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(54) Hydrogenated polyisoprene lubricating composition.

57) A lubricating composition is provided containing: a high viscosity synthetic hydrocarbon such as high viscosity, liquid hydrogenated polyisoprene olefin having a viscosity of greater than 3500 to 175,000 centistokes at 100°C; a low viscosity synthetic hydrocarbon and/or a low viscosity ester; and optionally an additive package to impart desirable performance properties to the composition.

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HYDROGENATED POLYISOPRENE LUBRICATING COMPOSITION

This application is a continuation-in-part of copending application Serial No. 473,841 filed March 9, 1983, the entire disclosure of which is incorporated herein by reference and which is a continuation-in-part of application Serial No. 356,665 filed March 10, 1982, now abandoned.

This invention relates to compositions useful as lubricating oils having high viscosity index, improved resistance to oxidative degradation and resistance to viscosity losses caused by permanent or temporary shear.

According to the instant invention a lubricating composition is provided comprising (1) a high viscosity, hydrogenated polyisoprene having a viscosity of from greater than 3500 to 175,000 centistokes at 100°C; (2) a low viscosity synthetic hydrocarbon, such as alkylated benzene or low viscosity polyalphaolefin and/or a low viscosity ester, such as monoesters, diesters, polyesters, and optionally (3) an additive package.

An object of the invention is to provide a lubricating composition with properties not obtainable with conventional polymeric thickeners.

A further object of the invention is to provide lubricating compositions exhibiting improved shear stability, superior oxidative stability and excellent temperature-viscosity properties.

The viscosity-temperature relationship of a lubricating oil is one of the critical criteria which must be considered when selecting a lubricant for a particular application. The mineral oils commonly used as a base for single and multigraded lubricants exhibit a relatively large change in viscosity with a change in temperature. Fluids exhibiting such a relatively large change in viscosity with temperature are said to have a low viscosity index. The viscosity index of a common paraffinic mineral oil is usually given a value of about 100. Viscosity index (VI) is determined according to ASTM Method D 2770-74 wherein the VI is related to kinematic viscosities measured at 40°C and 100°C.

Lubricating oils composed mainly of mineral oil are said to be single graded. SAE grading requires that oils have a certain minimum viscosity at high temperatures and, to be multigraded, a certain maximum viscosity at low temperatures. For instance, an oil having a viscosity of 10 cSt. at 100°C (hereinafter all viscosities are at 100°C unless otherwise noted) would be an SAE 30 and if that oil had a viscosity of 3400 cP. at -20°C, the oil would be graded 10W-30. An unmodified mineral oil of 10 cSt. can not meet the low temperature requirements for a 10W-30 multigrade rating, since its viscosity index dictates that it would have a viscosity considerably greater than 3500 cP. at -20°C, which is the maximum allowed viscosity for a 10W rating.

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The viscosity requirements for qualification as multigrade engine oils are described by the SAE Engine Oil Viscosity Classification - SAE J300 SEP80, which became effective April 1, 1982. The low temperature (W) viscosity requirements are determined by ASTM D 2602, Method of Test for Apparent Viscosity of Motor Oils at Low Temperature Using the Cold Cranking Simulator, and the results are reported in centipoise (cP). The higher temperature (100°C) viscosity is measured according to ASTM D445, Method of Test for Kinematic Viscosity of Transparent and Opaque Liquids, and the results are reported in centistokes (cSt.). The following table outlines the high and low temperature requirements for the recognized SAE grades for engine oils.

25	SAE Viscosity	Viscosity (cP) at Temperature (°C)		osity (cSt.) 100°C
	Grade	Max.	Min.	Max.
	OW	3250 at -30	3.8	
	5₩	3500 at -25	3.8	
30	10W	3500 at -20	4.1	
	15W	3500 at -15	5.6	
	20W	4500 at -10	5.6	
	25₩	6000 at -5	9.3	
	20		5.6	Less than 9.3
35	30		9.3	Less than 12.5
	40		12.5	Less than 16.3
	50		16.3	Less than 21.9

In a similar manner, SAE J306c describes the viscometric qualifications for axle and manual transmission lubricants. High temperature (100°C) viscosity measurements are performed according to ASTM D445. The low temperature viscosity values are determined according to ASTM D2983, Method of Test for Apparent Viscosity at Low Temperature Using the Brookfield Viscometer and these results are reported in centipoise (cP), where (cP) and (cSt) are related as follows:

$$cSt = \frac{cP}{Density, kg/dm^3}$$

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The following table summarizes the high and low temperature requirements for qualification of axle and manual transmission lubricants.

15	SAE Viscosity	Maximum Temperature for Viscosity	Viscosity at 100°C, cSt.		
	Grade	of 150,000 cP, °c	<u>Minimum</u>	Maximum	
	70W	- 55			
	75W	-40	4.1		
	80W	-26	7.0		
20	85W	- 12	11.0	e e e e e e e e e e e e e e e e e e e	
	90		13.5	24.0	
	140	- - -	24.0	41.0	
	250				

It is obvious from these tables that the viscosity index of a broadly multigraded oil such as 5W-40 or 70W-140 will require fluids having considerably higher viscosity index than narrowly multigraded lubricants such as 10W-30. The viscosity index requirements for different multigraded fluids can be approximated by the use of ASTM Standard Viscosity-Tempearture Charts for Liquid Petroleum Products (D 341).

If one assumes that extrapolation of the high temperature (40°C and 100°C) viscosities to -40°C or below is linear on chart D 341, then a line connecting a 100°C viscosity of, for example, 12.5 cSt. and a low temperature viscosity of 3500 cP at -25°C would

give the correct 40°C viscosity and permit an approximation of the minimum viscosity index required for that particular grade of oil (10W-40).

The 40°C viscosity estimated by linearly connecting the 100°C and -25°C viscosities would be about 70 cSt. The viscosity index of an oil having K.V. $_{100}$ = 12.5 cSt. and K.V. $_{40}$ = 70 cSt. would be about 180 (ASTM D 2270-74). Unless the -25°C viscosity of a fluid is lower than the linear relationship illustrated, then an oil must have a viscosity index of at least 180 to even potentially qualify as a 10W-40 oil.

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In actual fact, many V.I. improved oils have viscosities at -25°C which are considerably greater than predicted by linear extrapolation of the K.V. $_{100}$ and K.V. $_{40}$ values. Therefore, even having a V.I. of 180 does not guarantee the blend would be a 5W-40 oil.

Using this technique minimum viscosity index requirements for various grades of crankcase or gear oils can be estimated. A few typical estimations are shown in the following table:

20	Crankcase Oil Grade	K.V. 100°C	Estimated K.V. _{40°C} cSt.	Required Viscosity Index
	10W-30	9.3	60	135
	5₩-40	12.5	70	180
	5₩ - 30	9.3	53	159
25	0W-50	16.3	75.5	232
	Gear Oil Grade			
	80W-140	24	270	112
	75W-140	24	200	149
	75W-250	41	318	184
30	70W-140	24	150	192

It can thus be seen that preparation of very broadly graded lubricants, such as 5W-40 or 75W-250 requires thickeners which produce very high viscosity indices in the final blends.

It has been the practice to improve the viscosity index of mineral oils or low viscosity synthetic oils by adding a polymeric thickener to relatively non-viscous base fluids. Polymeric thickeners are commonly used in the production of multigrade lubricants. Typical polymers used as thickeners include hydrogenated styreneisoprene block copolymers, rubbers based on ethylene and propylene (OCP), polymers produced by polymerizing high molecular weight esters of the acrylate series, polyisobutylene and the like. These polymeric thickeners are added to bring the viscosity of a base fluid up to that required for a certain SAE grade and to increase the viscosity index of the fluid, allowing the production of multigraded oils. Polymeric VI improvers are traditionally high molecular weight rubbers whose molecular weights may vary from 10,000 to 1,000,000. Since the thickening power and VI increase are related to the molecular weight of the VI improver, most of these polymers normally have a molecular weight of at least 100,000.

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The use of these high molecular weight VI improvers, in the production of multigraded lubricants has some serious drawbacks:

- 1. They are very sensitive to oxidation, which results in a loss of VI and thickening power and frequently in the formation of unwanted deposits.
- 2. They are sensitive to large viscosity losses from mechanical shear when exposed to the high shear rates and stresses encountered in crankcases or gears.
- 3. They are susceptible to a high degree of temporary shear.

Temporary shear is the result of the non-Newtonian viscometrics associated with solutions of high molecular weight polymers. It is caused by an alignment of the polymer chains with the shear field under high shear rates with a resultant decrease in viscosity. The decreased viscosity reduces the wear protection associated with viscous oils. Newtonian fluids maintain their viscosity regardless of shear rate.

We have found that certain combinations of fluids and additives can be used to prepare multigraded lubricants which outperform prior art formulations and have none or a greatly decreased amount of the above listed deficiencies found in polymerically thickened oils. Certain specific blends of high viscosity hydrogenated polyisoprenes (HPI), low viscosity synthetic hydrocarbons and/or low viscosity esters form base fluids from which superior crankcase or gear oils can be produced by the addition of the proper additive "packages". The finished oils thus prepared exhibit very high stability to permanent shear and, because of their nearly Newtonian nature, very little, if any, temporary shear and so maintain the viscosity required for proper wear protection. The oils of this invention have remarkably better stability toward oxidative degradation than those of the prior art. The unexpectedly high viscosity indices produced from our base fluid blends permit the preparation of broadly multigraded crankcase fluids, such as 5W-40 and gear oils such as 75W-140. Up to now it has been difficult if not impossible, to prepare such lubricants without the use of frequently harmful amounts of polymeric V.I. improvers.

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The polyisoprenes of this invention may be prepared by Ziegler-type or, preferably, anionic polymerization. Such polymerization techniques are described in United States Patent 4,060,492.

For the purposes of this invention, the preferred method of preparation for the liquid hydrogenated polyisoprenes is by the anionic alkyl lithium catalyzed polymerization of isoprene. Many references are available to those familiar with this art which describe the use of such catalysts and procedures. The use of alkyl lithium catalysts such as secondary butyl lithium results in a polyisoprene having a very high (usually greater than 80%) 1,4-content, which results in backbone unsaturation.

When alkyl lithium catalysts are modified by the addition of ethers or amines, a controlled amount of 1,2- and 3,4- addition can take place in the polymerization.

Hydrogenation of these structures gives rise to the saturated species represented below:

Structure (A) is the preferred structure because of its low Tg and because it has a lower percent of its mass in the pendant groups (CH₃-). Structure (B) is deficient in that the tetrasubstituted carbons produced serve as points of thermal instability. Structure (C) has 60% of its mass in a pendant (isopropyl) group which, if repeated decreases the thickening power of the oligomer for a given molecular weight and also raises the Tg of the resultant polymer. This latter property has been shown to correlate with viscosity index. Optimization of structure (A) is desired for the best combination of thickening power, stability and V.I. improvement properties.

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Another feature of alkyl lithium polymers is the ease with which molecular weight and molecular weight distribution can be controlled. The molecular weight is a direct function of the monomer to catalyst ratio and, taking the proper precautions to exclude impurities, can be controlled very accurately thus assuring good quality control in the production of such polymer. The alkyl lithium catalysts produce very narrow molecular weight distributions such that Mw/Mn ratios of 1.1 are easily gained. improvers a narrow molecular weight distribution is highly desirable since, at the given molecular weight, thickening power is maximized while oxidative and shear instability are minimized. If desired, broad or even polymodal M.W. distributions are easily produced by a variety of techniques well known in the art. Star-shaped or branched polymers can also be readily prepared by the inclusion of multifunctional monomers such as divinyl benzene or by termination of the "living" chains with a polyfunctional coupling agent such as dimethylterephthalate.

It is well known that highly unsaturated polymers are considerably less stable than saturated polymers toward oxidation. It is important, therefore, that the amount of unsaturation present in the polyisoprenes be drastically reduced. This is accomplished easily by anyone skilled in the art using, for instance, a Pt, Pd or Ni catalyst in a pressurized hydrogen atmosphere at elevated temperature.

Regardless of the mode of preparation, polyisoprenes require hydrogenation to reduce the high level of unsaturation present after polymerization. For optimum oxidation stability, 90%, and preferably 99% or more of the olefinic linkages should be saturated.

The low viscosity synthetic hydrocarbons of the present invention, having viscosities of from 1 to 10 cSt., consist primarily of oligomers of alphaolefins and alkylated benzenes.

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Low molecular weight oligomers of alphaolefins from C_8 (octene) to C_{12} (dodecene) or mixtures of the olefins can be utilized. Low viscosity alphaolefin oligomers can be produced by Ziegler catalysis, thermal polymerization, free radically catalyzed polymerization and, preferably, BF_3 catalyzed polymerization. A host of similar processes involving BF_3 in conjunction with a cocatalyst is known in the patent literature. A typical polymerization technique is described in United States Patent No. 4,045,508.

The alkylbenzenes may be used in the present invention alone or in conjunction with low viscosity polyalphaolefins in blends with high viscosity synthetic hydrocarbons and low viscosity esters. The alkylbenzenes, prepared by Friedel-Crafts alkylation of benzene with olefins are usually predominantly dialkylbenzenes wherein the alkyl chain may be 6 to 14 carbon atoms long. The alkylating olefins used in the preparation of alkyl benzenes can be straight or branched chain olefins or combinations. These materials may be prepared as shown in U.S.P. 3,909,432.

The low viscosity esters of this invention, having viscosities of from 1 to 10 cSt. can be selected from classes of esters readily available commercially, e.g., monoesters prepared from monobasic acids such as pelargonic acid and alcohols; diesters prepared from dibasic acids and alcohols or from diols and monobasic acids or mixtures of acids; and polyol esters prepared from diols, triols (especially trimethylol propane), tetraols (such as pentaerythritol), hexaols (such as dipentaerythritol) and the like reacted with monobasic acids or mixtures of acids.

Examples of such esters include tridecyl pelargonate, di-2-ethylhexyl adipate, di-2-ethylhexyl azelate, trimethylolpropane triheptanoate and pentaerythritol tetraheptanoate.

An alternative to the synthetically produced esters described above are those esters and mixtures of esters derived from natural sources, plant or animal. Examples of these materials are the fluids produced from jojoba nuts, tallows, safflowers and sperm whales.

The esters used in our blends ought to be carefully selected to insure compatibility of all components in finished lubricants of this invention. If esters having a high degree of polarity (roughly indicated by oxygen content) are blended with certain combinations of high viscosity synthetic hydrocarbons and low viscosity synthetic hydrocarbons, phase separation can occur at low temperatures with a resultant increase in apparent viscosity. Such phase separation is, of course, incompatible with long term storage of lubricants under a variety of temperature conditions.

The additive "packages" mixed with the recommended base oil blend for the production of multigraded crankcase fluids or gear oils are usually combination of various types of chemical additives so chosen to operate best under the use conditions which the particular formulated fluid may encounter.

Additives can be classified as materials which either impart or enhance a desirable property of the base lubricant blend into which they are incorporated. While the general nature of the additives might be the same for various types or blends of the base lubricants, the specific additives chosen will depend on the particular type of service in which the lubricant is employed and the characteristics of the base lubricants.

The main types of current day additives are:

1. Dispersants,

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- 2. Oxidation and Corrosion Inhibitors,
- 3. Anti-Wear Agents,
- 4. Viscosity Improvers,
- 5. Pour Point Depressants,
- 6. Anti-Rust Compounds, and
- 7. Foam Inhibitors.

Normally a finished lubricant will contain several and possibly most or all of the above types of additives in what is commonly called an "additive package." The development of a balanced additive package involves considerably more work than the casual use of each of the additive types. Quite often functional difficulties arising from combinations of these materials show up under actual operating conditions. On the other hand, certain unpredictable synergistic effects of a desirable nature may also become evident.

The only methods currently available for obtaining such data are from extensive full scale testing both in the laboratory and in the field. Such testing is costly and time-consuming.

Dispersants have been described in the literature as "detergents". Since their function appears to be one of effecting a dispersion of particulate matter, rather than one of "cleaning up" any existing dirt and debris, it is more appropriate to categorize them as dispersants. Materials of this type are generally molecules having a large hydrocarbon "tail" and a polar group head. The tail section, an oleophilic group, serves as a solubilizer in the base fluid while the polar group serves as the element which is attracted to particulate contaminants in the lubricant.

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The dispersants include metallic and ashless types. The metallic dispersants include sulfonates (products of the neutralization of a sulfonic acid with a metallic base), thiophosphonates (acidic components derived from the reaction between polybutene and phosphous pentasulfide) and phenates and phenol sulfide salts (the broad class of metal phenates includes the salts of alkylphenols, alkylphenol sulfides, and alkyl phenol aldehyde products). The ashless type dispersants may be categorized into two broad types: high molecular weight polymeric dispersants for the formulation of multigrade oils and lower molecular weight additives for use where viscosity improvement is not necessary. The compounds useful for this purpose are again characterized by a "polar" group attached to a relatively high molecular weight hydrocarbon chain. The "polar" group generally contains one or more of the elements-nitrogen, oxygen, and phosphorus. The solubilizing chains are generally higher in molecular weight than those employed in the metallic types; however, in some instances they may be quite similar. Some examples are N-substituted long chain alkenyl succinimides, high molecular weight esters, such as products formed by the esterification of mono or polyhydric aliphatic alcohols with olefin substituted succinic acid, and Mannich bases from high molecular weight alkylated phenols.

The high molecular weight polymeric ashless dispersants have the general formula:

where 0 = Oleophilic Group

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P = Polar Group

R = Hydrogen or Alkyl Group

The function of an oxidation inhibitor is the prevention of a deterioration associated with oxygen attack on the lubricant base fluid. These inhibitors function either to destroy free radicals (chain breaking) or to interact with peroxides which are involved in the oxidation mechanism. Among the widely used anti-oxidants are the phenolic types (chain-breaking) e.g., 2,6-di-tert.-butyl para cresol and 4,4' methylenebis(2,6-di-tert.-butylphenol), and the zinc dithiophosphates (peroxide-destroying).

Wear is loss of metal with subsequent change in clearance between surfaces moving relative to each other. If continued, it will result in engine or gear malfunction. Among the principal factors causing wear are metal-to-metal contact, presence of abrasive particulate matter, and attack of corrosive acids.

Metal-to-metal contact can be prevented by the addition of film-forming compounds which protect the surface either by physical absorption or by chemical reaction. The zinc dithiophosphates are widely used for this purpose. These compounds were described under anti-oxidant and anti-bearing corrosion additives. Other effective additives contain phosphorus, sulfur or combinations of these elements.

Abrasive wear can be prevented by effective removal of particulate matter by filtration while corrosive wear from acidic materials can be controlled by the use of alkaline additives such as basic phenates and sulfonates.

Although conventional viscosity improvers are often used in "additive packages" their use should not be necessary for the practice of this invention since our particular blends of high and low molecular weight base lubricants produce the same effect. However, we do not want to exclude the possibility of adding some

Alkylated Wax Phenol

amounts of conventional viscosity improvers. These materials are usually oil-soluble organic polymers with molecular weights ranging from approximately 10,000 to 1,000,000. The polymer molecule in solution is swollen by the lubricant. The volume of this swollen entity determines the degree to which the polymer increases its viscosity.

Pour point depressants prevent the congelation of the oil at low temperatures. This phenomenon is associated with the crystallization of waxes from the lubricants. Chemical structures of representative commercial pour point depressants are:

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Wax Naphthalene

Chemicals employed as rust inhibitors include sulfonates, alkenyl succinic acids, substituted imidazolines, amines, and amine phosphates.

Polymethacrylate

The anti-foam agents include the silicones and miscellaneous organic copolymers.

Additive packages known to perform adequately for their recommended purpose are prepared and supplied by several major manufacturers. The percentage and type of additive to be used in each application is recommended by the suppliers. Typically available packages are:

- 1. HITEC [trademark] E-320, for use in automotive gear oils,
- 2. Lubrizol [trademark] 5002 for use in industrial gear oils,
- 3. Lubrizol 4856 for use in gasoline crankcase oil, and
- 4. OLOA [trademark] 8717 for use in diesel crankcase oils.

A typical additive package for an automotive gear lubricant would normally contain antioxidant, corrosion inhibitor, anti-wear agents, anti-rust agents, extreme pressure agent and foam inhibitor.

A typical additive package for a crankcase lubricant would normally be comprised of a dispersant, antioxidant, corrosion inhibitor, anti-wear agent, anti-rust agent and foam inhibitor.

An additive package useful for formulating a compressor fluid would typically contain an anti-oxidant, anti-wear agent, an anti-rust agent and foam inhibitor.

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This invention uses blends of high viscosity hydrogenated polyisoprene (HPI), having a viscosity range of from greater than 3500 to 175,000 cSt. with one or more synthetic hydrocarbon fluids having viscosities in the range of 1 to 10 cSt. and/or one or more compatible ester fluids having a viscosity range of 1 to 10 cSt. Such blends, when treated with a properly chosen additive "package," can be formulated in broad range multigraded crankcase or gear oils having improved shear stability, improved oxidative stability, and nearly Newtonian viscometric properties. The blends of this invention also find uses in certain applications where no additive need be employed.

In discussing the constitution of the base oil blend, it is convenient to normalize the percentages of high viscosity liquid hydrogenated polyisoprenes, low viscosity synthetic hydrocarbons, and low viscosity esters in the final lubricant so that they total 100%. The actual percentages used in the final formulation would then be decreased depending on the amount of additive packages utilized.

Each of the ingredients, HPI, low viscosity synthetic hydrocarbons, and low viscosity esters are essential for this invention. The high viscosity liquid hydrogenated polyisoprenes provide thickening and V.I. improvement to the base oil blend. The V.I. improvement produced by HPI in blends with low viscosity synthetic hydrocarbons or low viscosity esters is shown in the examples.

The low viscosity synthetic hydrocarbon fluid is frequently the main ingredient in the base oil blend, particularly in finished lubricants having an SAE viscosity grade of 30 or 40. While certain low viscosity esters are insoluble in high viscosity synthetic hydrocarbons, the presence of low viscosity synthetic hydrocarbon, being a better solvent for low viscosity esters, permits greater variations in the type of esters used in base oil blends of high viscosity syn-

thetic hydrocarbons, low viscosity synthetic hydrocarbons, and low viscosity esters.

Crankcase and gear oils consisting solely of HPI and low viscosity synthetic hydrocarbons with the proper additives produce synthetic fluids having excellent oxidative and hydrolytic stability.

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Low viscosity esters can be used in combination with HPI and low viscosity hydrocarbons or alone with HPI. In the three component blend the proper choice of ester and hydrogenated polyiso-prene oligomers can produce crankcase and gear oil formulations having outstanding viscosity indices and low temperature properties.

Two component blends of HPI and esters can be used to prepare multigraded lubricants having outstanding viscometric properties, detergency, and oxidative stability. While some applications present environments having high moisture levels, which would be deleterious to certain esters, there are other applications such as automotive gear oils where the high ester contents found in the hydrogenated polyisoprene oligomers-ester blends can be used to advantage.

When it is deemed advantageous to use a low viscosity ester as part of the blend, the low viscosity hydrocarbons act as a common solvent for HPI and the added ester. Depending on the polarity of the ester, the latter two are frequently somewhat incompatible. Excellent multigraded lubricants can be formulated with or without ester.

The third component, low viscosity esters, can be added to produce the superior lubricants of this invention. HPI and low viscosity synthetic hydrocarbons can be used alone to produce multigraded lubricants. The addition of low levels of low viscosity esters, usually 1-25% results in a base oil blend superior to blends of high viscosity synthetic hydrocarbons and low viscosity synthetic hydrocarbons alone in low temperature fluidity.

Low viscosity esters usually constitute 10-25% of the synthetic base oil blend, more or less can be used in specific formulations. When the final application involves exposure to moisture elimination or limitation of the amount of ester in blends may be advantageous.

The components of the finished lubricants of this invention can be admixed in any convenient manner or sequence.

An important aspect of the present invention is in the use of the properly constituted base oil blend in combination with the proper compatible additive package to produce finished broad range multigrade lubricants having:

- 1. Improved temporary shear stability.
- 2. Excellent oxidation stability.
- 3. High viscosity index.

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The range of percentages for each of the components, i.e., high viscosity hydrogenated polyisoprenes, low viscosity synthetic hydrocarbons, low viscosity esters, and additive packages, will vary widely depending on the end use for the formulated lubricant, but the benefits of the compositions of this invention accrue when the base oil blend of high viscosity hydrogenated polyisoprenes, low viscosity synthetic hydrocarbons, and/or low viscosity esters contains (normalized):

From 1 to 99% HPI, from 1 to 99% low viscosity synthetic hydrocarbons, esters or mixtures thereof. It is preferred to blend from 10 to 80% HPI with correspondingly 90 to 20% of at least one low viscosity ester base fluid or hydrocarbon base fluid. The additive package can be used in from 0 to 25% of the total formulation.

The lubricants of this invention approach viscometrics of Newtonian fluids. That is, their viscosities are changed little over a wide range of shear rates. The HPI of the invention may, in themselves, display non-Newtonian characteristics, particularly at low temperatures, yet, the final lubricant products utilizing low viscosity oils as diluents are nearly Newtonian.

The non-Newtonian character of currently used VI improvers is well documented. An excellent discussion can be found in an SAE publication entitled, "The Relationship Between Engine Oil Viscosity and Engine Performance--Part III." The papers in this publication were presented at a 1978 SAE Congress and Exposition in Detroit on February 27 to March 3, 1978.

The reference of interest is Paper 780374:

"Temporary Viscosity Loss and its Relationship to Journal Bearing Performance," M.L. McMillan and C.K. Murphy, General Motors Research Labs.

This reference, and many others familiar to researchers in the field, illustrates how commercial polymeric VI improvers of molecular weights from 30,000 and up all show a temporary viscosity loss when subjected to shear rates of 10^5 to 10^6 sec⁻¹. The temporary shear loss is greater for any shear rate with higher molecular weight polymers. For instance, oils thickened to the same viscosity with polymethacrylates of 32,000; 157,000; and 275,000 molecular weight show percentage losses in viscosity at a 5 x 10^5 sec⁻¹ shear rate of 10, 22 and 32%, respectively.

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The shear rates developed in pistons and gears (equal to or greater than $10^6~{\rm sec}^{-1}$) is such that, depending on the polymeric thickener used, the apparent viscosity of the oils approaches that of the unthickened base fluids resulting in loss of hydrodynamic films. Since wear protection of moving parts has been correlated with oil viscosity, it is apparent that the wear characteristics of a lubricant can be downgraded as a result of temporary shear. The nearly Newtonian fluids of this invention maintain their viscosity under these use conditions and therefore afford more protection to and longer lifetime for the machinery being lubricated.

The currently used polymeric thickeners which show temporary (recoverable) shear are also subject to permanent shear. Extended use of polymeric thickeners leads to their mechanical breakdown with resultant loss in thickening power and decrease in VI. This is illustrated in Example 5. Paper 780372 (op. cit), "Polymer Stability in Engines" by W. Wunderlich and H. Jost discusses the relationship between polymer type and permanent shear. The multigrade lubricants of this invention are not as susceptible to mechanical shear.

This same paper also recognizes an often overlooked feature of high molecular weight polymeric VI improvers, i.e., their instability toward oxidation. Just as these polymers lose viscosity by shear they are also readily degraded by oxygen with the resultant breakdown of the polymer and decrease in viscosity index. The lubricating fluids of this invention suffer much less change in viscosity index upon oxidation.

As mentioned earlier, the small amount of temporary shear exhibited by the lubricants of this invention guarantees optimum viscosity for the protection of moving parts where high shear rates are encountered. The importance of this feature is widely recog-5 nized. In the past, SAE grading (e.g. SAE 30) relied only on a measurement of the viscosity of a fluid at 100°C under low shear conditions, despite the fact that in machinery such as a crankcase high temperatures and very high shear rates are encountered. This disparity has led to the adoption in Europe of a new grading system wherein viscosities for a certain grade are those measured at 150°C and 10⁶ sec⁻¹ shear rate. This more realistic approach is currently being considered in the United States. The advantages a Newtonian fluid brings to such a grading system are obvious to anyone skilled in the art. The viscosity of a Newtonian fluid can be directly extrapolated to 150°C under high shear conditions. A polymer thickened fluid, however, will invariably have a viscosity lower than the extrapolated value, frequently close to the base fluid itself. In order to attain a certain grade under high shear conditions, polymer thickened oils will require a more viscous base fluid. The use of thicker base fluids will produce higher viscosities at low temperature making it more difficult to meet the low temperature (5W for crankcase of 75W for gear oil) requirements for broadly multigraded oils.

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Stated another way, current high molecular weight VI improvers "artificially" improve the viscosity index, since realistic high temperature high shear measurements are not utilized in determining VI. Viscosity index is determined by low shear viscosity measurements at 40°C and 100°C. The nearly Newtonian lubricants of this invention not only produce high viscosity index multigraded fluids which stay "in grade", but the VI and multigrade rating are realistic since they are not very sensitive to shear.

While the specific compositions exemplified in this patent are fairly precise, it should be obvious to anyone skilled in the art to produce even further combinations within the scope of this invention which will be valuable lubricants.

The following examples illustrate some of the blends encompassed by our invention:

Example 1

This example illustrates the preparation of crankcase lubricants ysing HPI's of the kinematic viscosities shown:

		INGREDIENT	WT %
5	A.	$HPI (KV_{100} = 4030)$	9
		$\frac{\text{INGREDIENT}}{\text{HPI} (KV_{100} = 4030)}$ $PAO-4^{(1)}$.53
		Di-2-Ethylhexyl azelate	20
		Lubrizol 3940 ⁽²⁾	18
	в.	HPI (KV ₁₀₀ = 28,350)	6
10		PAO-4	56
		Di-2-Ethylhexyl azelate	20
		Lubrizol 3940	18
	С.	HPI (KV ₁₀₀ = 106,100)	, ,5
		PAO-4	57
15		Di-2-Ethylhexyl azelate	20
		Lubrizol 3940	18

The lubricants had the properties shown:

		$\frac{\text{KV}}{100}, \frac{\text{cSt}}{\text{cSt}}$	$\frac{KV}{40,cSt}$	<u>VI</u>	CCS, cP	SAE GRADE
	A.	13.4	77.6	177	2465 @ -20°C	10W-40
20	В.	10.1	54.3	184	2940 @ -30°C	0W-30
	c.	14.1	78.3	186	2610 @ -25°C	5W-40

- (1) 4 cSt polyalphaolefin
- (2) Additive package made by Lubrizol Corporation

Example 2

This example illustrates the preparation of lubricants using the HPI's of the kinematic viscosities shown in blends with only synthetic hydrocarbon.

		INGREDIENT	WT %
	-	- Crankcase -	
	A.	$HPI (KV_{100} = 4030)$	9
		PAO-4	79
5		Lubrizol 4856 ⁽¹⁾	12
	в.	HPI (KV ₁₀₀ = 28,350)	6
		PAO-4	82
		Lubrizol 4856	12
	:	- Automotive Gear Oil -	
10	c.	HPI (28,350)	13
		PAO-4	77
		Anglamol 6043 ⁽¹⁾	10

The lubricants had the properties shown:

		$\frac{\text{KV}}{100}$, $\frac{\text{cSt}}{\text{cSt}}$	$\frac{\text{KV}}{40}$, cSt	<u>VI</u>	Vis., cP	SAE GRADE
15	A.	13.6	81.6	171	3485 @ -25°C	5W-40
	В.	13.7	80.3	175	3315 @ -25°C	5W-40
	c.	25.2	164.0	188	47,300 @ -40°C	75W-140

(1) Additive package made by Lubrizol Corporation

Example 3

This example illustrates the preparation of crankcase lubricants using HPI's of the kinematic viscosities shown in blends with ester and additive package.

		INGREDIENT	WI %
	A.	$HPI (KV_{100} = 4030)$	9
25		Diisodecyl Adipate	79
		Lubrizol 4856	12
	В.	$HPI (KV_{100} = 28,350)$	7
		Diisodecyl Adipate	81
		Lubrizol 4856	12

The lubricants had the properties shown:

	$\frac{\text{KV}}{100}$, $\frac{\text{cSt}}{\text{cSt}}$	$\frac{KV}{40}$, cSt	<u>vi</u>	CCS, cP	SAE GRADE
A.	13.4	69.1	200	2245 @ -30°C	
В.	13.4	65.3	212	2180 @ -30°C	0W-40

5 Example 4 to the second of t

This example illustrates the preparation of automotive gear lubricants using HPI of the kinematic viscosity shown:

		INGREDIENT		WT %
	Α.	HPI $(KV_{100} = 28,350)$. 9 ,, :
10		PAO-4	en e	61 to
		Di-2-Ethylhexyl azelate		
		Anglamol 6043		10
	В.	HPI (KV ₁₀₀ = 28,350)		13
		PAO-4		57
15		Di-2-Ethylhexyl azelate		20
		Anglamol 6043		10

The lubricants had the properties shown:

		$\frac{\text{KV}}{100}$, $\frac{\text{cSt}}{\text{cSt}}$	$\frac{KV}{40}$, cSt	VI	Vis., cP	SAE GRADE
	A.		81.0	195	122,300 @ -55°C	
20	В.	27.0	166.5	200	54,650 @ -40°C	75W-140

CLAIMS:

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- 1. A lubricating composition characterised in that it comprises:
- (A) a hydrogenated polyisoprene having a viscosity of from greater than 3500 to 175,000 centistokes at 100°C, and
- (B) a synthetic hydrocarbon, ester or mixture thereof having a viscosity of from 1-10 centistokes at 100°C.
- 2. A composition according to claim 1 characterised in that it further comprises an additive package comprising at least one additive selected from dispersants oxidation inhibitors, corrosion inhibitors, anti-wear agents, pour point depressants, anti-rust agents, foam inhibitors and extreme pressure agents.