 °C | Wi<br>R29<br>5 bar /      |               |                                |
|----------|----------|--------------------------|---------------------------|---------------|--------------------------------|
| RENISO   | Base oil | kV<br>[mm²/s]            | <b>Conc.</b><br>[m% R290] | kV<br>[mm²/s] | kV =<br>kinematic<br>viscosity |
| KC 68    | MO       | 68                       | 8.0                       | 12.0          | viceouty                       |
| SYNTH 68 | PAO      | 68                       | 9.0                       | 18.5          |                                |
| SEZ 68   | POE      | 68                       | 6.5                       | 28.0          |                                |
| PG 68    | PAG      | 68                       | 5.5                       | 29.0          |                                |

Different oil types show different degrees of solubility:

PAG and POE:Lower solubility and higher mixture viscosityMineral 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





# RENISO refrigeration oils for Carbon Dioxide (CO<sub>2</sub>, R744)

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#### **Refrigeration oils for CO<sub>2</sub>** R744 / CO<sub>2</sub> 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









# High miscibility with liquid CO2 DE PAG PAO Low miscibility with liquid CO2

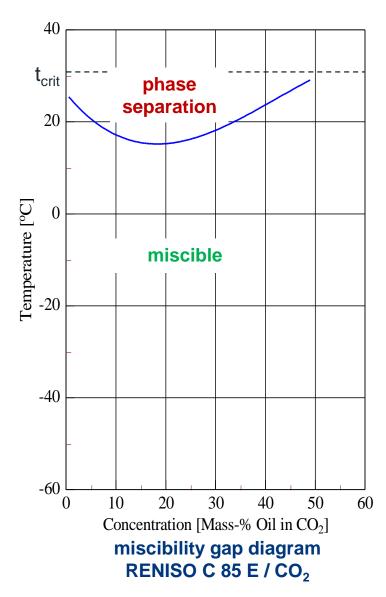
- $\rightarrow$  Polyalphaolefins (PAO) oils are not miscible with liquid CO<sub>2</sub>
- → Polyalkylene glycol (PAG) show a limited miscibility: used in compact systems (car a/c, heat pumps etc.)
- → CO<sub>2</sub> refrigeration oils based on polyol esters (POE): are the most important group because of the very good miscibility with CO<sub>2</sub>



### **Refrigeration oils for CO<sub>2</sub>** RENISO C: CO<sub>2</sub> refrigeration oils based on POE

Excellent miscibility of RENISO C with CO<sub>2</sub>

- 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 CO<sub>2</sub>**

CO<sub>2</sub>: Established technology in supermarkets in Central / Northern Europe

Installed in more than 1600 supermarkets



POE with special additive system for

Good CO<sub>2</sub> miscibility (oil return, heat transfer)

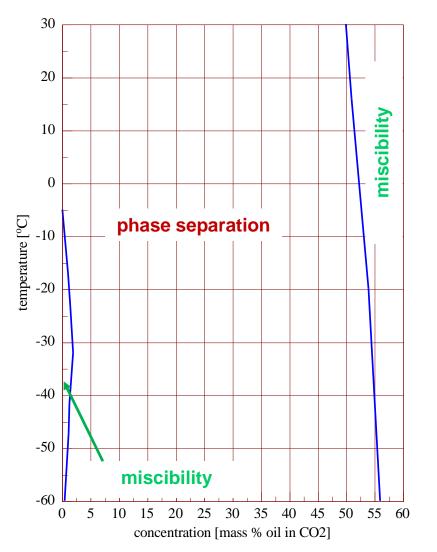
- High thermal stability (transcritical)
- Reliable lubricating properties (high pressure)



#### **Refrigeration oils for CO<sub>2</sub>** RENISO ACC 68: CO<sub>2</sub> refrigeration oil based on PAG (double end-capped)

 $\geq$ 





- Significant miscibility gap
  - Use in compact cooling systems
- Lower dilution under CO<sub>2</sub> atmosphere: higher lubricant film thickness
- → Very good practical experience in heat pump and air conditioning applications

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**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<sub>2</sub> 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)



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> 15 years of experience



# Why using anti-wear (AW) additives in CO<sub>2</sub> refrigeration oils ?



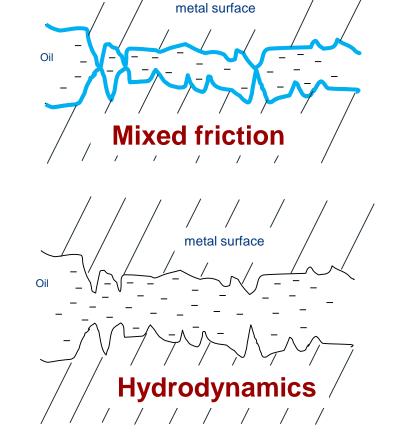
#### Anti-Wear (AW) additives are "activated" under mixed friction conditions :

→ 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  $CO_2$ : High oil dilution with  $CO_2$ 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 CO<sub>2</sub>** Additional reactant carbonic acid



#### **Carbonic acid: carbon dioxide and water**

 $CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$  carbonic <u>acid</u>

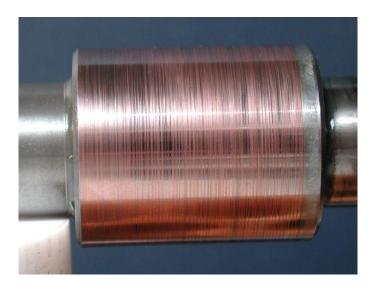
Possible consequences: Decomposition of the lubricant Attack of seals and metal surfaces→ corrosion, copper plating



# **Refrigeration oils for CO<sub>2</sub> Copper plating**

Example: polyol ester oil (POE) with a water content of 300 ppm in CO<sub>2</sub> 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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