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Synthetic Refrigeration Oils - Humidity Related Difficulties and Solutions

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SYNTHETIC REFRIGERATION OILS - HUMIDITY RELATED DIFFICULTIES AND SOLUTIONS

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Abstract

New lubricants have been developed to meet the performance demands of modern refrigerants and system components. A brief review of current refrigeration oil developments is presented.

It is well known that the new lubricants used with polar refrigerants tend to absorb water. The ester hydrolysis process and the effect on the essential lubricant properties are described. The effect of increased water content on compressor performance is outlined and a test method to determine the hydrolytic stability of ester lubricants is presented.

Polyglycol (PAG) lubricants are also discussed. Possible system problems associated with the hygroscopic nature of these lubricants are outlined.

Rechargeable container systems for filling compressors under exclusion of air, special oil dehydration techniques and innovative new lubricant developments are presented.

Introduction

Suitable lubricants had to be developed for the new generation of chlorine-free refrigerants like R 134a. Synthetic refrigeration oils, e.g. ester based lubricants and polyalkylene glycols, for use with polar refrigerants, have come to be firmly established in refrigeration technology. Meanwhile, the well known fluorocarbon (HFC) refrigerants are used nearly exclusively with polyol ester (POE) lubricants. An exception are automotive air conditioning applications where polyalkylene glycols are predominant.

As an alternative to HFCs, traditional refrigerants, such as propane and other hydrocarbons, carbon dioxide, and ammonia, are being discussed as replacements for chlorinated refrigerants. Considerable R&D work will be required to formulate suitable lubricants for novel refrigeration systems.

Innovative ammonia systems call for high stability lubricants with a specific solubility in ammonia refrigerant. These are polyglycol based lubricants stabilized and optimized by special additive packages. The insoluble refrigeration oils, e.g. mineral oils and alkylbenzenes, used in conventional ammonia systems, are mostly unadditized.

Some types of polyalkylene glycols with special additives have been found to be good soluble oils. Still, a number of problems remain to be solved. One of them is the protection of aluminum parts in the compressor against the harmful effects of humidity. Carefully keeping the system dry has shown to be the only viable solution. Chemical reactions of polyglycol and water with aluminum can occur as the water content in lubricants and refrigerant increases. Such chemical reactions - as indicated by e.g. discoloration of the lubricants, or varnish formation with jelly-type deposits in the compressor - cause corrosion damage to aluminum parts.

The combustible hydrocarbon refrigerants R 290 and R 600a are widely used in Central Europe, especially in Germany. In addition to refinery applications, the biggest potential for hydrocarbon refrigerants is in household refrigerators with direct cooling. The experience with hydrocarbon based lubricants (mineral and synthetic) containing dedicated additive packages is positive. Ester based lubricants also show good results with hydrocarbon refrigerants.

The professional discussion on natural refrigerants recently has even reverted to „historical" carbon dioxide. In the 1930s, when CFC refrigerants came to be popular, CO_2 was found unsatisfactory and disappeared almost completely, due for instance to the lubrication problems it caused. A sophisticated compressor design to effectively control the CO_2- related high pressure level in the system will have to go along with considerable lubricant development effort. Nothing final can be said on the future of CO_2 refrigerant before the current positive findings have been confirmed in sustained use.

Lubricants for alternative refrigerants

Alternative refrigerants	Suitable lubricants
Polar hydrofluorocarbons [HFC] e.g. R 23, R 134a, or mixtures like R 404 A, R 407C, R 507	**Polyol esters [POE]** (preferably without additives) *complex esters* *polyalkylene glycols [PAG]*
Ammonia (R 717) conventional systems	**Mineral oils, synthetic hydrocarbons (PAO, alkylbenzene)** unadditized
dry/direct evaporation (small systems) *flooded evaporation*	**Polyalkylene glycols**, additive-blended (soluble in ammonia)
Hydrocarbons propane (R 290), isobutane (R 600 a) *and mixtures*	**Mineral oil and semi-synthetic refrigeration oils** preferably additive-blended *ester based oils, PAG*
Carbon dioxide (R 744 - CO_2)	Ester based oils, PAG

Ester based oils

Ester based oils and the classical hydrocarbon based oils are now the most widely used refrigeration lubricants, as shown by the examples given above. Polyol ester products (POE) in combination with HFC refrigerant are the most popular.

Similarly positive results have not been achieved with any other lubricant. Additives are not needed because of the excellent lubricity, and the high thermal and chemical stability of POE. The only weakness seen is the esters' inherent hydrolytic capacity, although that can be controlled by the selection of the right synthetic components.

Ester based oils and materials compatibility

The materials used in compressors and refrigeration equipment, and all other operating conditions in the system must show good compability with both refrigerant and lubricant. The materials include different metals, seals, plastic components, coatings, and inserts for filters and dehydration equipment. During the initial phase of refrigeration oil development, the compatibility of materials and processes with lubricants and refrigerants was thoroughly tested in the laboratory.

Rubbers, elastomers and coatings

Laboratory tests initially led us to recommend against the use of chloroprene (also called neoprene) seals. However, these seals are significantly lower in price than certain FKM and HNBR seals classified good or excellent, so field tests were conducted jointly with our partners that led to clearly better results. Today, chloroprene seals continue to be successfully used in nearly all major compressor makes.

Tests of widely used elastomers and coatings with unadditized POE oils in most cases showed better compatibility than mineral oil and R 12 refrigerant. Until this time, non additive containing lubricants have not been found to cause malfunctions due to incompatibility with elastomers or coatings.

Metals

Laboratory and test facility experience shows that POE oils not containing additives have better compatibility with most metals than conventional lubricants and CFC. Zinc and silver (solder) are not recommended for use in refrigeration systems and compressors. Zinc reacts directly with ester based lubricants at temperatures as low as 100°C. Given the operating conditions in compressors, the risk of damage to parts made of zinc or alloys with a high zinc content is considerable. On the other hand, negative effects on brass or zinciferous bronze valves are not known. As to bearings, positive and negative experience is reported with zinc-containing metals and jewels.

State-of-the art compressor design is unthinkable without aluminum, although in use with ester based lubricants it may be problematic in refrigeration equipment in two important respects. In addition to pure metallic aluminum, there are two groups of aluminum alloys - cast and wrought - distinguished by properties and composition. It has shown in testing and in the field that economy-price cast aluminum, due to its hardness and rough surface, is not suited for connecting rods and pistons in refrigeration compressors with HFC refrigerant. An additive, e.g. chlorinated paraffin, is needed for better lubrication of rough surfaces. Chlorinated paraffins are formed in the use of CFC refrigerant. As CFCs are being phased out, phosphorous or sulfurous compounds would have to be used to achieve the same effect. These compounds, in turn, may be problematic in the longer term and, therefore, should not be used as anti-wear additives.

Secondly, a high water content of the lubricant-refrigerant mix in critical compressor sections, e.g. the lubricating points of connecting rod bearings, could cause hydrolytic reaction.

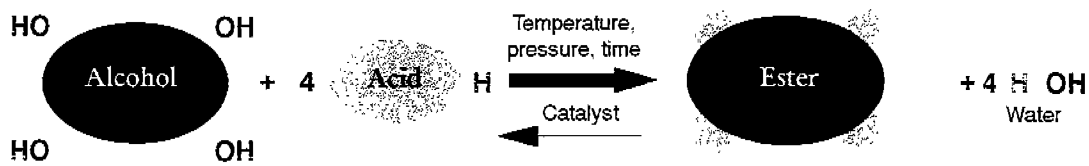
Ester based lubricants and humidity in the system

Esters are made in the following process:

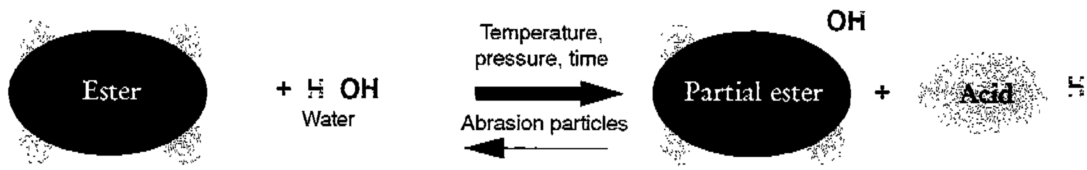
Under defined conditions, alcohols and acids react to form esters, releasing water. A law of nature says that chemical reactions will always take place in both directions, the prevailing conditions being the determinant. Hence, at the appropriate temperatures and pressures, the water present in the compressor will react with ester based lubricants to form acids and partial esters.

Refrigeration oils
Ester, e.g. alcohol (pentaerythritol) and carboxylic acids (C_6 - C_{12})

Ester-synthesis



Ester-hydrolysis



Extreme conditions (high pressure and temperature, catalytic effect of metals), such as existing e.g. at the lubricating points of connecting rod bearings, may cause the hydrolysis of polyol esters, with formation of partial esters and carboxylic acids.

Carboxylic acids will normally react with the metals used in refrigeration technology. The lubricant in the compressor will always contain suspended metal particles from the normal wear process. The acids will be gradually consumed in the chemical reaction described above.

Iron and copper form salts of different stability. While iron salts are highly stable and, in the authors' opinion, do not show any catalytic effect (as feared by others in the industry), copper salts are quite unstable. In field experience, copper plating showed to be rare and different in nature from that found in the past. In compressors with ester based lubricants, copper plating is not found to be a problem because it tends to be soft and will be rubbed off very easily.

Under the outlined conditions, aluminum - like other metals from the same group of elements - will react with organically linked hydroxyl groups. Partial esters have at least one free hydroxyl group and, under similarly extreme conditions, will react with the aluminum of metallic surfaces (e.g. connecting rod bearings) to form clearly more compact compounds than the soft reaction products that readily come off materials surfaces. In operation, striae and fissures will form first that fill with lubricant and initially do not show any apparent damage. If a sufficient quantity of water is present in the ester based lubricant, the undesirable process will go on. After a certain amount of time, the lubrication opening will become bigger, causing the compressor to run unsteadily before eventually it breaks down.

It should be noted in this connection that customary polyglycols normally have free hydroxyl groups and show similar reactions with aluminum. Problems will occur especially in insufficiently dehydrated ammonia systems using soluble PAG based lubricants. It is suspected that water accelerates the reaction of aluminum with the hydroxyl groups of polyglycols.

In light of these problems, the absence of humidity from the system is of paramount importance, and hydrolytically stable ester oils should be used.

Hydrolytic stability of ester based refrigeration oils

The Pneurop test, as provided for in DIN 51 352 and widely available at laboratories in the German petroleum industry, is used to determine the hydrolytic stability of synthetic ester based refrigeration oils in the following procedure:

> Fill test tubes with 0.8 g of deionized water + 0.4 g of aluminum grit + 40 g of test lubricant. Heat test tubes in a bath at a defined temperature under a reflux condenser over 24 hours. Thereafter, determine neutralization number as per DIN 51 558. In testing at a temperature of 140°C, most of the refrigeration oils on the market show positive results. The neutralization numbers found are up to 0.2 mg KOH/g. The first four test products (nos. 1-4) are products proven in the field.

Hydrolytic stability of ester based refrigeration oils

Oil no.	Identification		TAN (after 24 h/140°C)
1	POE MP	85% i-C_8	0.05
2	POE DPE	70% n-C_5	0.07
3	POE PE	50% n-C_7	0.33
4	POE PE	50% n-C_7 *	1.05
5	PEG	75% i-C_8	1.49

*) + additive

Humidity related difficulties - solutions and remedial actions

DEA participated in the development of rechargeable containers for filling compressor systems with hygroscopic refrigeration oils under exclusion of air in order to effectively control humidity related problems. Users may fill their compressors with lubricant from the special storage and transport containers at a pressure of up to 8 bar. Containers are recharged at a special loading station.

Innovative developments in dehydration techniques help control humidity related difficulties. Dryers installed in the compressor oil sump have shown positive results as related to the use of ester based lubricants. The dryers specially developed for ammonia systems and soluble oils are now being tested.

For retrofit applications in automotive air conditioning systems (overland buses with long refrigerant hoses), DEA is now working intensively on the development of a hydrocarbon based lubricant for use with polar refrigerants, e.g. R 134a. Thanks to a special additive technology, a lubricant of low hygroscopicity for problematic air conditioning systems now appears within reach. The basic concept is the exploitation of dispersion phenomena that can be enhanced by the use of special additives. This helps guarantee the flow of lubricant at evaporation temperatures of >-5°C.

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