Shrieve

# 低GWP制冷剂润滑油开发：挑战和瑞孚解决方案

## Lubricant Development for Low GWP Refrigerants: Challenges and Shrieve Solution

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# 内容提要

- **瑞孚公司简介**
- **制冷润滑油的特性及其对系统性能的影响**
- **不同制冷剂的特点及其对润滑油的挑战**
  - R32
  - R290及其它烃类
  - HFO及混合制冷剂
- **瑞孚制冷润滑油解决方案**
- **总结**

# Agenda

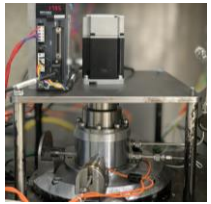
- **About Shrieve**
- **Introduction to Refrigeration Lubricants**
- **Features and Challenges for different refrigerants**
  - R32
  - R290 and heavy hydrocarbon
  - HFO & blends
- **Shrieve solutions**
- **Summary**

# 瑞孚简介

- **瑞孚化工（上海）有限公司成立于2008**
- **专注于压缩机油开发**
  - 制冷润滑
  - 空气压缩
  - 气体压缩
- **研发中心**
  - 基础油合成
  - 配方开发及测试
  - 模拟系统性能测试
  - 实际系统性能测试

# About Shrieve

- **Shrieve China operation started in 2008**
- **Focusing on compressor lubricant**
  - Refrigeration
  - Air compressor
  - Gas compressor
- **Shanghai R&D center**
  - Synthesis of new POE chemistry
  - Formulation development and testing
  - Measurement of lubricant property under application conditions
  - Real system testing



# 瑞孚简介 About Shrieve

# About Shrieve

- **全球最重要的制冷润滑油供应商之一**
  - 所有润滑油种类
  - 所有压缩机类型
  - 烷基苯：全球第一
  - 聚醚：全球第二
  - 酯类油：新结构

- **Global AC&R Lubricants Supplier**
  - all base type except PVE
  - all types of compressor
  - AB: No. 1 globally
  - PAG: No. 2 globally
  - Ester: new chemistry

| | 冰箱/冰柜 | 家用空调 | 工商业 | 汽车空调 |
|---|---|---|---|---|
| **Refrigerants** | R600a<br>R290<br>R134a | R410A<br>R32<br>R290 | R134a<br>HFO & blends<br>$CO_2$<br>$NH_3$ | R134a<br>R1234yf |
| **Compressor** | Reciprocal | Rotary | Screw/Centrifugal/<br>Reciprocal/Scroll | Scroll/Swash<br>plate/Rotary Vane |
| **Lube** | AB/MO/POE | POE/PAG | POE/AB/<br>MO/PAG | PAG/POE |

# 制冷润滑油的特性
# 及其对系统性能的影响

## Introduction to Refrigeration Lubricants

# 制冷润滑油的特殊性

- **密闭系统，受空气、水分影响小**
- **长寿命**
  - 小系统，终身不换油
  - 更加关注稳定性
- **受制冷剂的影响非常大**
  - 温度对油的性质影响更复杂
- **温度、压力变化范围非常大**
  - 固定工况下，高、低压侧T、P差别
  - 同一设备，用于不同环境温度
  - 同一制冷剂用于不同制冷应用

# Refrigeration Lube: Differences from All Other Industrial Lube

- **Sealed system: less impacted by air and moisture**
- **Long lifetime**
  - Small system: no oil change in lifetime
  - Stability is more important than other lubricant
- **Refrigerants change lube properties a lot**
  - Temperature effect is more significant
- **T/P varies a lot**
  - Fixed condition: high P/T and low P/T
  - Same unit used in different ambient condition
  - Same refrigerant for different application

## 润滑油选择考虑的主要因素

- 合适的工作粘度：润滑和回油
- 合适的相溶性：回油和性能
- 电绝缘性能：安全性
- 稳定性：长期可靠性
- 材料兼容性：长期可靠性
- 导热性能、比热容等其它性能

## Criteria for Refrigeration Lubricant Selection

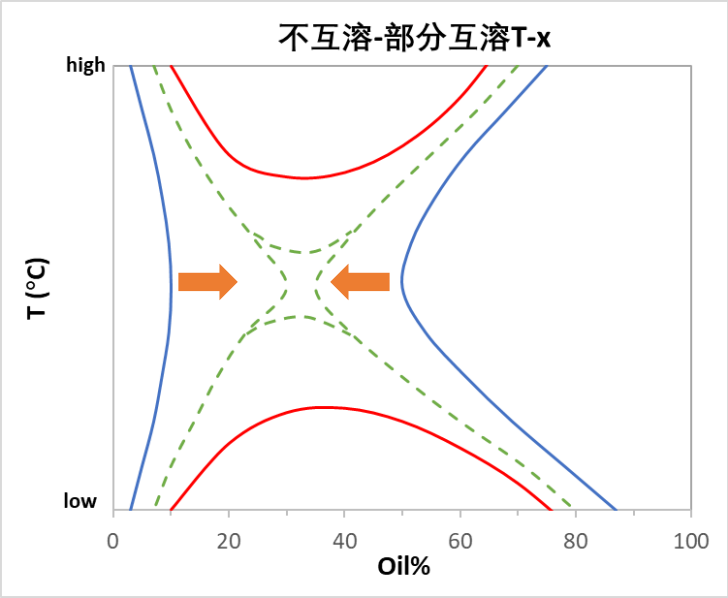
- Optimized Working Viscosity: lubricity & oil return
- Optimized Miscibility: oil return & efficiency
- Dielectric: Safety
- Stability: Durability
- Compatibility: Durability
- Others: Thermal conductivity, specific heat, et. al

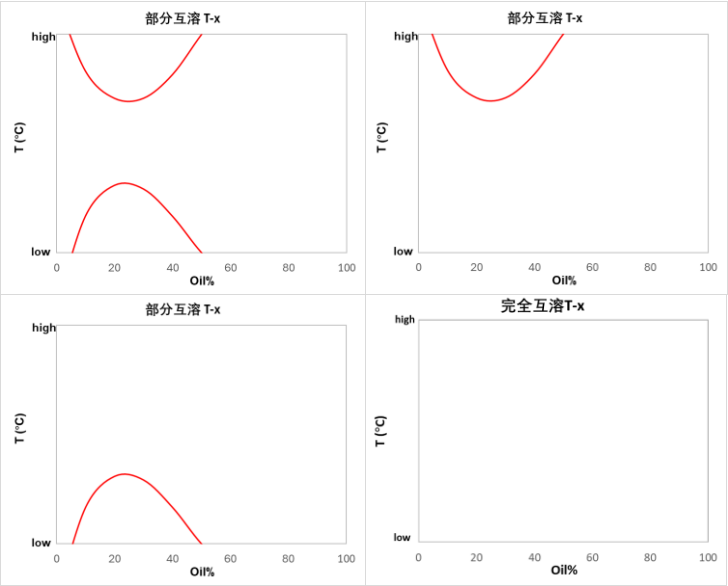
# 制冷剂和润滑油的互溶性

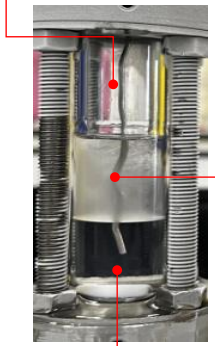
# Refrigerants/Lubricants Miscibility

- **不同制冷剂/润滑油组合可能表现为：不互溶、部分互溶、完全互溶**

- **Different combination of Ref/Lube may behave as immiscible, partially miscible, or fully miscible**

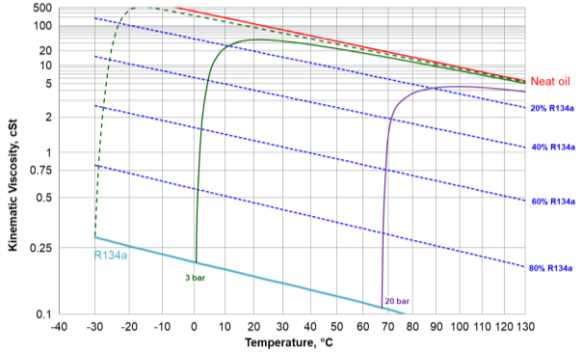


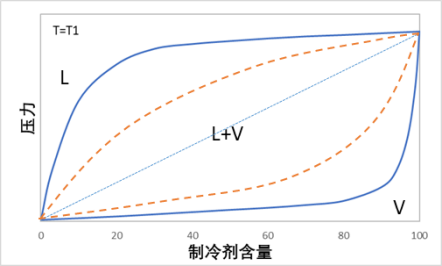



# 温度压力对溶解度及粘度的影响

- **制冷剂的溶解会大大降低混合物粘度**
- **恒温条件下，压力升高**
  - 制冷剂溶解度增加
- **恒压条件下，温度升高**
  - 制冷剂溶解度降低
  - 混合物粘度先增加后降低
- **接近制冷剂饱和点时，溶解度变化大**
  - 固定温度，压力升高接近制冷剂饱和压力
  - 固定压力，温度降低接近制冷剂露点




# T&P Effect on Solubility and Viscosity

- **Dissolving ref. into lubricant reduces viscosity significantly**
- **At constant T, as P rises**
  - Solubility of ref. increases
- **At constant P, as T rises**
  - Solubility of ref. decreases
  - Viscosity increases first, but then decreases
- **When reaching saturation condition, solubility changes dramatically**
  - T is constant, increasing P to saturation pressure of refrigerants
  - P is constant, decreasing T to saturation temperature of refrigerants

| T (°C) | P (bar) | Maximum Viscosity | | |
|---|---|---|---|---|
| | | T(°C) | Ref. content (wt%) | Viscosity (cSt) |
| -30 | 0.84 | -16 | 5.5 | 532 |
| 0.7 | 3 | 22 | 11.6 | 37.3 |
| 67.5 | 20 | 99 | 15.6 | 4.5 |

# 制冷剂演变

# Refrigerant Transition

# 制冷剂替代演变

# Refrigerant Transition

| R134a | R404A | R410A | R22 | *Other* |
|---|---|---|---|---|
| R600a | R290 | R32 | R32 | ***R1233zd*** |
| R290 | R455A | R290 | R290 | ***R1336mzzz*** |
| R1234yf | R454A | R452B | R444B | ***R-1234ze(E)*** |
| R1234ze(E) | R744 | R447B | R454C | ***R1224yd(Z)*** |
| R450A | | R454B | | ***R600*** |
| R513A | | | | ***R601*** |
| R744 | | | | |

CFC/HCFC

↓

HFC

↓

HFO/HFC; HCFO; HC; $CO_2$; $NH_3$

## 重要LGWP替代制冷剂的润滑油挑战与应对方案

- **HFC (R32)**
  - 互溶性 → 新化学结构
- **HFO**
  - 稳定性 → 添加剂
  - 溶解度 → 新化学结构
- **HC**
  - 溶解度 → 新化学结构
- **共同挑战：越来越多的极端工况**
  - 超高温、超低温

## Challenges & solutions for major LGWP alternatives

- **HFC (R32)**
  - Miscibility → New chemistry
- **HFO**
  - Stability → Additives
  - Solubility → New chemistry
- **HC**
  - Solubility → New chemistry
- **More and more extreme working conditions**
  - Super high/low temperature

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# R32润滑油开发

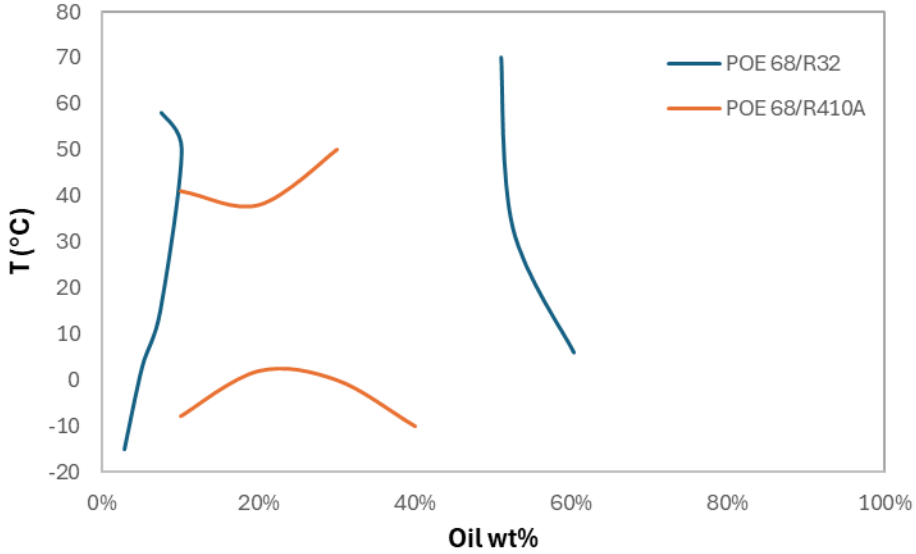
# Lubricant Development for R32

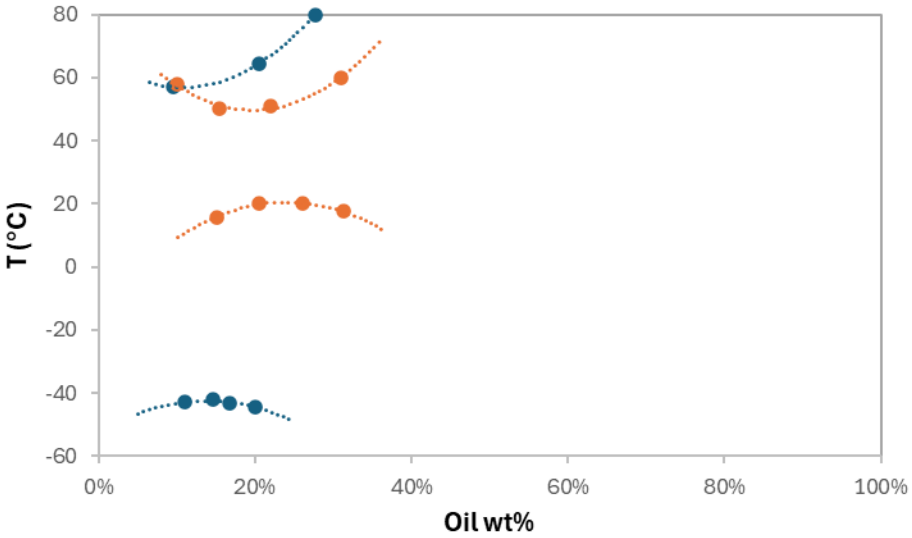
# R32 互溶性

- R32润滑油的主要挑战是互溶性
- 小型系统走向了不互溶的润滑油

# R32 Miscibility

- The major challenge for R32 lubricant is miscibility
- Small system goes to immiscible lube.



# 瑞孚R32润滑油解决方案

# Shrieve Lube Solution for R32

| 润滑油 | 基础油类型 | 压缩机类型 Compressor | R32 UCST |
|---|---|---|---|
| ZEROL® RA 68EH | POE | 滚动转子 Rotary | Immiscible |
| ZEROL® RA 70EF | POE | 滚动转子 Rotary | 20 |
| ZEROL® RA 68EC | POE | 滚动转子 Rotary | 0 |
| ZEROL® RA 68EM | POE | 滚动转子 Rotary | -40 |
| ZEROL® RA 74AE | POE | 滚动转子 Rotary | Immiscible, low cost |
| | | | |
| ZEROL® RC 40EM | POE | 涡旋 Scroll | -32 |
| ZEROL® RC 55EM | POE | 涡旋 Scroll | -40 |
| ZEROL® RC 68ED | POE | 涡旋 Scroll | -30 |
| ZEROL® RC 68EA | POE | 涡旋 Scroll | 0 |
| ZEROL® RC 32XA | PAG | 涡旋 Scroll | -30 |

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# R290润滑油开发

# Lubricant Development for R290

## R290及更重烃类制冷剂的特点和挑战

- **特点**
  - 环境友好，全球接受
  - 能力和能效都比较好
  - 和很多类型的润滑油都有良好的互溶性
  - 密度低
- **挑战 (或机会)**
  - **对润滑油稀释较大**
  - 多种选择
  - 对电性能要求相对较低

## Features & Challenges for R290 and heavier hydrocarbons

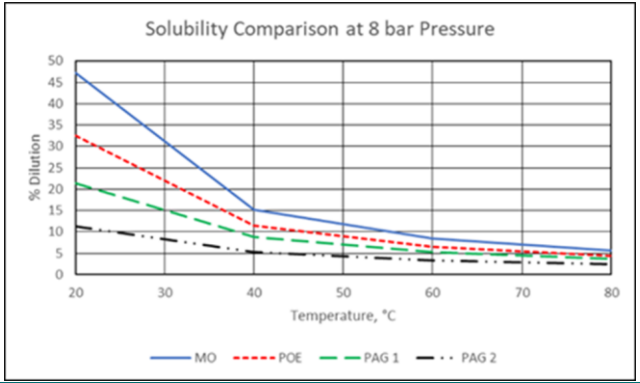
- **Features**
  - Global environmental acceptability
  - Good miscibility with different type of lubricants
  - Good capacity and efficiency
  - Low density
- **Challenges (or Opportunities)**
  - **High dilution to lubricants**
  - Multiple options
  - Less demand for dielectric property

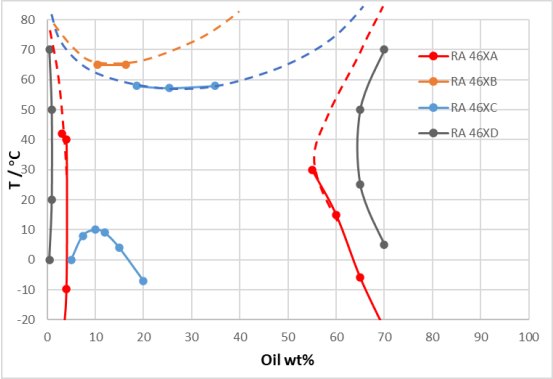
# 互溶性可控

- 对润滑油溶解性好，容易稀释润滑油
- 改变化学结构可以调节R290的互溶性
- 对高背压压缩机，不互溶润滑油能提升能效
- 对于结构复杂的系统，互溶型润滑油可帮助回油

# Adjustable Miscibility

- R290 dilutes many kind of lubes.
- Miscibility with R290 is adjustable by fine tuning the chemistry.
- Immiscible lube help improve energy efficiency.
- For large complicate system, miscible lube help oil return



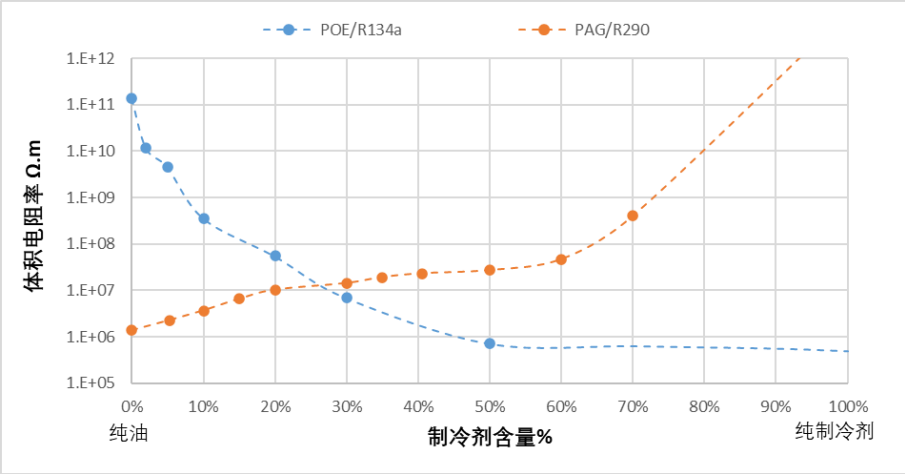



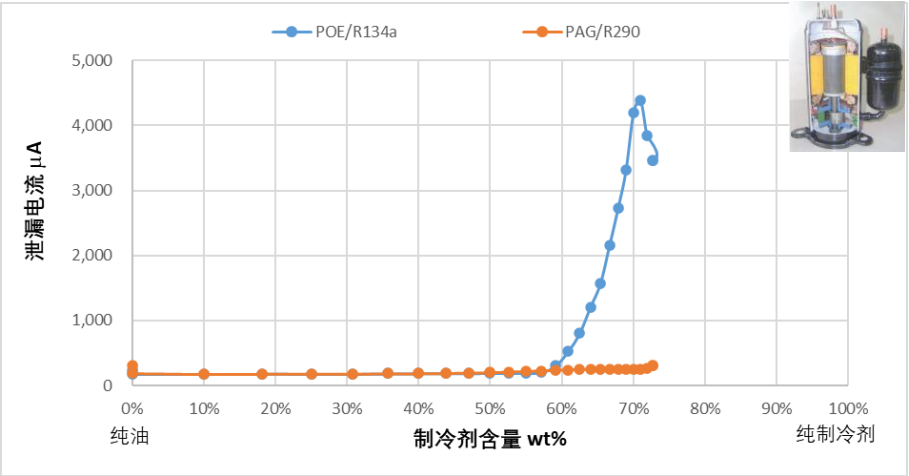
# 电绝缘性能优异

# Excellent dielectric property

- 对润滑油电绝缘性能要求不高
- 给使用电绝缘性能相对较差的润滑油提供了可能

- Less demand for lubricant dielectric property
- Enable to use PAG



# 瑞孚R290润滑油解决方案

# Shrieve Lube Solution for R290

| 润滑油 | 基础油类型 | 压缩机类型 Compressor | 应用 Application |
|---|---|---|---|
| **ZEROL® RA-XA** | PAG | 滚动转子 Rotary | 家用除湿 Dehumidifier<br>干衣机 dryer<br>移动式空调Portable AC<br>分体式空调Split RAC |
| **ZEROL® RA-XB** | PAG | 滚动转子 Rotary | 家用除湿 Dehumidifier<br>干衣机 dryer<br>移动式空调Portable AC<br>分体式空调Split RAC |
| **ZEROL® RFL-EPH** | PAG | 半封活塞 Semi-hermetic Recip<br>涡旋 Scroll | 采暖 House heating<br>热泵热水器 HP Water Heater、<br>汽车空调 Mobile AC |
| **ZEROL® ESTER** | POE | 全封活塞 Hermetic Recip | 轻商冷冻冷藏<br>Light commercial refrigeration |
| **ZEROL® AB** | AB | 全封活塞 Hermetic Recip | 轻商冷冻冷藏<br>Light commercial refrigeration |
| **Progiline LPG** | PAG | 半封活塞 Semi-hermetic Recip<br>螺杆Screw | 工业制冷及气体压缩<br>Industrial refrigeration and gas compression |

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# HFO及其混合物润滑油开发

# Lubricant Development for HFO and Blends

## HFO及其混合物的特点和挑战

- **一般来说，不如HFC稳定**
  - R1234ze(E) > R1234yf > R1233zd(E)
- **R1234ze(E) 和 R1233zd(E) 对润滑油稀释严重**
  - 螺杆压缩机要求的工作粘度难于达到
- **混合物太多选择**
  - 需要耗费大量资源进行全面评价

## Features & Challenges for HFO & Blends

- **Generally, less stable than HFC.**
  - R1234ze(E) > R1234yf > R1233zd(E)
- **R1234ze(E) and R1233zd(E) dilute lubricant.**
  - Difficult to achieve the working viscosity requirement of screw compressor
- **Too many blends**
  - It takes lots of efforts to fully evaluate.

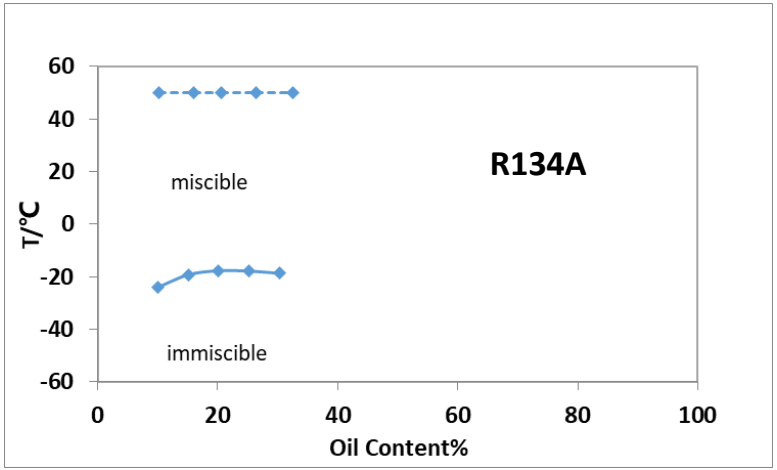
# R1234yf

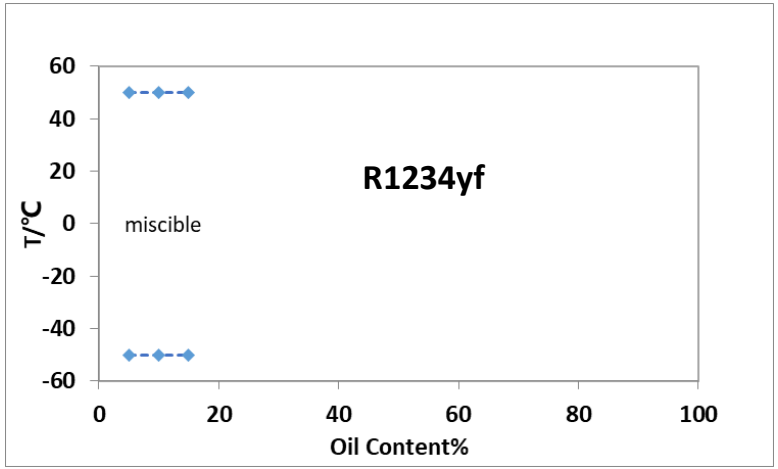
## R134a vs R1234yf

- 同样的油，R1234yf相溶性更好
- 结构差不多的油，R134a用VG 68就可以，R1234yf则要用到VG85

## R134a vs R1234yf

- Same lubricant, much more miscible with R1234yf
- Similar chemistry, R1234yf needs VG 85 while R134a needs VG 68.



## R134a vs R1234yf

- 为R134a开发的油不宜直接用于R1234yf
- 有空气条件下，R1234yf测试前后酸值变化更大，金属腐蚀更严重

## R134a vs R1234yf

- R134 cannot be used for R1234yf
- R1234yf test has higher TAN and metal corrosion if air presented.

| | R134a | | R1234yf | |
|---|---|---|---|---|
| Air | N | Y | N | Y |
| 酸值 mgKOH/g | 0.1 | 0.5 | 0.1 | **3.5** |
| 油色 | | | | |
| 金属外观 | 无腐蚀 | 无腐蚀 | 轻微腐蚀 | 严重腐蚀 |

## R134a vs R1234yf

- **优化添加剂后，酸值和金属腐蚀得到改善**

## R134a vs R1234yf

- **Further optimization on additives controls TAN and metal corrosion even better.**

| | R134a | | R1234yf | |
|---|---|---|---|---|
| Air | N | Y | N | Y |
| 酸值 mgKOH/g | <0.05 | 0.2 | <0.05 | **1.0** |
| 油色 | | | | |
| 金属外观 | 无腐蚀 | 无腐蚀 | 无腐蚀 | 轻微腐蚀 |

## R134a vs R1234yf

- **进一步优化添加剂后，酸值得到控制，金属腐蚀被抑制**

## R134a vs R1234yf

- **TAN and metal corrosion has been improved with optimized additives**

| | R134a | | R1234yf | |
|---|---|---|---|---|
| Air | N | Y | N | Y |
| 酸值 mgKOH/g | <0.05 | 0.1 | <0.05 | 0.1 |
| 油色 | | | | |
| 金属外观 | 无腐蚀 | 无腐蚀 | 无腐蚀 | 无腐蚀 |

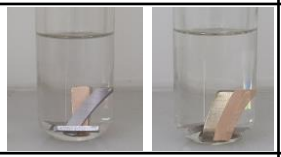
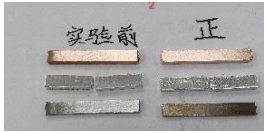
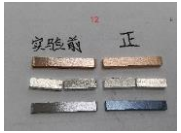
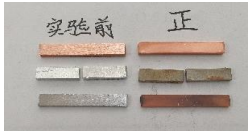
# R1233zd(E)

# 稳定性测试

- A油：没有冷媒250°C稳定，有冷媒225 °C不稳定
- B油：有冷媒225 °C不稳定
- R1233zd(E) 稳定性不如油

# Stability test

- Oil A: Stable at 250°C if no R1233zd(E), not stable at 225°C if with R1233zd(E).
- Oil B: not stable at 225°C if with R1233zd(E).
- R1233zd(E) impacts the stability of the oil.

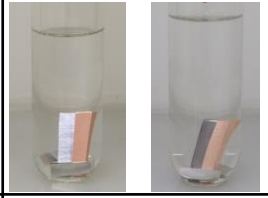
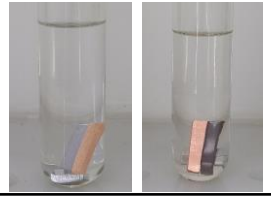
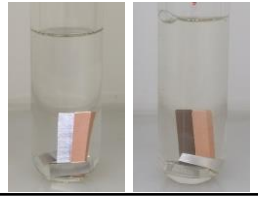
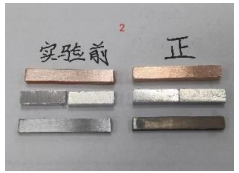
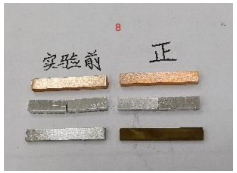
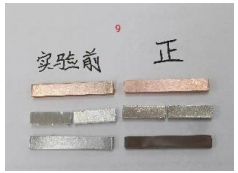
| | | Oil **A** (no R1233zdE) | Oil **A**/R1233zdE | Oil **B**/R1233zdE |
|---|---|---|---|---|
| Temperature °C | | 250 | 225 | 225 |
| Appearance | Oil |  | | |
| | Metal |   |   |   |
| | Comment | 油：良好<br>金属：良好 | 油：严重变质<br>金属：良好 | 油：严重变质<br>金属：腐蚀明显 |
| TAN, mg KOH/g | | 0.02→0.13 | 0.03→**1.25** | 0.04→**2.67** |
| Viscosity, cSt | | 365→367 | 360→370 | **213→52** |

# 稳定性测试

- 有冷媒225°C 油C稳定
- 250°C酸值略提高。

# Stability test

- Oil C was very stable under 200, 225°C.
- Under 250°C, started to see TAN rise.

| Temp °C | | 200 | 225 | 250 |
|---|---|---|---|---|
| Appearance | Oil |  |  |  |
| | Metal |  |  |  |
| | | 油：良好<br>金属：良好 | 油：良好<br>金属：无明显腐蚀 | 油：良好<br>金属：无明显腐蚀 |
| TAN, mg KOH/g | | 0.01→0.03 | 0.01→0.02 | 0.01→0.38 |
| Viscosity, cSt | | 326→324 | 326→325 | 326→313 |

# 瑞孚HFO润滑油解决方案

# Shrieve Lube Solution for HFO

| Ref. | 产品 Product | 压缩机类型 Compressor | 应用 Application |
|---|---|---|---|
| **R1234yf** | ZEROL HD 46/100<br>ZEROL RM 68EX/85E | 斜盘式活塞Swash plate<br>涡旋Scroll | 汽车空调 MAC |
| **R1234ze(E)** | ZEROL PE-X / ZEROL ESTER | 螺杆 Screw | 高温热泵/商用空调<br>HTHP/Chiller |
| **R1233zd(E)** | ZEROL HPL 320A | 螺杆 Screw | 高温热泵 HTHP |
| **R514A** | ZEROL RC ED | 离心 Centrifugal | Chiller |
| **R515B** | ZEROL PE-X<br>ZEROL ESTER | 涡旋Scroll<br>离心 Centrifugal | 高温热泵/商用空调<br>HTHP/Chiller |
| **R454B** | ZEROL RA 68EC | 滚动转子 Rotary | 家用空调<br>RAC |
| **R454C** | ZEROL RM 68EX | 涡旋Scroll | 汽车空调MAC |
| **R473A** | ZEROL HD | 活塞 Reciprocal | 冷藏车Reefer |

# 总结

- 制冷润滑油的选择要充分考虑稳定性、材料兼容性、制冷剂互溶性、及合适的工作粘度
- 润滑油可以从很多方面影响制冷系统的性能，系统设计时需要充分考虑润滑油的影响
- 不同制冷剂，面临不同的挑战
- 对多种LGWP制冷剂，瑞孚化工都有完备的润滑油方案

# Summary

- Stability, material compatibility, refrigerant miscibility, and working viscosity shall be considered when developing lubricants for refrigeration system
- Lubricants affect the performance of the system from multiple respects. Lubricant effects need to be considered when designing a refrigeration system.
- Challenges are different for different refrigerants.
- Shrieve has a comprehensive lubricant solution for various LGWP refrigerants.

# Q&A

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# THANK YOU

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