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**POTENTIALLY USEFUL POLYOLESTER LUBRICANT ADDITIVES.  
AN OVERVIEW OF ANTIOXIDANTS, ANTIWEAR AND ANTISEIZE COMPOUNDS.**

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**ABSTRACT**

Reliable service lubrication of compressors with polyolesters that do not contain additives is the optimal goal for hermetic compressor use. Chlorine derived from CFC and HCFC refrigerants is reported to have effective antiwear properties and negates the widespread use of additives in mineral oil lubricated systems. The use of antioxidants for mineral oil and polyolesters have been reported; antioxidant additive activity seems essential for polyolesters. Antiwear and antiseize additives seem to be a short term goal for use with polyolesters. High silicone aluminum to steel wear seems to be a primary target for additive use. The interaction of specific heteroatom organic compounds with highly polar surface active synthetic polyolester lubricants is complex. Results of an extensive literature search describe results from a service base determined at ambient conditions. Known lubricant additives used in the hermetic compressor industry, the mode of action of several types of additives and some lubricant additive chemistry that demonstrates selective thermal stability in conjunction with the chemical structure are examined.

**INTRODUCTION**

This paper summarizes a literature search that was conducted as part of a research project for the Air-Conditioning and Refrigeration Institute [ARTI] and the Materials Compatibility of Lubricant and Refrigerants program [MCLR] (1). An objective of the literature search was to investigate commercially available additives and review published information on the class of chemical compounds used as additives with polyolesters. The search identified any chemical compound that could be added to a pentaerythritol [PE] and trimethylpropane [TMP] polyolester base stock lubricant in order to alter and improve its antioxidant [AO], antiwear [AW] and anti seize [AS] properties.

Many reviews discuss the need for polyolesters (2, 3, 4), their benefits (5) and how carboxylic acid and alcohol selection affects thermal stability and viscosity (3, 6). Early work focused on development of ester lubricants (2) that would out perform mineral oils. The HVAC industry has settled on the PE and TMP base stocks; however, the chemistry and types of polyolesters in refrigeration compressors is relatively new and nearly all of chemical and additive formulations of current refrigeration grade polyolester lubricants are proprietary. The paucity of this information made performance correlations of currently used refrigeration grade polyolesters with that of new and old published information nearly impossible. However, the ASHRAE and MCLR research programs have provided funding to develop fluid property data on most of the currently used polyolesters (7, 8).

The choice of polyolesters selected by HVAC engineers was first based on historical CFC and HCFC mineral oil miscibility characteristics. Perhaps assumptions were made on the lubricity of the esters in the hermetic system based on viscosity and how well esters lubricated gears and rolling element bearings in jet aircraft. Within the last three years, proactive lubricant suppliers developed polyolesters suitable for durable compressor service. Currently available polyolesters differ chemically in one way or another; however, there is still a need to better understand the sensitivity of various compressor designs and engineering characteristics to obtain optimum lubrication.

Alcohol and carboxylic acid are the primary modifiers of HFC miscibility, thermal stability and fluid properties. Alkyl branching of the carboxylic acid promotes HFC miscibility whereas linear acids promote immiscibility. A wide variety of structurally different esters were studied. Esters made of linear acids were better than mixed and branched esters (3). Hermetic engineers require miscibility for good lubricant return properties and they have dictated reduced lubricity. By properly tailoring the carboxylic acid composition of polyolesters, an effective balance of liquid/liquid miscibility and lubricity can be obtained.

Sufficient evidence exists that suggests lower miscible polyolester lubricants can return to the compressor. Refrigerant gas equilibrium solubility studies, with single and blended refrigerants, almost equally reduce the viscosity

of fully and partially miscible polyolester lubricants at identical conditions (7). This information should help in selecting polyolesters that would have better lubricity at the start, namely a more linear product. We cannot expect esters and mineral oils to behave identically. They are two different class of chemicals and have completely different physical and chemical properties.

The characteristics of a good compressor lubricant are to seal gas spaces, provide a tough hydrodynamic film, provide a dense lubricant sealing wedge on the leading edges of piston rings and provide good impact films. Chlorine bearing refrigerants promote a mono layer of ferric chloride. Ferric chloride on surfaces is known to provide a lubricious layer resulting in the lubrication performance of mineral oils with CFC and HCFC refrigerants (9).

Unlike naturally occurring hydrocarbon fluids, polyolesters are synthetic materials that can be widely varied by altering the ratio of linear and branched carboxylic acids. Synthetic polyolesters can have totally different performance properties amongst suppliers of identical viscosity grades, whereas supplies of refrigeration grade hydrocarbons have a more narrow variance. The potential variance among compressors was minimized by the presence of chlorine in chlorine bearing refrigerants.

The most common 32 ISO VG mineral oil used in the refrigeration industry for the last 35 years is a blend of two straight distillation cuts of hydrocarbons. When early lubricants were combined with CFC refrigerants, severe copper plating and thermal instability of hermetic system lubrication was the predominate failure mode. Eventually, a very light acid treatment followed by clay filtration of the same lubricants improved thermal stability of the chlorinated refrigerant lubricant mixture and compressor performance.

#### ADDITIVE SELECTION

The use of synthetic polyolester lubricants in compressors must at least parallel the performance hydrocarbons have with CFC and HCFC refrigerants. If we want additive free polyolesters, we need to synthesize into the ester lubricious properties for an additive free system. The properties of viscosity, low temperature miscibility and lubricity need to be built into the structure of the polyolester by the selection of the appropriate acids and alcohols.

Perhaps the overall lubricity of a lubricant is a surface energy phenomena. Metals have high surface energies and lubricants are easily adsorbed to them (6, 10). Compared to mineral oil, esters are polar and are easily attracted to the surfaces of metals. This fact makes the selection of lubricant additives for PE and TMP polyolesters suitable for refrigeration service very complex. Increased molecular weight improves the lubricity of an ester (6). Esters of high molecular weight and carbon content approach the non-polar index properties of mineral oils (11). Non-polar mineral oil or ester fluids have a lesser attraction to the metal surfaces allowing polar additives to be adsorbed. However, these same non-polar esters are not suitable for refrigeration service due to immiscibility and low temperature viscosity.

When the polarity index of esters increase (11), so does refrigerant miscibility and metal surface competition for potentially useful polar additives. The additive that must be selected to either deactivate the surface or provide a polymeric lubricating surface may already be too active to be thermally and chemically stable for compressor service (12, 13). Depending on the compressor design, bearing stresses dictate the degree of metal to metal contact. Therefore, the ester base fluid selected for compressor service will cover the metal surfaces preferentially and not the additive. This then results in higher wear characteristics (6).

Mineral oils respond to additive treatment. When mineral oil is exposed to an acid clay clean up process, heterocyclic materials that contain nitrogen, sulfur and phosphorus are removed. Some of the natural lubricity of naphthenic lubricants and antioxidant qualities of the lubricant are subsequently lost. Fully refined USP grade white mineral oils are another example that require the antioxidant  $\alpha$ -tocopherol [Vitamin E] for storage purposes.

Millions of HVAC system compressors have been produced that also use a fully refined white oil with HCFC-22. To compensate for the poor lubricity of a white oil, either tricresyl phosphate [TCP] or butylated triphenyl phosphate [BTTP] are used as lubricant additives. These same lubricant additives have been used with pale yellow oils as well.

Although the structure of esters does not affect lubricity (3), it may play a role in additive selection as it does with mineral oils. The additive BTTP is more efficacious than TCP with white oil and R-22. However, the same additives are only half as efficient with pale oils and R-22.

Some applications for 32 ISO VG pale mineral oils demanded improved thermal stability properties and better sealed tube responses. The antioxidant and metal surface deactivating properties of a metallo dithiodiphosphate were used to promote this effect (14).

The use of additives in mineral oil systems is a good example of their longevity. If additives are required to make a polyolester survive the expected life time of a compressor, then that additive has a definite life time. When an additive provides a good lubrication layer, the presence of that film must not be removed from that surface by the lubricant. In cases when the additive is removed by the polyolester, wear debris can form and become a circulating contaminant in compressor systems. The comparison is made with the ferric chloride layer formed in mineral oil CFC systems. When the system is dry and free of circulating HCl, the ferric chloride layer is permanent to a degree and is not removed by esters or non polar mineral oils.

### ANTIOXIDANT

In storage, polyolesters can adsorb water and oxygen to form hydroperoxy oxidation products (15, 16). The chemical structure of PE and TMP esters promote significantly higher thermal stability but can include homolytic decomposition reactions involving free radicals (15). Although these fluids provide extreme temperature capabilities, it may be unnecessary for compressor use. Many of the 95 compounds identified as suitable AOs also perform well as AW and AS agents. Limited space allows only a sample of the structural types to be identified here.

Alkylated 1, 3, 4 thiadiazoles derived from 2, 5-dimercapto-1, 3, 4 thiadiazole were effective AO and AW agents (17). The free radical that is formed at elevated temperatures is quenched with bis[p-( $\beta$ -naphthylamino)phenyl]thiophosphoro diethylamide (18). 1-[di (4-octylphenyl)amino methyl]tolutriazole is synergistic with the typical butylated hydroxytoluene AO (19) and is reportedly due to the formation of a phenoxy radical and thioether adducts (20).

Several primary and secondary amines are high performance AOs effective at elevated temperatures. Some of the most common are phenyl  $\alpha$  naphthylamine [PANA Uniroyal] (21), which is less effective alone but synergistic with diphenyl sulfoxide (22). Octyl  $\alpha$  Naphthylamine [Irganox LO-6] (23) and p,p' dioctyldiphenylamine [Irganox L57] (23) are widely used but appear to be sensitive to light causing some polyolester formulations to turn light orange in color.

Hindered phenols 2, 6-Di-tert-butyl-dimethylamino-p-cresol and 4, 4' methylene bis(2, 6-bis-tert-butylphenol) (24) are found to be effective AOs at elevated temperatures in heat pumps [200°C]. The effectiveness of AOs is dependent on the structure of the ester, including the type of branching, alkyl side chain length and structure of the AO (25).

Commercial esters of C<sub>5</sub> to C<sub>9</sub> composition respond favorably to bis(4-phenylaminophenyl) N,N-diethylamidophosphate at 240°C (26). Unreacted zinc dialkyldithiophosphates [ZDTP] are the primary AOs that terminate peroxy radicals in esters (27) and promote good lubricity and AO activity with polyalkylene glycols as well (28).

Simple phosphates like TCP in AO amine mixtures further promote stability of oils and esters (29). When used alone, dialkyl phosphates, phosphonates and phosphites (9) protected compressor lubricants. Multiple activities are reported with low levels of triphenyl or tributyl phosphite (30), dibutyl hydrogen phosphite (31) or dimethyl phosphite (32).

## ANTIWEAR

The mode of action of AW agents is dictated by the temperature and surface energies of the wear zone. Phosphorus derivatives predominate this class of materials and are sulfur and chlorine containing products. Chlorine containing products show reduced sliding energies.

Specifically related to polyolesters, about 63 compound classes were identified as potentially suitable additives. The singular AW activity of TCP is surpassed with diaryl ether phosphate esters (33, 34) but is found to be synergistic with diphenyl octylphosphite (35). When a thin phosphate lubricant layer is easily replaced by an oxide layer, wear is increased and suggests the importance of selecting the proper molecular structure of the amine and phenolic AOs which compete for the same surface (36). A minimum of 5% TCP was needed in some applications to adequately cover all of the reactive metal surfaces. In other applications, the metal surface was coated with a very thin oxidation layer of TCP and polyolester (37).

Superior results were obtained when the active portions of a phenolic AO and wear properties of a phosphonate were synthesised in the form of di-butyl-3, 5-di-tert-butyl-4-hydroxy benzyl phosphonate (38). An ashless derivative dialkyl or diaryl dithiophosphates can be obtained by neutralizing with an amine AO like N-octylphenyl-1-naphthylamine instead of metal oxides. This forms a substantially effective AO and AW derivative useful in polyolesters at elevated temperatures (39).

Secondary phosphite esters such as di-2-hexyl, di-lauryl or di-oleyl hydrogen phosphate (40), the halogenated compounds chlorobenzylchlorotoluene (41) and 1,1,1-trichlorononane (42), are excellent AW and extreme pressure additives. Applications using chlorotrifluoroethylene oligomers have been published without reports of wear data (43); however, specific chemical structures that contain relatively inactive chlorine atoms and are still safe materials to use. Chlorinated polyolesters from the Ferro Corporation have excellent boundary lubricant additive qualities, are deemed safe by the EPA and may be useful.

## ANTISIEZE

Many of the same substances that are effective AW agents are also effective AS compounds. The AS activity of many of the compounds contain sulfur and phosphorous. The mode of action and efficiency of these compounds are governed by both adsorption activity and thermal decomposition characteristics. With sulfur additives, the AS activity is mainly controlled by the thermal decomposition characteristics on the rubbing iron surfaces. When phosphates are used, the most important parameter is surface adsorption. The structure of metallo dithiodiphosphates is directly controlled by adsorption activity of the additive on rubbing surfaces. Then, thermal decomposition properties become the main feature of the compounds (9, 44). The activity was compared with mineral oil, diesters, TMP and PE esters. The additives in the polyolesters had the least beneficial activity (44).

## MODE OF ACTION

The mode of action for many of the additives is a reaction of the metallic surface with one of the heteroatom components of that substance. Whether the hot wire process (45) or extreme pressure 4 ball tests were used (46, 47), the surfaces, when examined by XPS, found that additives containing chlorine always seemed to predominate over sulfur or phosphorous derivatives when contained in the same lubricant.

## SUMMARY

A soft lubricious surface is formed *in situ* on steel surfaces in CFC and HCFC refrigerant compressor systems. The desired lubrication with HFC compressor systems is with polyolesters that have a great affinity for metal surfaces. If the polyolester base fluid is more polar than the additive, then the additive is less adsorbed onto the surface and wear occurs in the absence of an ester film.

Apart from this program, separate studies are under way to examine the thermal dependency of additives under specified loads and metal combinations under refrigerant pressure and dynamic conditions. The instrumentation is designed to study friction during additive depletion rates at either specified loads or bearing surface temperatures, surface speeds, lubricant dilution and refrigerant type. Commercially available additive free lubricants are used as the base stocks.

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