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OF ADVANCED RESEARCH****REVIEW ARTICLE****Chemical additive for viscosity enhancement****Shailesh N. gadhvi and Ajit V. pandya**

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Abstract

This paper briefly reviews the development of different chemical additive for enhancing viscosity of diesel oil and other lubricants. petroleum diesel is an attractive renewable energy source, however some time due to change in crude blend or changing the distillation range of various stream of refinery we are getting resulting value of diesel viscosity is lower than specified requirement. In this review, different additive discussed to enhance the viscosity or viscosity index of diesel. Factors affecting the viscosity of fuel are discussed. In addition, various additive used to improve the viscosity of diesel are also presented, with a special emphasis laid on the effects of these additive on pour point of oil.

*Copy Right, IJAR, 2013,. All rights reserved.***Introduction**

Probably the most important single property of a lubricating oil is its viscosity. A factor in the formation of lubricating films under both thick and thin film conditions, viscosity (Rizvi, 2009, Ludema, 1996, Leslie, 2003 and Margareth, et. al., 2010), affects heat generation in bearings, cylinders, and gears; it governs the sealing effect of the oil and the rate of

consumption or loss; and it determines the ease with which machines may be started under cold conditions. For any piece of equipment, the first essential for satisfactory results is to use an oil of proper viscosity to meet the operating conditions.

In selecting the proper oil for a given application, viscosity is a primary consideration. It must be high enough to provide proper lubricating films but not so high that friction losses in the oil will be excessive. Since viscosity varies with temperature, it is necessary to consider the actual operating temperature of the oil in the machine. Other considerations,

such as whether a machine must be started at low ambient temperatures, must also be taken into account. The kinematic viscosity of a fluid is the quotient of its dynamic viscosity divided by its density, both measured at the same temperature and in consistent units. The most common units for

reporting kinematic viscosities now are the stokes (St) or centistokes

(cSt; 1 cSt = 0.01 St), or in SI units, square millimeters per second (mm²/s; 1 mm²/s = 1 cSt). The viscosity of any fluid changes with temperature, increasing as the temperature is decreased, and decreasing as the temperature is increased. Thus, it is necessary to have some method of determining the viscosities of lubricating oils at temperatures other than those at which they are measured. This is usually accomplished by measuring the viscosity at two temperatures, then plotting these points on special viscosity-temperature charts developed by ASTM. The two temperatures most used for reporting viscosities are 40°C (104°F) and 100°C (212°F). VI improvers are long chain, high molecular weight polymers that function by causing the relative viscosity of an oil to increase more at high temperatures than at low temperatures. Generally this result is due to a change in the polymer's physical configuration with increasing temperature of the mixture. It is postulated that in cold oil the molecules of the polymer adopt a coiled form so that their effect on viscosity is minimized. In hot oil, the molecules tend to straighten out, and the interaction between these long molecules and the oil produces a proportionally greater thickening effect. As temperature increases, solubility improves, and polymer coils eventually expand to some

maximum size and in so doing donate more and more viscosity. The process of coil expansion is entirely reversible as coil contraction occurs with decreasing temperature (see Figure 1.9). Different oils have different rates of change of viscosity with temperature. For example, a distillate oil from a naphthenic base crude would show a greater rate of change of viscosity with temperature than would a distillate oil from a paraffin crude. The viscosity index is a method of applying a numerical value to this rate of change, based on comparison with the relative rates of change of two arbitrarily selected types of oil that differ widely in this characteristic. A high VI indicates a relatively low rate of change of viscosity with temperature; a low VI indicates a relatively high rate of change of viscosity with temperature. For example, consider a high VI oil and a low VI oil having the same viscosity at, say, room temperature: as the temperature increased, the high VI oil would thin out less and, therefore, would have a higher viscosity than the low VI oil at higher temperatures. The VI

of an oil is calculated from viscosities determined at two temperatures by means of tables published by ASTM. Tables based on viscosities determined at both 104°F and 212°F, and 40°C and 100°C are available. Finished mineral-based lubricating oils made by conventional methods range in VI from somewhat below 0 to slightly above 100. Mineral oil base stocks refined through special hydroprocessing techniques can have VIs well above 100. Additives called VI improvers can be blended into oils to increase VIs; however, VI improvers are not always stable in lubricating environments exposed to shear or thermal stressing. Accordingly, these additives must be used with due care to assure adequate viscosity over the anticipated service interval for the application for which they are intended. Among the principal VI improvers are methacrylate polymers and copolymers, acrylate polymers, olefin polymers and copolymers, and styrene butadiene copolymers, Figure (1.10). The degree of VI improvement from these materials is a function of the molecular weight distribution of the polymer. The long molecules in VI improvers are subject to degradation due to mechanical shearing in service. Shear breakdown occurs by two mechanisms. Temporary shear breakdown occurs under certain conditions of moderate shear stress and results in a temporary loss of viscosity. Apparently, under these conditions the long molecules of the VI improver align themselves in the direction of the stress, thus reducing resistance to flow. When the stress is removed, the molecules return to their usual random arrangement and the temporary viscosity loss is recovered. This effect can be beneficial in that it can temporarily reduce oil

friction to permit easier starting, as in the cranking of a cold engine. Permanent shear breakdown occurs when the shear stresses actually rupture the long molecules, converting

www.intechopen.com Lubricating Oil Additives 263 them into lower molecular weight materials, which are less effective VI improvers. This results in a permanent viscosity loss, which can be significant. It is generally the limiting factor controlling the maximum amount of VI improver that can be used in a particular oil blend. VI improvers are used in engine oils, automatic transmission fluids, multipurpose tractor fluids, and hydraulic fluids. They are also used in automotive gear lubricants. Their use permits the formulation of products that provide satisfactory lubrication over a much wider temperature range than is possible with straight mineral oils alone.

Polymethacrylates (PMA): These are polymerised esters of methacrylic acid. They normally exhibit pour-point depressing activity. Dispersant properties can be obtained by incorporating polar groups in the molecular structure.

Polyisobutenes (PIB): These are non-dispersant polymers and they have no effect on the pour point of formulated lubricants. They have limited use in modern formulations.

Olefin co-polymers (OCP): These are usually co-polymers of ethylene and propylene. Dispersant properties can be obtained incorporating polar groups in the molecular structure.

Styrene/diene co-polymers: The molecular weight distribution is optimised to give good shear stability in crankcase applications. Its uniquely effective thickening power in solution gives an overall thickening efficiency that is superior to other polymers of equivalent shear stability. To produce oil with good viscosity temperature property use is made of high molecular weight compound – specifically polymer, was proposed as far back as 1967 but its instability with heat and shear stress ruled out any completely satisfactory result. Later mainly in last 20 or 30 years other compounds have been proposed. Some of the most important additives of this type have been discussed widely in the foreign and domestic literature. These additives include polyisobutylenes, copolymer of isobutylene with styrene, polymethacrylate and polyacrylate (plexol, viscoplexes, Glysoviscals, Acryloids) polymer of vinyl ethers (vinipols), polyalkyl styrene (Santodexes, certain copolymer of lauryl methacrylate and nitrogen containing monomer etc.

The principle behind the production of most such polymer in the very strong susceptibility of compounds containing the vinyl group $\text{CH}_2=\text{CH}$ -polymerisation reaction, isobutylene, $\text{CH}_2\text{C}(\text{CH}_3)_2$, is used to produce polyisobutylene: styrene $\text{CH}_2=\text{CHOC}_6\text{H}_5$, to produce polystyrene: acrylic acid ester $\text{CH}_2=\text{CHCOOR}$ TO PRODUCE POLYACRYLATES: vinyl n-butyl ether $\text{CH}_2=\text{CHOC}_4\text{H}_9$ to produce vinipol etc. in the majority of the cases the polymerization reaction proceeds by an ionic mechanism and is catalyzed by acidic agent.

Numerous investigation and the accumulated experience in use of high molecular weight compound as additive to produce oil with given property of viscosity are now opening up possibility in the development of multifunctional additives that have not only viscosity improving property but also antiwear and pour point depressant properties.

In recent years. One notes in the domestic and foreign patent literature an ever increasing trend towards improving the mechanical stability of various polymeric thickness. This trends was brought about by the need for developing formulations for not only motor oils but also oils for hydromechanical gear boxes, transmission oil and speciality fluid in which viscosity temperature characteristic are particular important.

Stabilization of polymeric additives is brought about various methods, for example patent describe the homogenization of a solution of 18000molecular weight polyisobutylene in mineral oil in the presence of secondary amines produce from coconut oil. The viscosity additive thus obtained showed a good mechanical stability during test and the viscosity of the thickened oil decreased only 1% during the test. An oil compound with unhomogenized polyisobutylene under the same conditions showed a 15% decrease in viscosity.

An analogous methods was used to obtain a thickening additive on the basis of a polymethacrylates which also had pour-point depressant and detergent effects.

One of the patent propose the use of polypeptide of molecular weight 10,000 to 1,000,000 as a thickening additive for lubricative oil, said to be better than polyisobutylene or polymethacrylate in mechanical stability for example, the addition of 0.5% of a 1,60,000molecular weight polypeptide containing about 90% of lauryl glutamate and 10% benzyl glutamate group increased the viscosity of mineral oil from 4.9 to 12.2 cst. Increasing the viscosity of same mineral oil to 12.2cst require the use of approx. 3% Acryloid 763(commercial 400,000MW. Polymethacrylate) or paratone N (commercial 120,000M.W. polyisobutylene).in the

test of mechanical stability of the compound oil by exposure to ultrasonic radiation the viscosity of the oil containing 0.3% of the polypeptide decreased by 2.8% that of the oil with 3.0%Acryloid 763 by 30% and that of the oil with 3% polyisobutylene by 6%

In soviet author certificate with the aim of preventing mechanical breakdown of a polymeric thickening additive used in gear lubrication, the addition of 2% stabilizer to the oil is recommended, this stabilizer consisting of quaternary ammonium salt of aminophenol compound. In this case mechanical breakdown of the polymer was reduced by factor of 1.2-1.4.

A real possibility was shown for reducing the mechanical breakdown of polyisobutylene by the addition of antioxidant to the polymer compounded oil, these antioxidants being effective at the bulk working temperature of the oil. The most active stabilizer under the condition investigated proved to be 2-diethylaminomethyl-p-hydroxydiphenylamine, which reduced the polyisobutylene breakdown by a factor of 1.7-1.8.

Thus in the current development of new type of thickening additives, special attention of investigations and users is being turned to the mechanical stability of the polymeric compound that are obtained. Almost all patent contain comparisons of the thickening power and mechanical stability of the additive being patented with those of the classical commercial additives based on polyisobutylene or polymethacrylate, polymers of approximately the same molecular weight are generally selected for such comparisons.

For example, a polymer of 4-methylpentane-1 has been used as a thickening additive for mineral and synthetic oil. the addition of 3.25% of this polymer to an oil increased its viscosity from 6.5 to 12.4cst at 99°C. after 250 cycle of pumping the oil through a nozzle (mechanical stability test). Its viscosity had dropped 6.5%. in an analogous test on the same base oil thickened with 3.05% polyisobutylene (to 12.4cst at 99°C) the viscosity dropped 37.5%.

A similar comparison is made in patent describing the use of a butadiene polymer, molecular weight 1,000 to 10,000, consisting mainly of cis - units. It is stated that the polymer in oil solution has a high resistance to mechanical breakdown.

Sometimes atoms of active elements are introduced in to the polymer composition during synthesis- material such as sulfur, chlorine, phosphorous together. Such additives in addition to their thickening action have good antiwear and antiscuff properties, which are extremely valuable these material are recommended even as additives for gear and transmission oil for extreme pressures.

An example is given in patent for the use of low molecular weight halogenated and sulfohalogenated polymers as extreme pressure oils. The viscosities of such polymers, containing 0.3-1.3% sulfur or 0.6-10.9% chlorine are approximately 13-16cst. At 99°C. In US patent there is description of sulfur containing polymer used as viscosity improver additives that are stable to the action of high shear stresses.

The introduction of 0.1-5.0% phosphorous into polymers gives them antiwear properties. For example an oil compounded with the polymer proposed is gave a seizure load of 137kg in a four ball tester in comparison with 65kg for the base oil.

The polymer chosen for introduction of active elements or groups are as a rule fairly low molecular weight materials (800 to 10,000) which are more susceptible to addition reaction. For example in a 850 molecular weight polyisobutene was subjected to phosphosulfurization and the starting material was 940MW. Polyisobutylene. This phosphosulfurized low molecular weight polyisobutylene after treatment with barium oxide was used as the detergent component of a thickening additive consisting of 19,000MW. Polyisobutylene. In other patent the detergent component is a barium or calcium salt of hydrolyzed phosphosulfurized low molecular weight polyisobutylene. The phosphosulfurization reaction is carried out at 180-230°C for 5-8hrs with a P₂S₅ concentration of 10-15%. As a result of such reaction the polymer usually adds about 5% sulfur and 3% phosphorous.

In recent years specialists are becoming interested in low molecular weight polymer that are used in the synthesis of certain additives e.g. succinimide or are used as a lube oil component. One of the promising methods of obtaining high quality lube oil is to start with a mineral oil and add polyisobutylene with a molecular weight close to that of the oil. An interesting feature of such polymer when used as a lube oil component is its ability to burn without forming deposits. The high adhesivity of low molecular weight polyisobutylene (with respect to metal surface) ensures that the lubricating oil will have a good oil film. Hence the oil containing the polyisobutylene gives less deposits and provides more effective lubrication.

For the production of motor oils or transmission oil other comparatively low molecular weight polymers may be used. Formulations are given in the literature for such oil based on polyethylene oil and fractions of hydrogenated lignite tar.

The increase in demand for petroleum fuels and consequent depletion of their reserves has given rise to the need for investigating new energy

resources or finding the optimum way of using the present resources. In this regard, two approaches are pursued: a) Improving refining processes for producing better quality fuel from different crude oils, that is, tailoring fuel at the refining stage, and b) Using some additives for improving the quality of existing fuels to a desired level,

which is, improving performance of available fuel. The effects of fuel quality variations on diesel engine emissions is complicated by the wide variation of the engine response to the fuel quality changes and the extent of inter-correlation of the various fuel variables. In engine literature, many investigators have reported. Betz et al. (1993) suggest that the particulate emission reduction could be attained using the ash less additive technology. The different fuel characteristics are

given in Table 2.1. They found that it is necessary to use a conditioning period prior to emission tests. Kouremenos et al. (1999) examined the effect of the fuel composition and physical properties on the mechanism of combustion and pollutant formation. A number of fuels having different density, viscosity, chemical composition, (especially aromatics type), are used in their investigation and found that the fuel properties namely density and viscosity are more important than fuel composition (aromatics) in respect of engine performance and emissions. The total aromatic content, however, has more influence on engine performance and emissions rather than the individual aromatics. Hajdukovic et al. (2000) reported that the toxicity of diesel fuel is generally attributed to soluble aromatic compounds. Alkyl derivatives of benzene and polycyclic aromatic hydrocarbons are considered as most harmful. New oxygen and nitrogen derivatives of hydrocarbons are formed as a result of oxidative and pyrolytic processes during combustion. The diesel fuel being heavier and having higher carbon content has some problems when used in an engine. Due to its high freezing point, it is known to cause

blockage of filters and nozzles especially under cold conditions. The routine use of fuel additive in diesel began in 1960's in Europe as cold flow improvers. The additives added in parts per millions (ppm) levels achieve a specific objective of either improving the physical or chemical characteristics of the fuel or improving the combustion characteristics. There are many other functions of additives. Based on the function and additive concept, they are reported to be classified (Owen Kiehl et al, 1990) as antioxidants and stabilizers, metal deactivators, cetane improvers, combustion improvers, detergents, corrosion inhibitors, anti-static additives, dehazers and demulsifiers, anti-icers, biocides, anti-foamants, odor masks and odorants, dyers and markers and drag

reducers. Kidoguchi et al. (2000) in their investigations reported that in fuels with higher aromatics content, the pyrolysis of fuel will not be satisfactory and therefore there are local high temperature regions on account of higher adiabatic flame temperature capability of ring structure hydrocarbons. The aromatic compounds are very compact with very less surface to volume ratio compared to long chain normal polymers. They have higher C/H ratio and also cm ratio per unit volume. They are also more reactive because of lower C-C bond strength compared to C-H bonds.

Hence, in the absence of air, they are prone to higher cracking, pyrolysis and agglomeration with other aromatic molecules nearby during the initial stages of combustion. Their adiabatic flame temperatures are also very high and as a result, soot formation increases (Hirao et al., 1988). Due to higher bond strength of O-H bonds compared to C-H and C-C bonds, O-H bonds break up in presence of high local temperatures and bring the local temperatures down. This decreases the possibility of formation of NO_x. The O-H bonds are reformed as the temperatures decrease and the absorbed energy is given back. Jensen et al (1983) observed that the concentrations of alkyl homologues of PAH and oxy-PAH in the particulates were found to decrease with increasing cylinder exhaust temperatures. The degree of alkylation for the most abundant homologue of these compounds increased by one to two carbons as the cylinder exhaust temperature decreased. The inverse relationship between engine temperature and production of extractable organics suggests one possible emission control strategy. The post combustion reactor might achieve reduction of PM associated with organics. To evaluate the feasibility of such an engine modification, both particulate and vapour emissions need to be collected simultaneously. This will allow proper correlation of particulate vapour with the engine conditions. Alkyl homologue analysis of diesel emissions provides information which may lead to selection of engine operating conditions that will reduce the environmental impact of diesel emissions. It is reported that

- a) Iso-propyl nitrate reduces both aldehyde and CO level without much effect on NO_x.
- b) Iso and Iso-amyl nitrate and di-tertiary butyl peroxide reduce NO_x by generating alkoxyl radicals.

Stage de Caro et al. (2001) studied the effect of two organic additives for their properties and to investigate their effect on diesel - ethanol mixture they tested them in the DI and IDI engines. Additives bring stability to the diesel ethanol mixture. Cetane number decreased in the presence of alcohol and also

the dynamic viscosity, and heat content increases the volatility. Diesel / ethanol blends with low ethanol content have little effect on the contents of the pollutant gases from the indirect injection engines whereas a reduction is observed with DI engines. DI engines are more sensitive than IDI engines to the fuel cetane number. Adding ethanol leads to a reduction in the smoke and particulates levels emitted in the exhaust. In the presence of additive, the cycle-to-cycle variation of IMEP was reduced. Kulinowski et al. (1993) in his review suggested that diesel fuel additives such as cetane improvers, combustion improvers, diesel detergents, low aromatic and sulphur content in fuel and lubricity additives can give a desirable effect. They concluded that a properly formulated diesel additive with the above measures will result in desirable changes in the emissions and performance of the engine.

API project 42(Whitemore, 1940-66) measured several physical properties of a variety of synthetic hydrocarbon structure. This data was reviewed recently by Denis (1984) in an attempt to determine which structure give the best balance of pour point against viscosity-temperature variation as defined by viscosity index (VI). Four from API 42 (normal alkanes and midchane branched isoalkanes, cyclohexyl alkanes and phenyl alkanes), two commercial available synthetic (Poly decenes and polyisobutenes) and a broad range for naphthenic structures typical of those found in naphthenic mineral oils.

It is interesting that in 1962, synthesized hydrocarbon 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 material were the main reason for lack of promise at the time. There have been significant process development since then and synthesized hydrocarbon based products are now commercially available for almost every lubrication application. There are four major classifications of synthesized hydrocarbons:

Polyalphaolefins : Alpha olefins are straight chain hydrocarbons with a reactive olefinic tail they are made commercially by fractionating oligomerized ethylene and can be polymerized to form branched hydrocarbon which like something like a section of flexible fish backbone. The length of the backbone depends on the number of olefin combined in the polymer molecule and, for a given starting olefin, viscosity increases and volatility decreases with backbone length. The length of branches depends on the size of the starting alphaolefine and viscosity-Temperature performance viscosity index improves with increasing branch length. However pour point

also increases with branch length and the best compromise between viscosity index and pour point is obtained by using 1-decene as the starting olefin. Polydecenes therefore form the largest segment of the PAO market. Further information on polydecene synthesis procedure can be found in papers by Brennan(1979) and Isa (1986).

Polyisobutenes: polyisobutenes are produced by polymerizing the relatively inexpensive butane/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 viscosity improvers. The low thermal stability can be put to good use in high temperature metal working 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.

Alkylated aromatics: Alkylated aromatics are synthesized by alkylating an aromatics with olefin. The fluid properties are a function of the structure of the alkyl groups. The most common aromatic used in benzene and it comes with either one alkyl benzene or two alkylbenzene. Alkylbenzene have very low pourpoint and low viscosity index. Dialkyl benzene can have viscosity index around 100 and are less volatile and more stable.

Cycloaliphatics: 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) branches have high shear strength and current commercial traction fluids are typically twin ringed cycloaliphatic. These have low viscosity index are only available in low viscosity and have higher volatility than mineral oils of equivalent viscosity

The Vegetable oils in use prior to the mineral oil takeover were organic esters. Their main disadvantages were low temperature gelation and high temperature deposit 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 review of the synthesis and properties of esters have been presented by Klamann (1984) and Szydywar(1984). Those of commercial

interest have high viscosity index, 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 polyolefin products. A review of the effect of esters on seal materials was given by van der Waal (1985). Hydraulic instability of some esters can lead to storage problem if water is encountered. 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).

Polyglycol is 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 property was reviewed by Kussi (1965). And on traction properties in particular by Hentschel (1985).

The most obvious attractive feature of polyglycols is the combination of high viscosity index (>200) with low pour point (<-50C) possible with certain structures. Viscosity index and pour as a function of structure was discussed by Denis (1984). Pressure-viscosity coefficient is lower for high viscosity index 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 make their gear efficiency improvements less predictable.

Phosphoric acid esters, or phosphate esters, have been known for over 130 years and a wide variety of structure 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 additives 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. Maintenance procedure to avoid problems with degraded phosphate esters were reviewed by Shade (1987) based on experience with compressors reaction with steel surface give phosphide film makes phosphates esters excellent boundary lubricants.

Silicones and silicates esters are two classes of specialty synthetic lubricants with unusual properties. They are again new and warranted a chapter each in Gunderson Hart (1962). Silicones consist of alternating silicon-oxygen backbone with organic side-chains attached to the silicon. They have extremely high viscosity index (>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 silicone were reviewed recently by Huber (1986).

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 type 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. 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 problem. 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.

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