

Synthetic versus Mineral Fluids in Lubrication

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SUMMARY Deciding whether to choose a synthetic lubricant or a mineral oil is governed by two factors: Can the initially more expensive synthetic save money in the long run or can it provide some key performance characteristic not obtainable with a mineral oil? This paper reviews the physical and chemical differences between synthetic and mineral oils in the context of lubricant performance and discusses the characteristics of three major classes of synthetics, hydrocarbons, esters and polyglycols, and four minor classes. Performance benefits which can make a synthetic the best choice for many applications are improved energy efficiency, wider operating temperature range, increased design ratings, reduced maintenance costs, better reliability and safer operation. Each of these benefits is discussed in terms of physical and chemical property differences between minerals and synthetics.

1. INTRODUCTION

Hyperbole is the currency of much of modern advertising and lubricant advertising is no exception. Premium mineral oils are often named or described as super, excellent, high performance, universal, extra, heavy duty, multipurpose, all purpose, ultra, superior, special and so on. What more can a customer expect from a synthetic when mineral oils sound so good? This paper addresses this question by discussing which properties affect performance and how these properties differ between mineral and the various types of synthetic lubricants. The differences are often so striking that the advertising agencies may have to invent some new adjectives.

Mineral-based lubricants have been in wide use for over a century. They displaced animal and vegetable oils after becoming readily available at low cost as byproducts of kerosene refining from crude oil, production of which rapidly expanded in the second half of the nineteenth century. Advances in refining technology combined with the development of property-enhancing additives during the last fifty years have led to a broad range of mineral lubricants which perform satisfactorily in most applications.

Satisfactory performance is not necessarily optimum and there is room for improvement in many areas. The perfect lubricant would have no friction, allow no wear and be able to operate at any temperature for any length of time without any change in its properties. The place for synthetics is somewhere between the finite limitations of mineral oils and perfection. To be commercially viable, a synthetic product must

- a. meet a need which a mineral oil can not, or
- b. show an economic benefit in operation.

Early developments in synthetic lubricants primarily addressed the need to provide some performance characteristic unattainable with mineral oils. Organic esters were developed in the 1940's in response to a military need for

lubricants which would perform satisfactorily at high temperatures and still remain fluid at low temperatures. Much current research is aimed at lubricants that can function at temperatures far higher than either mineral oils or most current synthetics can survive. Although these developments are important, they are not the main focus of this paper since they concern applications where mineral oils are not appropriate and hence the title comparison has no meaning.

In the last decade or so, field experience has shown that certain types of synthetics can give economic benefits when used in place of mineral oils which were working satisfactorily. This will be the main subject of this paper. The benefits fall in five general areas:

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| <ol style="list-style-type: none">a. Improved energy efficiencyb. Wider operating temperature rangec. Increased design ratingsd. Reduced maintenancee. Better reliability and safer operation |
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Ongoing research is improving our understanding of the relationship between these benefits and the physical and chemical properties of the synthetics, leading to an optimization of the synthetic molecular structures for particular applications. The above benefit classes will be discussed in Section 4.

The history of synthetic lubricants has been presented in many publications and will not be covered again here. However, it is worth noting that there is a significant anniversary in 1987. It is 25 years since the publication of "Synthetic Lubricants" by Gunderson and Hart (1962), the first comprehensive text on the subject and an excellent source of historical information on lubricants in general and synthetics in particular. This book is still the starting point for research projects on synthetics and lists over 500 references. Synthetics are not new, but it is only recently that they have become widely available as products for the full range of industrial and automotive applications.

2. SYNTHETICS - "ENGINEERED LUBRICANTS"

This is the fifth major tribology conference in 1987, the 21st anniversary of the introduction of tribology as a discipline. One concept of tribology is that the lubricant should be treated as an equal partner to other engineering components in machines rather than as an unfortunate necessity to make them work. It is in this context that the value of synthetics must be judged.

Within the two main classes of mineral oils, paraffinic or naphthenic, processing variations can improve low or high temperature performance but most of the engineering characteristics are fixed once a viscosity has been selected. This lack of choice of engineering properties is a major reason why lubricants have not been given high priority in engineering design. With synthesized basestocks, molecular structure variations can produce a range of engineering properties independent of viscosity and we are now in a position to produce "engineered lubricants" with properties optimized for particular applications. In a nutshell, synthetics succeed by matching the molecule to the machine to give the performance benefits and the payback we are looking for.

The main advantage of mineral oils is their low cost. In the crude oil from which they are derived, we get millions of years of nature's hydrocarbon synthesis efforts simply for the cost of finding it and pumping it. The resulting crude oil contains an enormous assortment of hydrocarbon molecules. The main limitation of mineral oils, however, is that when nature put together this hydrocarbon assortment she used wide artistic licence rather than strict tribological principles. As a result, the lubricant-sized molecules have a variety of structures ranging from the best to the worst, tribologically speaking. Most refining processes are there to take out or restructure the worst, leaving a composition whose properties vary from average to good.

API Project 42 (Whitmore, 1940-66) measured several physical properties of a variety of synthetic hydrocarbon structures. This data was reviewed recently by Denis (1984) in an attempt to determine which structures give the best balance of pour point against viscosity-temperature variation as defined by viscosity index (VI). Figure 1 plots VI versus pour point for seven classes of hydrocarbons; four from API 42 (normal alkanes and mid-chain branched isoalkanes, cyclohexylalkanes and phenylalkanes), two commercially available synthetics (polydecenes and polyisobutenes) and a broad range for naphthenic structures typical of those found in naphthenic mineral oils.

Superimposed on Figure 1 is the range for dewaxed, solvent-refined paraffinic mineral oils. Such an oil contains a mixture of isoalkanes, cycloalkanes, naphthenics and aromatics and its physical properties are an average of those of its constituents. VI remains constant at around 100, independent of viscosity, because that is how VI was defined in the first place - seven vacuum distilled paraffinic lube fractions were arbitrarily assigned a VI value of 100 and seven naphthenic fractions were assigned a VI of 0 (Dean, 1929). Denis showed that using thermal diffusion instead of vacuum distillation to fractionate a mineral oil separates out various structures and the dashed line shows the VI-pour relationship for these.

We could plot many other physical properties such as pressure-viscosity coefficient, limiting shear

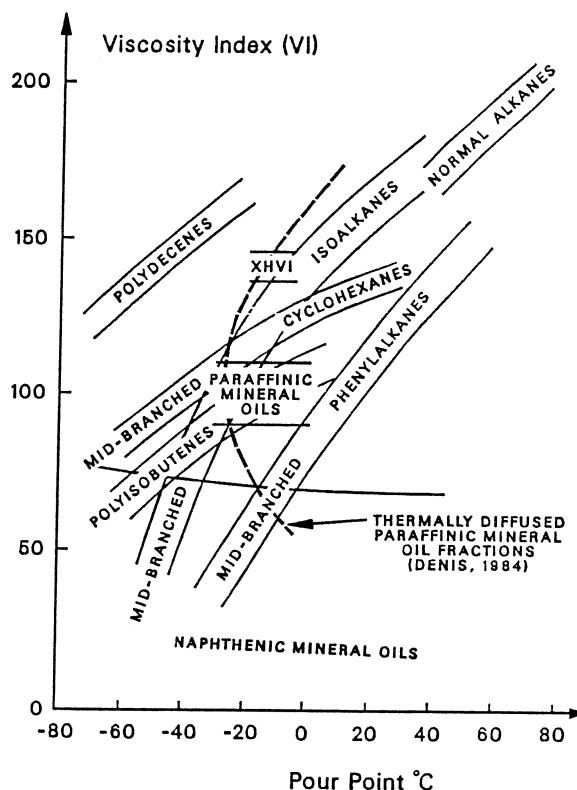


Figure 1. VI versus pour point for various hydrocarbons.

stress, volatility, thermal stability, density and so on and would find similar separations for the individual classes of hydrocarbons with an average for the mineral oil. The net result of this is that mineral oils are average performers for many applications but optimum for few. Alternative processing schemes to solvent extraction, such as hydrocracking, can remove aromatics and open up some ring structures, which can increase VI. Wax hydroisomerization produces the so-called extra-high VI (XHVI) stock which fits in the isoalkane range on Figure 1. Commercially available XHVI is limited to low viscosities and has a higher pour than synthetic hydrocarbons.

Synthetic lubricants are not an attempt to recreate mineral oil. It would be an impossible task to identify and synthesize all the mineral oil hydrocarbon structures and mix them together to make a synthetic mineral oil. To come close would cost a fortune and its only use would be as a museum-piece. There are many other structures in addition to hydrocarbons, such as esters, polyethers, silicones and halogenated fluids, which do not even occur in mineral oil but have unique and useful lubrication properties. Within each of these classes a variety of structures can be created with properties ranging from poor to excellent. Only those structures with particularly useful tribological properties are chosen for synthesis.

It should be remembered, however, that individual synthetic lubricants cannot be all things to all machines. One type of basestock may be perfect for one application but not good for another. A certain structural change may enhance one property at the expense of another. Additive differences in the same basestock can make or break a product. It is the lubricant formulator's job to select the

correct basestock and additive system so that the synthetic formulation shows measurable application benefits over mineral oils. The promise of synthetics has generated considerable research efforts to this end in recent years. This has resulted in a broad spectrum of products which, in most cases, depend on unique additive systems to fully realize that promise.

Assured long-term availability of synthetic products enables the development of advanced designs whose successful operation depends on the properties of a synthetic. Ester-based lubricants, for example, are used in essentially all commercial and military jet engines due to the high temperatures encountered and mineral oils are out of the picture. The cost of a lubricant fill, even with synthetics, is small compared with the development and production costs of most equipment and as the engineering properties of synthetics become better appreciated, the trend to exclusive use of synthetics in certain applications will increase.

3. SYNTHETIC BASESTOCK OVERVIEW

This section is intended as a review of the various types of synthetics currently in competition for parts of the mineral oil market rather than a thorough description of the synthesis and properties of synthetic fluids in general. A good starting point for a more thorough study is Gunderson and Hart (1962). Recent progress in synthetics was reviewed by Klamann (1984) in Chapter 6 of his 1984 book "Lubricants" and a study of commercial applications of synthetics was published by Mobil (1985). Sixty-six papers were presented at a conference entitled "Synthetic Lubricants and Operational Fluids" held at the Technische Akademie Esslingen, West Germany in January, 1984, and the conference volume (editor W. J. Bartz) is well worth reading. Many of these papers have appeared in the Journal of Synthetic Lubrication, volume 1 of which was published in the UK in 1984.

In terms of sales volume, there are three major classes of synthetic basestocks; hydrocarbons, organic esters and polyglycols. Other categories, sold in lower volumes and usually at higher cost, but with some exceptional properties, include phosphate esters, silicon-containing fluids, halogenated fluids and polyphenyl ethers. Brief descriptions of the fluids in each of these classes follow.

3.1. Synthesized Hydrocarbons

It is interesting that in 1962, synthesized hydrocarbons did not merit one of the ten chapters dedicated to each significant type of synthetic lubricant in Gunderson and Hart. Low yield processes and expensive raw materials were the main reason for lack of promise at the time. There have been significant process developments since then and synthesized hydrocarbon based products are now commercially available for almost every lubrication application. There are four major classifications of synthesized hydrocarbons:

(a) Polyalphaolefins

Alphaolefins are straight chain hydrocarbons with a reactive, olefinic tail. They are made commercially by fractionating oligomerized ethylene and can be polymerized to form branched hydrocarbons which look something like a section of flexible fish backbone. The length of the backbone depends on the number of olefins combined in the

polymer molecule and, for a given starting olefin, viscosity increases and volatility decreases with backbone length. The length of the branches depends on the size of the starting alphaolefin and viscosity-temperature performance (VI) improves with increasing branch length. However, pour point also increases with branch length and the best compromise between VI and pour is obtained using 1-decene as the starting olefin. Polydecenes, therefore, form the largest segment of the PAO market. Further information on polydecene synthesis procedures can be found in papers by Brennan (1979) and Isa (1986).

After hydrogenation, polydecenes have excellent oxidative stability when combined with appropriate antioxidants. Hydrogenated polydecene lubricant basestocks are made commercially in viscosity grades from 4 to 100 mm²s⁻¹ (cS) at 100C for polymers from three to about twenty decene molecules, respectively. At 4 mm²s⁻¹, VI is 130 and pour point is -70C and at 100 mm²s⁻¹, VI is 170 and pour point is -30C. Since there are no molecules smaller than C₃₀, volatility at low viscosity is much better for polydecenes than for mineral oils. Polydecenes also have low shear strength (low traction) at the pressures encountered in elastohydrodynamic lubrication (EHL), which leads to significant energy savings in gears, as will be described in Section 4.1. For some very low temperature applications, polydecenes containing a significant amount of dimer (C₂₀) with viscosities as low as 2 mm²s⁻¹ are available.

The combination of high VI, low pour point, low traction, low volatility, excellent oxidative stability and the availability of a wide range of viscosities has made polydecenes uniquely suitable for the majority of industrial and automotive applications. They do not damage painted surfaces but can shrink certain seal materials and are not good solvents for certain additives. Low (~15%) concentrations of diesters are often added to polyalphaolefin products to enhance seal performance and improve additive solubility.

(b) Polyisobutenes

Polyisobutenes are produced by polymerizing the relatively inexpensive butene/isobutene biproducts from crude oil refining. They cost less than other synthetics but are limited in their application as lubricants by their poor thermal stability. Higher molecular weight versions are used as VI-improvers. The low thermal stability can be put to good use in high temperature metalworking applications, the high temperature stages of some gas compressors and in two-stroke engines where they decompose to gases without leaving an oily residue. A high dielectric constant also makes polyisobutenes an appropriate choice for electrical insulating oils.

(c) Alkylated Aromatics

Alkylated aromatics are synthesized by alkylating an aromatic with olefins. The fluid properties are a function of the structure of the aromatic and the number and structure of the alkyl groups. The most common aromatic used is benzene and it comes with either one (alkylbenzene) or two (dialkylbenzene) alkyl groups of 10 to 14 carbon atoms in length. Alkylbenzenes have very low pour points and good miscibility with fluorocarbon refrigerants and are used either alone or in blends with low pour point mineral oils or with other synthetics in refrigeration compressors. However, they have low VI (~0) and are not very effective as boundary lubricants. Dialkylbenzenes can have VIs around 100 and are less volatile and more stable to

oxidation than equivalent viscosity mineral oils but are limited to low viscosities. Typical applications are for low (subzero) temperature operation of gears, hydraulic systems, power transmissions and IC engines.

(d) Cycloaliphatics

Considerable research has gone into the design of fluids which have high shear strength (high traction) at high pressure (>1 GPa) for use in traction drives. Traction drives may be thought of as gearboxes without teeth, where the EHL film is used to transmit torque between the gears. Their main advantage is that the lack of teeth allows the design of continuously variable gear ratios.

At high pressure, lubricants behave like glassy solids and have an upper limit to the shear stress which can be applied before they deform significantly. This limit is determined by the shape of the molecules but is independent of the size and, hence, viscosity. A study of structural effects on traction has recently been reported by Hentschel (1985). Cyclic structures and those with small (methyl) branches have high shear strength and current commercial traction fluids are typically twin ringed cycloaliphatics. These have low VI, are only available in low viscosity and have higher volatility than mineral oils of equivalent viscosity. They are generally unsuitable for applications other than traction drives.

3.2. Organic Esters

The vegetable oils in use prior to the mineral oil takeover were organic esters. Their main disadvantages were low temperature gelation and high temperature deposits due to the glycerine portion of the molecule. Prompted by German wartime military needs, Zorn studied over 3500 synthetic esters in the search for those with the best mix of high and low temperature properties. A review of this early work can be found in Gunderson and Hart (1962) and more recent reviews of the synthesis and properties of esters have been presented by Klamann (1984) and Szydywar (1984). Current commercial esters fall into two classes:

(a) Dibasic Acid Esters

Diester are produced by the reaction of a dibasic acid which contains two carboxylic groups, with an alcohol. The acid forms the backbone of the structure with the alcohol attached to its ends. A variety of structures can be made by changing the diacid or alcohol used and the physical properties of many such esters were summarized by Denis (1984). Those of commercial interest have high VI, low pour points, low traction, low volatility, good thermal and oxidative stability, good solvency and hence the ability to reduce deposit formation. On the negative side, esters can damage painted surfaces and cause elastomer swelling, although as mentioned earlier this property is often put to good use in enhancing the seal swelling capability of polyalphaolefin products. A review of the effect of esters on seal materials was given by Van der Waal (1985). Hydrolytic instability of some esters can lead to storage problems if water is encountered.

Diester were originally developed as aviation engine oils and were designated Type I. They have largely been displaced by Type II and III oils based on polyol esters. Current uses for diester, in addition to blending with polyalphaolefin products, are in air compressors, IC engines and as

basestocks for high temperature greases.

(b) Polyol Esters

Polyol esters are synthesized by reacting a monobasic acid with a polyhydric alcohol (one with more than one hydroxyl group). In this case, the polyhydric alcohol forms the backbone with the acid groups attached to it. Again, fluid properties are a function of the type of acid and alcohol used and have been summarized by Klamann (1984) and Denis (1984).

The main advantages of polyol over dibasic acid esters are much better high temperature stability, when used with heat-resistant antioxidants and metal passivators, and the ability to generate reaction films which protect metal surfaces under thin-film, boundary lubrication. Polyol structures can be made with similar volatility and low temperature properties to dibasic acid esters but VIs are slightly lower and they are potentially more damaging to painted surfaces and seals. Their widest use is in advanced aviation engines, but they are also used as air compressor oils, hydraulic fluids, heat exchange fluids, gear oils, high temperature grease basestocks and at low concentrations in polyalphaolefin products, silicones, silicate esters and rolling oils.

3.3. Polyglycols

Polyglycol is the commonly used name for a wide range of polymers of epoxides and heterocyclic oxides. Also known as polyethers and polyalkylene glycols, they have been commercially available in many forms since 1945. The major initial use was as brake fluids but they are now available as lubricant basestocks with a wide variety of properties. A comprehensive study of the synthesis and properties of polyglycols can be found in Gunderson and Hart (1962). More recently, the effect of structure on physical properties was reviewed by Kussi (1985) and on traction properties in particular by Hentschel (1985).

Common starting materials for polyglycols are ethylene oxide, propylene oxide, epoxides with longer alkylene chains and tetrahydrofuran. Random and block copolymers of these can be synthesized in various lengths and the physical properties are a function of the amount and chain position of each. From an application viewpoint, they fall roughly into two categories, water soluble and hydrocarbon soluble. Water solubility increases as the proportion of ethylene oxide in the polymer increases. Hydrocarbon solubility increases with the amount of long-chain epoxides.

The most obvious attractive feature of polyglycols is the combination of high VI (>200) with low pour point (<-50C) possible with certain structures. VI and pour as a function of structure was discussed by Denis (1984). Pressure-viscosity coefficient is lower for high VI polyglycols than for equivalent viscosity mineral oils. Limiting shear strength (traction) is a strong function of structure and copolymers have been found with very low traction which give significant gear efficiency improvements (Kussi, 1985), particularly at high contact temperatures. Polyglycols show a greater variation in traction with temperature than do hydrocarbons which makes their gear efficiency improvements less predictable.

Oxidative stability of polyglycols is not as good as polyalphaolefins, but with the correct choice of molecular structure and appropriate antioxidants can exceed that of mineral oils. Unlike

hydrocarbons, there is no polymerization of the decomposition products and no coke or sludge formation although a loss of viscosity occurs. The polar nature of polyglycols enhances boundary lubricating ability and generally reduces wear. Water-soluble polyglycols also pick up water from the atmosphere, which can lead to rusting during idle periods unless appropriate corrosion inhibitors are used.

Careful selection of additives is needed to match the solubility characteristics of a particular polyglycol structure and care must be taken not to contaminate hydrocarbon insoluble polyglycols with hydrocarbons or vice-versa when changing from one to the other in a machine. Some polyglycol structures can be harmful to paints and some seal materials and compatibility should be established before they are used.

Water soluble polyglycols are primarily used as brake fluids. They also are effective metalworking fluids, with or without added water, since they are resistant to bacteria, have low toxicity, and are not corrosive to most metals. They can also be easily removed from finished components with a water wash. They are mixed with water to form fire-resistant hydraulic fluids and the polyglycol also lowers the freezing point allowing low temperature use. They can also be used as water viscosifiers for low pressure elastomeric bearing lubricants but these are not shear stable and can not protect rolling bearing or gear contacts. They also are effective screw compressor lubricants for hydrocarbon gases since low gas solubility minimizes dilution and viscosity loss.

Water insoluble polyglycols are used as base fluids for a variety of industrial oils, including gear oils, bearing and circulating oils, compressor lubricants and hydraulic fluids.

3.4. Others

Much of the recent research effort in synthetic lubricants is directed towards higher temperature capability for such uses as advanced aviation engines and adiabatic IC engines. Since these are improvements over existing synthetics rather than over mineral oils a discussion of these fluids is outside the scope of this paper. An overview of progress in aviation lubricants was given by Loomis (1982). There are, however, a few fluid types outside the three major classes discussed above that are worth a brief review:

(a) Phosphate Esters

Phosphoric acid esters, or phosphate esters, have been known for over 130 years and a wide variety of structures have been synthesized. A chapter in Gunderson and Hart (1962) is dedicated to the synthesis and properties of many of these. Those of current commercial interest as synthetic lubricants are the triaryl type, synthesized by catalyzed reactions of phenols with phosphorus oxychloride. Although higher in cost, they have replaced PCBs as the synthetic fire-resistant lubricant of choice for environmental reasons. Other structures used as lubricants are trialkyl and mixed alkyl-aryl types.

Phosphate esters are used as hydraulic fluids, lubricants for compressors with high discharge temperatures, gas turbine main bearing lubricants and occasionally in steam turbines. They have a high bulk modulus, which is of value in hydraulic control systems. Thermal, oxidative and hydrolytic stability of phosphate esters varies with

structural type and is in general only fair. Maintenance procedures to avoid problems with degraded phosphate esters were reviewed by Shade (1987) based on experiences with compressors. Reaction with steel surfaces to give phosphide films makes phosphate esters excellent boundary lubricants.

(b) Silicon-containing Fluids

Silicones and silicate esters are two classes of specialty synthetic lubricants with unusual properties. They are again not new and warranted a chapter each in Gunderson and Hart (1962).

Silicones consist of an alternating silicon-oxygen backbone with organic side-chains attached to the silicon. They have extremely high VIs (>300), low pour points, low volatility, are relatively unreactive and have excellent oxidative and thermal stability. Their disadvantages are high cost, up to 100x that of mineral oils, and they are poor boundary lubricants, the use of additives to correct the problem being limited by poor solubility. The synthesis and properties of silicones were reviewed recently by Huber (1986). Applications include specialty high temperature greases, hydraulic fluids, brake fluids and compressor lubricants.

Silicate esters are similar in structure to silicones but with an oxygen atom between each organic side-chain and the silicon to which it is attached. The properties of silicate esters are similar to silicones but they have very poor hydrolytic stability and can only be used in moisture-free, enclosed systems. They are used as hydraulic and heat exchange fluids.

(c) Halogenated Fluids

Chlorine and/or fluorine can be used to replace part or all of the hydrogen in hydrocarbons, polyethers and silicones, resulting in many fluids which are inert, non-flammable, resistant to solvents and have a high thermal and oxidative stability. Chlorofluorocarbon and fluorester synthesis and properties were covered in Gunderson and Hart (1962). Applications are generally specialized because of the high cost of these materials. The June 1987 issue of Tribology International had a news item on what they thought was the most expensive lubricant in the world, a perfluorinated polyether grease costing over US\$450/kg. Uses include hydraulic fluids with extreme fire-resistance and lubricants for oxygen compressors, pumps for corrosive materials and many small volume, high temperature systems.

(d) Polyphenyl Ethers

A variety of polyphenyl ether structures have been synthesized and among them are some of the most thermally and oxidatively stable lubricants currently available. Again, these types of fluids are covered by Gunderson and Hart (1962) and by Klamann (1984). They are generally of high viscosity and have high pour points which restricts their application. They are chemically inert, radiation resistant, have very low volatility and find use in diffusion pumps, heat transfer fluids and in radiation resistant greases.

4. PERFORMANCE BENEFITS WITH SYNTHETICS

In order to be commercially viable as a mineral oil replacement, a synthetic must be able to give a reasonable return for the additional investment. A recent review (Engineer's Digest, 1986) gave 58

industrial case studies of savings achieved by replacing mineral oils with synthetics, with an average saving of US\$35000 per case. Principal benefits cited in the review were labor and material savings, reduction in power requirements, reduced failure rates and elimination of cold weather starting problems. The benefits of various types of synthetics in industrial applications were also recently reviewed by Miller (1984). In the introduction to the current paper, five general areas of performance benefit for synthetics were listed. These areas will be discussed in more detail in the following subsections, with emphasis on the property differences which give the benefit.

When we refer to "synthetic" or "mineral" we mean the type of basestock which makes up most of the lubricant. All modern lubricants, synthetic or mineral, rely heavily on additives to give many of their performance characteristics. However, since the structure of synthetic basestocks is closely controlled, additives can be tailor-made for optimum response resulting in improved performance over mineral oils. In addition, lubricant manufacturers in general are prepared to spend more on additive systems for the higher-priced synthetics, resulting in performance improvements over and above those to be expected from the structural differences between mineral and synthetic basestocks. This section will concentrate mainly on those lubricant properties which are functions of the basestock type, where there are inherent differences between minerals and synthetics.

4.1. Improved Energy Efficiency

Energy savings compared with mineral oils have been well documented for synthetics in internal combustion engines (eg: SAE, 1981) and gears (eg: Murphy, 1981, Godet, 1984 and Jacobson, 1985). However, the physical reasons for improved energy efficiency are different for each.

In IC engines, friction losses are split roughly 70:30 between hydrodynamic and boundary friction. The primary advantage for appropriate synthetics comes from the ability to reduce viscosity, and hence reduce hydrodynamic friction, without running into volatility problems and without compromising high temperature wear performance, as discussed in Section 4.2. A secondary benefit comes from reduced traction and pressure-viscosity coefficient. The overall fuel economy benefit from these improved rheological characteristics is 2-3% on average compared with multigrade mineral oils with the same high temperature protection. An additional 1% or so improvement can be gained from the use of friction modifiers to reduce boundary friction, but this approach is also valid for mineral oils.

In gears, friction losses come from a combination of viscous drag and contact loss. The mode of lubrication of the gear contacts is elastohydrodynamic and the major benefit for synthetics comes from a reduction in traction, which reduces the energy consumed in shearing the film between the gear teeth. Figure 2 shows a schematic of the EHL film between two spur gear teeth and the contact traction forces generated with a mineral oil and a low traction synthetic. Lubricants being sheared in the high pressure gear contacts behave like plastic solids with a limiting shear stress. The reduction in contact friction loss corresponds to the area between the traction force curves and is proportional to the reduction in the stress limit.

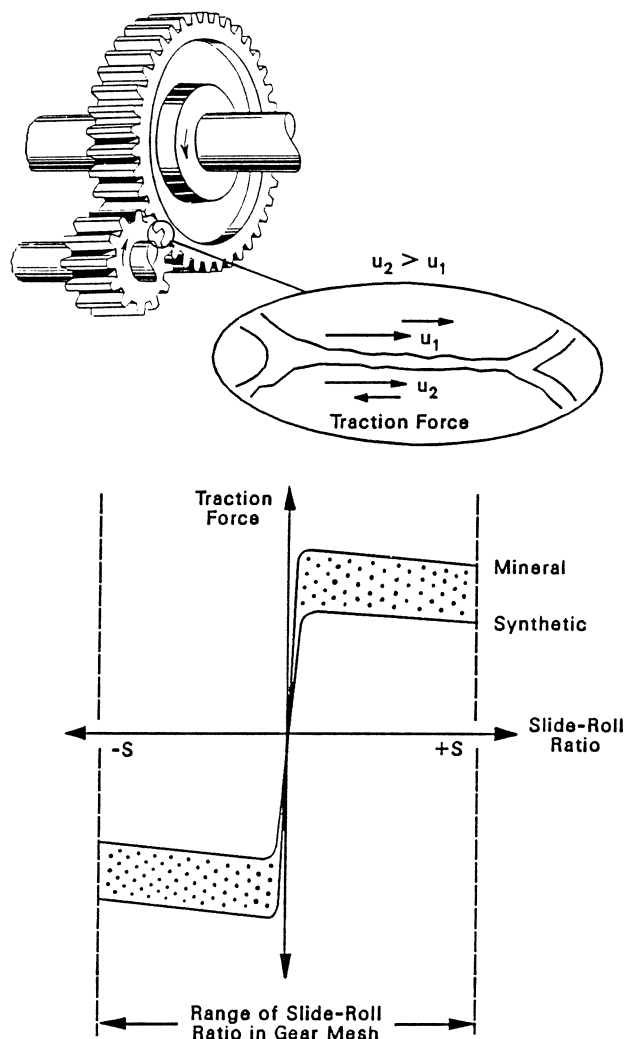


Figure 2. Schematic of traction forces in gear contacts. Energy savings with synthetics are proportional to the area between the mineral and synthetic curves.

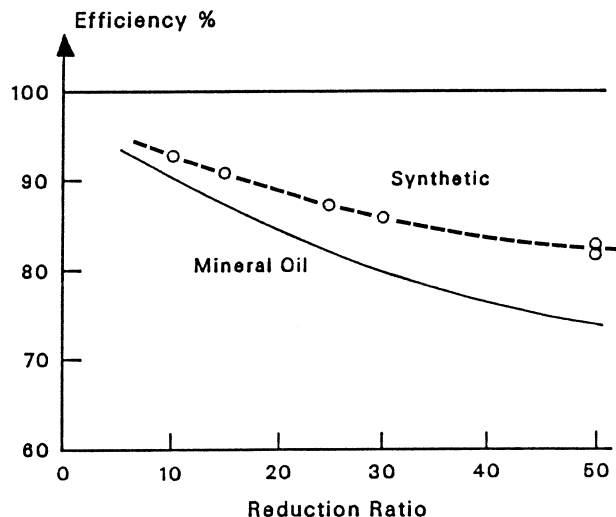


Figure 3. Worm gear efficiency versus reduction ratio for polydecene-based synthetics versus mineral oils.

The limiting shear stress is a function of small scale molecular structure. Linear structures, with or without long side branches, generally have low traction, examples being polydecenes and linear polyglycols or esters which have 30-70% reduction in the gear stress range. Approximate efficiency increases possible by changing from a mineral oil to a low traction synthetic are 0.5% for each stage of a spur or helical gear reducer, 1.5% for hypoid gears and, as shown in Figure 3, from 2% to 8% for worm gears as the ratio increases from 10:1 to 50:1. Since the annual cost of the energy being transmitted by the box is of the order of 100 times the cost of a synthetic oil charge, the extra cost of the synthetic will be repaid in a few weeks for a high ratio worm gear and in a few months for a triple reduction helical box.

4.2. Wider Operating Temperature Range

Four factors contribute to a wider operating temperature range for certain synthetics compared with mineral oils; lower pour point, higher VI, better oxidative stability and lower volatility.

The optimum lubricant viscosity grade for any application is the one which gives the minimum acceptable hydrodynamic or EHL film at the highest operating temperature to be encountered. The upper temperature limit of mineral oils is determined not by the lack of availability of sufficient viscosity but by their oxidative stability limit. Figure 4, presented by Beerbower (1982), compares life expectancy versus temperature for mineral oils and various synthetics. Allowable temperature increases over mineral oils to give the same life are about 75C for polyglycols, 100C for polydecenes/diesters, 120C for polyol esters and 220C for polyphenyl ethers.

Where a low viscosity is needed at a temperature below the oxidation limit for mineral oils, volatility is the next barrier. Volatility is a function of molecular structure and size. The wide

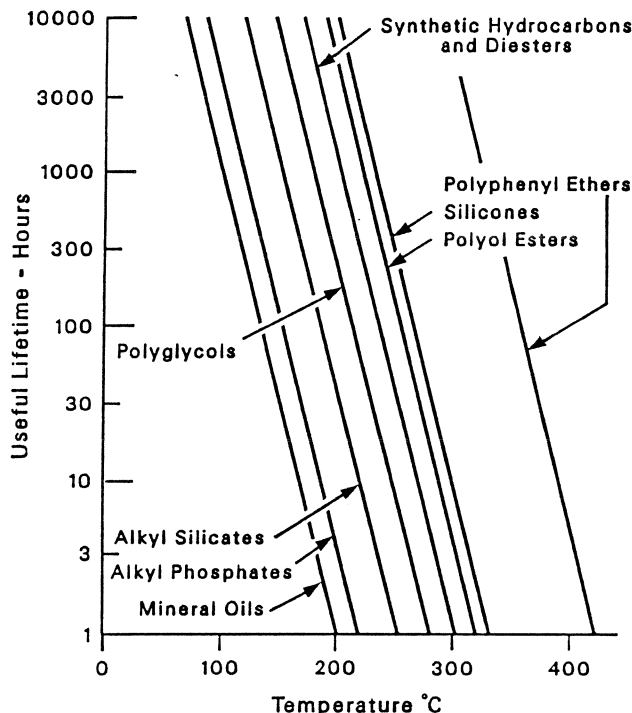


Figure 4. Life expectancy of inhibited lubricants in air (Beerbower, 1982).

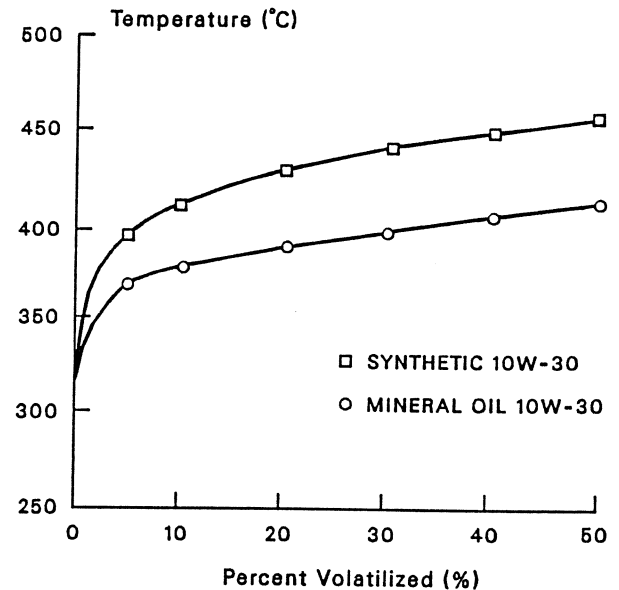


Figure 5. Comparison of the volatility (ASTM D1160) of polydecene- and mineral-based SAE 10W-30 oils.

distribution of structures and sizes in a mineral oil means there are more volatile components than in a similar viscosity synthetic composed of either a smaller number of isomers or of structures with lower volatility. Polydecenes, for example, are generally distilled to remove all dimer (C_{20}) leaving only trimer, tetramer and higher oligomers. A polydecene-based SAE 10W-30 engine oil can go to 30-40C higher temperatures before volatility equals that of an SAE 10W-30 mineral oil, as shown in Figure 5. This results in typically 25% lower oil consumption, except in the small percentage of engines with high leakage rates.

Assuming a high temperature viscosity requirement can be met without oxidative stability or volatility problems, the next limitation is the temperature below which the oil viscosity becomes too high to operate the machine or one of its components, such as a circulating pump. For a mineral oil, the limit may be set by the pour point at which wax crystallization causes the oil to solidify. A major advantage for synthetics is that isomers which solidify at moderate temperatures either do not occur during synthesis or can be excluded by process design.

If there is no pour point problem, the low temperature limit will be set by the lubricant's viscosity-temperature behavior, commonly represented by viscosity index, VI. VI is determined by a standardized method from kinematic viscosity at 40C and 100C and many synthetics have considerably higher VI than mineral oils. Paraffinic mineral oils have a higher VI than naphthenics, but they also have higher pour points so a balanced combination is often used for low temperature applications. The benefit at low and high temperatures from an increase in VI is shown in Figures 6(a) and 6(b) respectively. It can be seen that VI increases with high viscosity lubricants are more significant than for low viscosity, which is a quirk from the way the viscosity index system was initially designed.

From a lubrication engineering viewpoint, the meaning of VI has been confusing ever since the introduction of polymeric VI-improvers to generate crossgraded engine and hydraulic oils. The polymers add relatively more kinematic viscosity at

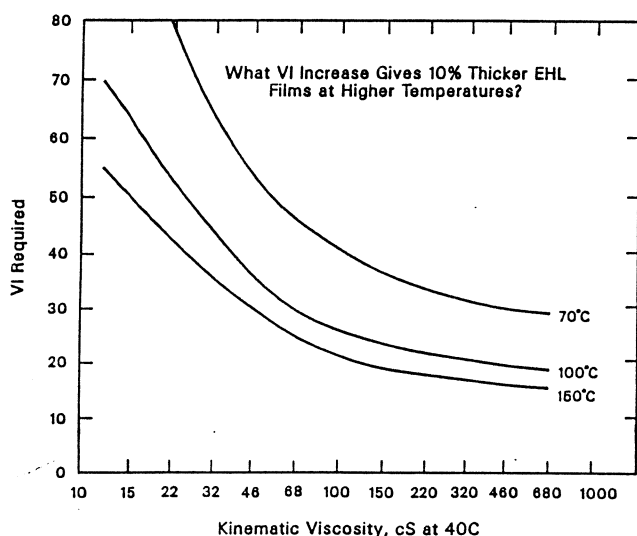
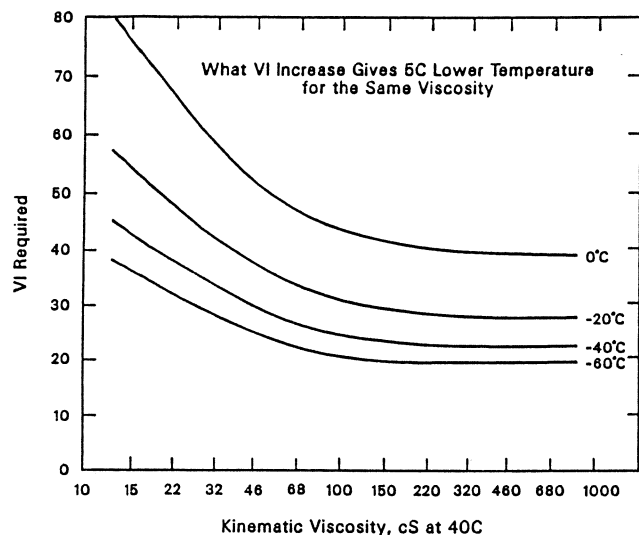


Figure 6. The significance of viscosity index (VI) in terms of lubricant performance at low and high temperature.

100C than at 40C and therefore boost VI as well as viscosity. Although the viscosity and VI boost increases with increasing polymer molecular weight and/or concentration, the blend also becomes increasingly non-Newtonian. Dynamic viscosity decreases with increasing shear rate in hydrodynamic bearings due to polymer disentanglement and alignment and in EHL contacts by mechanical degradation to lower molecular weights. As a result, film thicknesses are lower than for lubricants without polymer.

Comparison of VI-improved mineral oils with high-VI synthetics of the same crossgrade may be misleading. Synthetics with high natural VI allow multigrade oils to be made either without polymer or with less polymer and with a higher viscosity basestock than for mineral oils. An SAE 5W-30 polydecene/ester based synthetic engine oil has about 30% higher viscosity at 150C and 10^6 sec^{-1} shear rate than a typical SAE 5W-30 mineral oil. Automotive engine builders now set minimum high temperature, high shear rate viscosities for initial fill oils and these can be met with better overall viscosity-temperature performance and hence fuel economy with synthetics than with mineral oils.

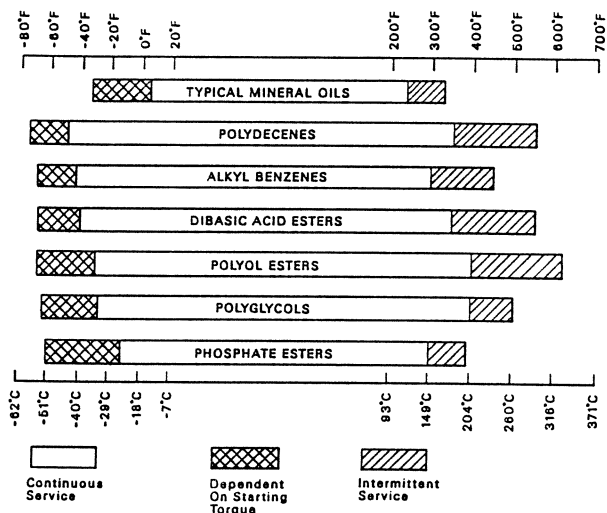


Figure 7. Comparative temperature limits for mineral and some synthetic lubricants.

As a result of the four advantages of synthetics discussed above, significant extensions in both the low and high end of the operating temperature range are possible. Figure 7 gives a general idea of the increased range possible with various types of synthetic.

4.3. Increased Design Ratings

Making use of the advantageous engineering properties of synthetic lubricants has allowed machines to be either uprated to a higher power throughput, replaced by a smaller unit with the same rating or run at the same power with a longer life expectancy. All represent improvements in design rating. The extreme example of uprating is in aviation jet engines where no reasonable rating would be possible without polyol esters. A polydecene-based lubricant helped make possible the non-stop, 9-day, round the world flight by the internal combustion engine-powered Voyager in December 1986. Experience with mineral oils suggested they would not last the required 200 hours in this engine. The following are some examples where mineral oils can perform satisfactorily but synthetics do better.

The power throughput of most worm gears is limited not by their mechanical strength but by the maximum temperature rise above ambient, the thermal rating. Reduced contact losses with a low traction synthetic not only save energy but also give a significantly lower temperature rise, allowing a thermal rating increase. Two worm gear manufacturers in the US now give 10-15% increased ratings for their boxes when polydecene-based lubricants are used. In addition, since the maximum temperature allowable for a synthetic is much higher than for a mineral oil, a further increase in thermal rating is possible. These two factors allowed a 65% increase in the power rating of a spur gear reducer used in farm tractors.

A marine diesel engine has been operated at 20% overload with no evidence of the piston ring scuffing which might be expected with a mineral oil. Increased cleanliness and the lack of deposits in the top ring land prevented ring sticking and allowed overload running. These benefits come from improved response of the synthetic basestock to tailored antioxidants and dispersants.

The effect of traction on the life of machines can go either way. The maximum torque possible in traction drives is proportional to the limiting shear strength of the lubricant films which transmit power between the rolling elements. Cycloaliphatic traction fluids have about twice the shear strength of mineral oils and can therefore double the drive throughput capability.

Alternatively they can halve the contact load needed between the rolling elements and give an eightfold increase in drive life for the same throughput. In gears, on the other hand, where the teeth are forced to slide over each other, the tangential shear stresses on the gear teeth are proportional to the limiting shear stress. Reducing these shear stresses reduces the degree of crack-opening on the slower moving surface, which is in tension as it enters the contact zone, and this reduces the rate of pit formation. A comparison of a mineral oil and a polydecene with 30% lower traction in a gear simulator, operating with a thick ($\lambda=2$) EHL film, showed a factor of 4 reduction in the rate of pit growth for the synthetic.

Low-speed heavily loaded rolling bearings and gears need shear stable high viscosity lubricants to provide a reasonably thick EHL film, prevent surface damage and meet their design lives. Mineral oils are generally limited to ISO 680 grade before pour point rises above 0C. The use of polymeric VI improvers gives little additional benefit for the added viscosity due to polymer degradation in the EHL contact inlet. Asphaltic open gear lubricants are appropriate for some applications, but most enclosed systems are better served by shear-stable synthetic hydrocarbon formulations which are available to ISO 6800 grade.

4.4. Reduced Maintenance

Reduced maintenance costs can come, for example, from extended oil life, improved cleanliness, longer component life, eliminating summer/winter oil changes and reduced oil consumption. Examples of such benefits have been documented in just about every paper on synthetic lubricants. This subsection will briefly review the reasons behind the benefits.

Oil drain intervals in both industrial and automotive applications can be extended typically by a factor of four due to the improved oxidative stability of appropriately additized synthetics. A heavier dose of dispersant and antiwear additives is usually included in synthetic engine oil formulations to ensure optimum performance throughout the extended oil life. The lack of sludge and deposit formation due to the improved stability of the synthetics also leads to improved machine cleanliness, preventing machine failures due to piston ring sticking, filter or separator plugging, improper valve function, exhaust gas turbocharger bearing coking and the like.

Longer gear and bearing lives due to thicker hydrodynamic and EHL films at high operating temperatures result from the use of synthetics where the high VI is not due to shear unstable polymeric additives. Component lives are also increased by a reduction in the number of circulation problems such as line starvation at low temperatures and filter problems at high temperatures. Low traction synthetics can give longer gear pitting lives. Aircraft wheel bearings are subjected to extreme cold and then rapid heating due to their proximity to the braking surfaces which reach temperatures over 1000C. Greases based on synthetic hydrocarbons have proven

very effective by being sufficiently fluid to allow bearing rotation when cold and still provide protection during braking. Wear with mineral-based greases was excessive in this application.

In construction and other off-highway equipment operating in locations subjected to cold winters and hot summers, changing oil between seasons is still the norm. The additional inventory cost, changeover labor cost, and the risk of operating or being unable to start the equipment with the wrong oil due to rapid weather changes can be eliminated by switching to a wax-free, high VI synthetic. The use of synthetics for improved cold starting as well as fuel efficiency is gaining wide acceptance in the US truck and bus industry. Reduced volatility of the synthetics can also lead to significant oil consumption reductions.

4.5. Better Reliability and Safer Operation

There are many lubricant applications where there is more at stake than the added downtime and maintenance cost if something goes wrong. Many of the advances in aerospace technology have been driven by the need for extreme reliability and it is in such applications that the expensive, specialty lubricants find a home. Expensive is a relative term - what is \$1000 for a few pounds of lubricant if it keeps some critical component in a \$100 million satellite from breaking down? It is here that the true role of the lubricant as an engineering component is seen.

Enhanced component reliability has resulted in widespread use of synthetics in the automobile racing business. Polydecene-based engine oils, gear oils and wheel bearing and CV joint greases are used by many winning teams for extra protection. Cars have been able to finish races with synthetic engine oils where it would not have been possible with minerals. Two examples were with overheated engines, one due to a plugged air intake on the oil cooler and the other due to loss of coolant. Another lost two-thirds of its synthetic axle lubricant but kept on running despite considerable heat generation.

Human safety is a vital concern and synthetics can play a significant role in allowing safer operation of many systems. It is difficult to put a figure on the true economic benefit of safer operation but the cost of liability insurance premiums is one measure. Eliminating fire hazards by the use of fire-resistant hydraulic fluids can significantly enhance insurability.

5. CONCLUDING REMARKS

The advantage of synthetics over mineral oils comes from the ability to synthesize selected molecular structures which are beneficial in lubrication. This usually is only possible at some cost penalty and a synthetic product is only of value if it can more than repay the additional investment or provide some critical performance need which a mineral oil can not.

Performance factors which can lead to overall cost savings are improved energy efficiency, reduced maintenance costs, increased design ratings, improved reliability and safer operation. In addition, performance beyond the capability of mineral oils can be obtained through a wider operating temperature range and the ability to operate in hostile environments.

The introduction of tribology as a scientific discipline has helped make these benefits more

readily recognizable. The lubricant is an important engineering component, not an unfortunate afterthought, and its performance characteristics contribute to the overall economics of any design. Synthetics in widest use as mineral oil replacements due to better performance are synthetic hydrocarbons, polyglycols and esters. Synthetics which offer special properties at higher cost are phosphate esters, silicones, halogenated fluids and polyphenyl ethers.

Future developments in synthetics will come from current research towards understanding the relationship between molecular structure and physical or chemical properties. Those properties where significant advantages are seen over mineral oils are thermal and oxidative stability, traction, volatility, viscosity-temperature/pressure/shear behavior and pour point. Matching lubricant molecules to machine needs will lead to exclusive use of synthetics in many applications.

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