

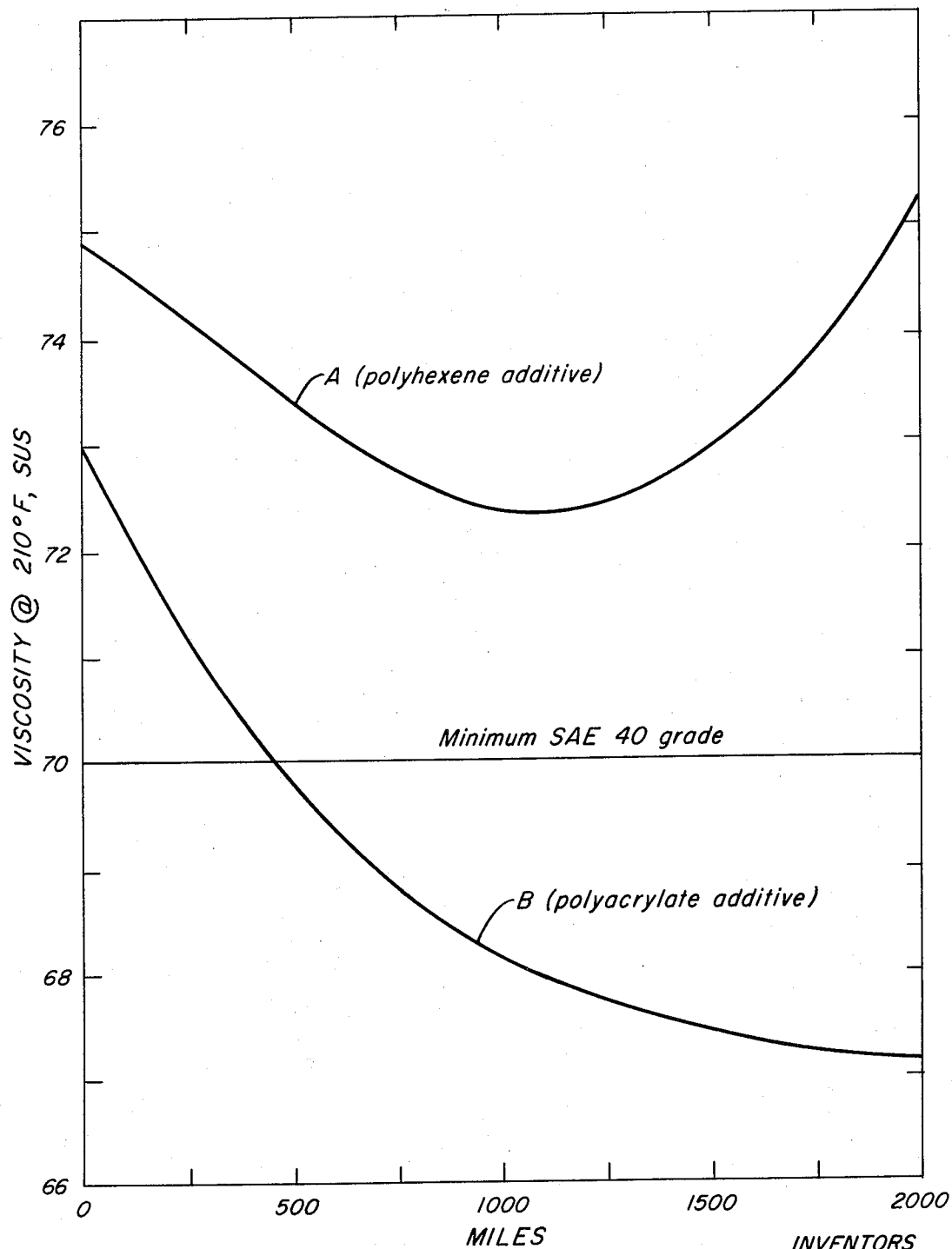
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SHEAR STABLE, MULTIVISCOSITY GRADE LUBRICATION OILS

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SHEAR STABLE, MULTIVISCOSITY GRADE LUBRICATING OILS

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ABSTRACT OF THE DISCLOSURE

Compounded lubricating oils having improved properties, including viscosity properties, are obtained by the use of higher alpha-olefin polymers of controlled molecular size and narrow molecular weight distribution. A shear stable, multiviscosity grade lubricating oil is produced by adding the alpha-olefin polymer to a lubricating oil.

This application is a continuation-in-part of our patent application Ser. No. 152,505, filed June 14, 1971, and now abandoned.

The present invention relates to novel, shear stable lubricating oil compositions comprising an alpha-olefin polymer of controlled molecular size and narrow molecular weight distribution. More particularly, the invention relates to a novel, shear stable lubricating oil composition containing the alpha-olefin polymer of controlled molecular size and narrow molecular weight distribution to significantly enhance the oil's viscosity grade as determined by established ASTM testing procedures.

In early days lubricating oils were selected for automobiles, trucks and similar vehicles on their ability to protect the engine's components against wear and surface damage during operation. Kerosene addition to the oil in winter was generally recommended to thin the oil for improved cold weather starting, even though this degraded the lubricating quality of the oil. Later when it was discovered that oils differed in their change in viscosity with changes in temperature, the existing oils were rated in this property, and selection of the more satisfactory oils could be made from the existing oils for cold weather use. This viscosity-temperature relationship of an oil, expressed as its viscosity index, was based on the viscosity temperature relationship of two known oils which were selected as standards. However, since no reliable method was known for determining the 0° F. viscosity of an oil, viscosities were obtained at substantially higher temperatures and its 0° F. viscosity was determined by extrapolation. Sometime after this, high molecular weight organic polymers were added to lubricating oils to decrease the temperature effect on the viscosity, that is to increase the viscosity index of the oils. It was later discovered that the viscosity index as derived from an ASTM D341 chart did not truly represent the cold weather cranking characteristics of the polymer-modified oil since the viscosity-temperature curve of the polymer modified oil did not faithfully respond to extrapolation. Thus it became known that viscosity index is not a reliable indicator of the properties desired in a polymer-modified oil.

Originally automotive-type lubricating oils were classified by operating temperature viscosity in accordance with SAE specification and assigned a grade number such as SAE 20. This system has proven to be inadequate because it does not provide an accurate indication of an unmodified oil's cold weather starting characteristics. Furthermore, this system is not a reliable in-use indi-

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cator of polymer-modified oils' quality and cannot be used in conjunction with viscosity index, which, as indicated, is not a reliable index for these modified oils.

Today's automotive-type lubricating oils are to an increasing extent marketed under multiviscosity grade designations, such as SAE 10W-30 grade, SAE 10W-40 grade and the like in accordance with SAE classification J300a. The first number in the grade designation is an indication of the cold temperature viscosity as determined at 0° F. by the cold cranking simulator procedure (ASTM D2602-70) and the second number is an indication of the high temperature viscosity as determined at 210° F. by a kinematic viscometer (ASTM D445). The high performance oils have a wider spread in the numbers with SAE 5W-50 being the broadest possible category in this SAE classification. Since adequately high viscosity is desired to protect the engine's bearing components during operation of the engine when heated to operating temperatures and adequately low cold weather viscosity is desired in the same oil to permit easy winter starting, the multiviscosity grade designation, which is the result of viscosity determinations on an oil at 0° F. and 210° F., is a more reliable indicator of the most important physical properties of the lubricating oil.

As pointed out, special polymeric viscosity modifiers have been incorporated into petroleum based lubricating oils or suggested for incorporation in these oils for the intended purpose of improving their inherent viscosity-temperature characteristics for automotive uses, as measured by viscosity index. These materials include polyisobutylenes, polyacrylates, polyalkylstyrenes, poly-alpha-olefins, ethylene-propylene copolymers and the like. As indicated, multiviscosity grading and the introduction of the cold cranking simulator procedure have now superseded viscosity index grading of automotive-type lubricating oils as being more reliable and meaningful, particularly with oils containing these high molecular weight, organic polymer viscosity modifiers. When a polymer additive is used in conjunction with multiviscosity grading, it is desired by the use of the polymer additive to produce a lubricating oil having the same 210° F. viscosity but a much lower 0° F. viscosity than a non-modified oil.

Although these polymeric materials can significantly improve the viscosity grade of a compounded oil prior to use, they are highly susceptible to mechanical shear in the engine. Thus instability to shear results in rapid in-use degradation of the 210° F. viscosity of the compounded oil. In a relatively short time these viscosity-modified oils fail to meet the labeled SAE specifications. Thus, a 10W-40 grade oil can quickly degrade to an SAE 10W-30 grade oil or even a 10W-20 grade oil as the viscosity modifier is fragmented by the shearing forces in the engine. Furthermore, the fragments resulting from the rupture of the polymer tend to become chemically active, particularly acidic in nature, leading to engine corrosion such as valve corrosion. This corrosion is particularly accentuated in the case of engines having positive crankcase ventilation since the corrosive products are retained within the crankcase rather than being vented to the atmosphere. So general is this in-use oil shear problem that essentially all commercially available viscosity-modified oils fail the labeled viscosity grade prior to the completion of the minimum miles of vehicle operation recommended by the manufacturer before oil change.

Another problem with these high molecular weight polymer-modified lubricating oils is related to the non-Newtonian character of these oils as a result of the polymer additives. These high molecular weight polymers introduce non-Newtonian characteristics to the compounded oil and can cause test failure in the cold cranking simu-

lator test (ASTM D2602-70) by causing the oil to leave the shear area and climb the rotor shaft of the cold cranking simulator. When this happens, it constitutes a test failure of the oil because it demonstrates the likelihood that the oil will leave the bearing surface in actual use. Thus, a lubricating oil which is properly viscosity modified by means of a high molecular weight polymeric additive must satisfy a number of requirements which are almost mutually exclusive, particularly for the higher performance multiviscosity oils. That is, the polymer modified oil must (a) produce a useful 210° F. SAE viscosity, (b) it must not severely degrade under mechanical shear as determined by the sonic shear test (ASTM D2603) or a 10-hour shear test in the L-38 test engine (MIL-L-46152), or shear in an engine to an extent that the oil will reduce in grade (SAE J300a) prior to the manufacturer-recommended miles before oil change, (c) it must permit easy engine starting as determined by the cold cranking simulator test (ASTM D2602-70), and (d) it must not leave the shear area and climb the rotor shaft of the cold cranking simulator during the test.

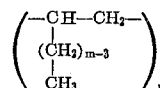
We have discovered that a high quality multiviscosity grade lubricating oil that meets all of these requirements can be prepared by adding to the oil a minor amount of a poly(1-olefin) of controlled molecular weight and molecular weight distribution. The resulting lubricating composition is shear stable for extended periods of operation and will therefore maintain its SAE multiviscosity grading. It exhibits good viscosity characteristics at 210° F. and good 0° F. viscosity as determined by the cold cranking simulator test. Furthermore, it will not leave the shear area and climb the cold cranking simulator rotor shaft. This lubricating oil when fully compounded as a motor oil meets required lube oil specifications and maintains these specifications over a long period of use.

The drawing is a graph comparing the viscosity stability of two oils in actual use under identical conditions. Both oils were compounded as SAE 10W-40 grade oils from the same base stock oil. Oil A contained 4.8 percent of our novel polyhexene while oil B, commercially sold for automotive use, contained 2.9 percent of a polyacrylate viscosity modifier. Both oils were identically tested in identical 1968 Chevrolet V-8 automobiles, each having an engine displacement of 307 cubic inches. A magnetic tape was first made by driving a third automobile over a city-suburban route for a total of 2,000 miles to provide a representative balance of driving conditions. The test automobiles containing oil A and oil B, respectively, were placed side-by-side on dynamometers in a temperature controlled test laboratory and their operation was controlled by the tape. A full simulation of the operation of the third automobile was effected in each test automobile including low speed and high speed driving, acceleration, braking, stopping, starting, hill climbing, ambient temperature, and the like, for the equivalent 2,000 miles. Periodic studies of the test oils, including viscosity, and engines were made. The graph shows that the 210° F. viscosity of oil A, the novel polyhexene modified oil, decreases about 2.5 SUS after 1,000 miles of operation and then increases the remaining 1,000 miles. On the other hand the 210° F. viscosity of oil B, the commercial polyacrylate-modified oil decreases continuously, about three SUS the first 500 miles and about six SUS for the full 2,000 miles. This test fully demonstrates the remarkable stability of our novel poly(1-hexene) modified oil in actual engine use.

The poly(1-olefin) which we add to the lubricating oil can be the polymer of any single straight or branched-chain alpha-olefin monomer from 1-pentene to 1-dodecene and preferably from 1-pentene to 1-decene. In addition, copolymers of any of the above alpha-olefins can be used as well as copolymers of the above with propylene, isobutene and 1-butene. The polymers formed from monomers larger than about 1-dodecene and those

smaller than about 1-pentene tend to crystallize out of oil at low temperatures and this property interferes with their utilization. For example, three and four carbon polyolefins are solids at low temperatures and cannot be used unless they are copolymerized with at least about 20 mol percent and preferably at least about 50 mol percent of a higher alpha-olefin such as 1-hexene. The most preferred monomer is 1-hexene either polymerized alone or copolymerized with one or more of 1-butene, 1-octene or 1-decene. The useful branched chain monomers include 4-methyl-1-pentene. The alpha-olefins of odd carbon numbers within the defined range are usable but are much less plentiful than the even-numbered carbon olefins.

The poly(1-olefins) can be described as a mixture of long chain molecules formed with a series of repeating units having the structural formula



in which m is the carbon number of the starting alpha-olefin and n is the number of repeating units in an individual molecule. When 1-hexene is the monomer, m is six. When 1-decene is the monomer, m is ten, etc. When a mixture of alpha-olefins is used, such as 1-hexene and 1-decene, the different alpha-olefins join together in the chain randomly in essentially the same molar ratio that each alpha-olefin occurs in the initial mixture. The polymer chains terminate with hydrogen or with a double bond.

The high quality, shear stable, multiviscosity grade lubricating oil is obtained under our invention when the molecular weight and the molecular weight distribution of the alpha-olefin polymer additive are controlled within critical limits. High molecular weight organic polymers generally contain a mixture of molecules occurring over a vast range in molecular weight. This includes polymers of alpha-olefins. A high molecular weight polymer can be defined in terms of the weights and distribution of the molecules forming it by means of its weight average molecular weight M_w , its number average molecular weight M_n and the distribution factor M_w/M_n . Values for these concepts, as represented by the specified symbols, provide a good indicator of the distribution of the molecules and molecular weights in the polymer and, as stated, are the basis for the definition of the useful alpha-olefin polymer additives described herein.

The classification SAE J300a specifies viscosity numbers for multiviscosity oils (together with the viscosity ranges defining each number) in the order listed as follows: 5W, 10W, 20W, 20, 30, 40 and 50. The viscosity numbers with the letter W are based upon the 0° F. viscosities and the numbers without a W are based upon the 210° F. viscosity. A multiviscosity numbered oil is one whose 0° F. and 210° F. viscosities fall within one of the prescribed viscosity ranges for both 0° F. and 210° F. Multiviscosity numbered oils having a difference in viscosity numbers as set out in the above list of less than three are either not desired or are readily obtainable and therefore do not require high molecular weight polymer additives. These oils are SAE 10W-20, 20W-20 and 20W-30 oils.

However, the novel poly(1-olefins) described herein are particularly useful for producing high quality, shear stable, multiviscosity numbered oils having a difference in the listed viscosity numbers of three or more and more particularly four or more. The greater the difference in the SAE multiviscosity numbers, the more difficult it is to compound the oil. Therefore, the greater the difference in the SAE multiviscosity numbers the more beneficial as well as necessary are these poly(1-olefins) for producing a satisfactory oil that can pass lube oil specifications. Those oils having a difference of three in their SAE multiviscosity numbers are SAE 5W-20, 10W-30 and 20W-40 oils; those with a difference of four in their multiviscosity

numbers are SAE 5W-30, 10W-40 and 20W-50 oils; those with a difference of five in their multiviscosity numbers are SAE 5W-40 and 10W-50 oils, leaving SAE 5W-50 as the only multiviscosity numbered oil having a difference of six in its multiviscosity numbers.

We have discovered that the high quality, shear stable, multiviscosity grade lubricating oil having a difference of at least three in the SAE multiviscosity number is obtained with poly(1-hexene) when its weight average molecular weight M_w is between about 50,000 and about 1,000,000; its number average molecular weight M_n is between about 4,000 and about 1,000,000, and its distribution factor M_w/M_n is between 1 and about 12 with M_w/M_n being between 1 and about 12 when M_w is about 50,000 and being between 1 and about 2 when M_w is about 1,000,000 with the upper range of the distribution factor proportionately increasing from about 2 to about 12 as the M_w decreases from about 1,000,000 to about 50,000.

When the novel poly(1-hexene) is used to produce a shear stable, multiviscosity numbered lubricating oil having a difference of at least four numbers in the SAE multiviscosity number, the weight average molecular weight M_w is between about 100,000 and about 1,000,000, the number average molecular weight M_n is between about 12,000 and about 1,000,000, and the distribution factor M_w/M_n is between 1 and about 9 with M_w/M_n being between 1 and about 9 when M_w is about 100,000 and between about 1 and 2 when M_w is about 1,000,000 with the upper range of the distribution factor M_w/M_n proportionately increasing from about 2 to about 9 as the weight average molecular weight M_w decreases from about 1,000,000 to about 100,000.

When the novel poly(1-hexene) is used to produce a shear stable, multiviscosity numbered lubricating oil having a difference of at least five numbers in its SAE multiviscosity number, the weight average molecular weight M_w is between about 150,000 and about 1,000,000, the number average molecular weight M_n is between about 35,000 and about 1,000,000 and the distribution factor M_w/M_n is between 1 and about 6 with M_w/M_n being between 1 and about 6 when M_w is about 150,000 and between about 1 and 2 when M_w is about 1,000,000 with the upper range of the distribution factor M_w/M_n proportionately increasing from about 2 to about 6 as the weight average molecular weight M_w decreases from about 1,000,000 to about 150,000.

When the novel poly(1-hexene) is used to produce a shear stable, multiviscosity numbered lubricating oil having a difference of six numbers in its SAE multiviscosity number, the weight average molecular weight M_w is between about 200,000 and about 1,000,000, the number average molecular weight M_n is between about 90,000 and about 1,000,000 and the distribution factor M_w/M_n is between 1 and about 3 with M_w/M_n being between 1 and about 3 when M_w is about 200,000 and between 1 and about 1.5 when M_w is about 1,000,000 with the upper range of the distribution factor M_w/M_n proportionately increasing from about 1.5 to about 3 as the weight average molecular weight M_w decreases from about 1,000,000 to about 200,000.

The lower the weight average molecular weight M_w of a poly(1-olefin) the more difficult it is to produce a multiviscosity numbered lubricating oil having a difference of at least three numbers in its SAE multiviscosity number, since the 0° F. viscosity value tends to be too high to pass the desired grade. However, the lower the weight average molecular weight of the polymer the more shear stable it becomes. On the other hand the higher the weight average molecular weight M_w , the more likely it is that the lubricating oil will leave the shear area and climb the shaft of the cold cranking simulator to fail the test. Furthermore, the lower the distribution factor at the same weight average molecular weight, the less increase in 0° F. viscosity for a given amount added to a specific base oil to get a desired 210° F. viscosity.

The critical distribution of molecular weights as indicated by M_w and M_n depends on the specific monomer used. Thus, the critical ranges for M_w and M_n varies directly with the ratio of the molecular weights of the alpha-olefin monomers or the average molecular weight of the alpha-olefin monomer mixtures. However, the range of critical distribution factors does not change regardless of the monomer or mixture of monomers from which they are made. For example, the molecular weight of 1-decene is 5/3 times the molecular weight of 1-hexene. Thus the critical ranges of weight average molecular weight and number average molecular weight for poly(1-decene) is 5/3 that of poly(1-hexene). These ranges are calculated for any poly(1-olefin) from the ranges specified above for poly(1-hexene) using the molecular weight ratio of the monomers. In like manner the critical distribution of molecular weights as indicated by M_w and M_n for a poly(1-olefin) made from a mixture of monomers containing 80 mol percent 1-hexene and 20 mol percent 1-decene is about 95.2/84 times the equivalent values for poly(1-hexene), since the average molecular weight of the mixture is about 95.2.

We have discovered, as the above values indicate, that the desirable properties in the poly(1-olefin) are directly related to the number of repeating units in the poly(1-olefin) regardless of the starting monomer or mixture that is used. Thus the molecular weight at the weight average molecular weight can be expressed by the equation $M_w = n_w M$ where n_w represents the calculated number of repeating units n at the weight average molecular weight and M is the molecular weight of the monomer, and the molecular weight at the number average molecular weight can be expressed by the equation $M_n = n_n M$ where n_n represents the calculated number of repeating units n at the number average molecular weight. The effect of the small terminal groups in these molecules is excluded from the equations since their effect is inconsequential in view of the large size of the molecules. Furthermore,

$$n_w = M_w / M = M_w / M_o$$

and $n_n = M_n / M = M_n / M_o$ where M_o represents the average molecular weight in a mixture of alpha-olefin monomers. Thus, as stated, the ranges for n_w and n_n are found to be constants regardless of the alpha-olefin monomer or mixture of alpha-olefin monomers that is used. From these equations it is apparent that $M_w / M_n = n_w / n_n$, verifying that the critical distribution factor herein is independent of the molecular weight of the starting alpha-olefins.

The addition to a base stock lubricating oil of only a minor amount of the poly(1-olefin) having weight and number average molecular weights, M_w and M_n , and a molecular weight distribution M_w/M_n within the limits specified herein, is required to produce a multiviscosity graded oil having a difference of at least three in the SAE multiviscosity number. For example, we have determined that the addition of a poly(1-hexene) as defined herein will produce desirable results in the lubricating oil when it constitutes from about 0.5 to about 10 weight percent of the oil, preferably between about 1.0 and about 6.0 percent and most preferably about 1.0 to about 3.5 percent of the oil. In general, the higher the weight average molecular weight M_w for a series of polymers made from the same monomer at equivalent distribution factors, the less polymer required for a given oil to produce equivalent results. Also, the lower the viscosity of the base oil, the more polymer additive that is necessary to produce the desired viscosity grade.

Furthermore, we have discovered that the effect of the poly(1-olefin) upon the lubricating oil is a function of the number of repeating units in the polymer and is therefore a function of the molecular weight of the monomer or average molecular weight of the mixture of monomers from which the polymer was made. Thus, we have deter-

mined that the weight percent of any polymer to be used in a lubricating oil can be determined by reference to the amounts of poly(1-hexene) used or required. The amount of the poly(1-olefin) to be used is obtained by multiplying the percent of poly(1-hexene) used or required by the ratio of the molecular weight of the alpha-olefin from which the poly(1-olefin) is made and the molecular weight of 1-hexene, M/M_6 or M_0/M_6 , wherein M is the molecular weight of the alpha-olefin, M_0 is the average molecular weight of the mixture of alpha-olefins and M_6 is the molecular weight of 1-hexene. Thus, if four percent of a particular poly(1-hexene) is required to produce a desired result in a lubricating oil then four percent times (M_{10}/M_6) or 6.67 percent of a poly(1-decene) having equivalent properties is required to produce a similar result. Since the amount of a poly(1-olefin) required to produce a given effect increases with an increase in the molecular weight of the starting alpha-olefin, other things being equal, it is generally preferred to use a poly(1-olefin) prepared from a lower alpha-olefin such as 1-hexene.

A fully compounded lubricating oil as prepared for automotive use contains many additives that must be used to meet various specifications or to overcome various deficiencies. One advantage of the poly(1-olefin) additive described herein for improvement of the viscosity characteristics is that it is fully compatible with and does not interfere with or detract from the functioning of other additives. Other additives which are added to the oils are preferably those which have demonstrated their effect by actual use and include pour point depressants, antioxidants, blooming agents, detergents, dispersants, rust inhibitors, anti-wear agents, anti-foam agents, extreme pressure agents, corrosion inhibitors, sludge inhibitors, metal deactivators, anti-scuffing agents, and the like. These additives are selected and used to meet desired specifications or overcome deficiencies in the base oil with respect to the intended use in accordance with procedures which are conventional and well known to those in the field of compounding lubricating oils.

The poly(1-olefins) of this invention which have the critical ranges of weight average molecular weights M_w , number of average molecular weights M_n and molecular weight distribution M_w/M_n are preferably made, by catalyzing the alpha-olefin or mixture of alpha-olefins using a Ziegler-Natta type catalyst. Either continuous, semi-continuous in which only the alpha-olefin is added during reaction, or batch polymerization can be used, provided that all conditions and proportions of chemical species present in the reaction mixture are properly correlated with each other to obtain the necessary molecular weights and distribution. Any Ziegler-Natta type catalyst can be used which is useful for the polymerization of propylene. Particularly useful are titanium and vanadium salts, primarily the chlorides, in conjunction with aluminum alkyls and alkyl chlorides. We have found that purple titanium trichloride together with aluminum triethyl constitutes an excellent catalyst. A catalyst containing from about one to about ten gram atoms of aluminum per gram atom of titanium is useful with a ratio of about 1.8 to about three being preferred. The reaction is suitably carried out using about 300 to about 6,000 grams of olefin per gram of catalyst and preferably from about 1,500 to about 3,000 grams of olefin per gram of catalyst.

Hydrogen or another suitable molecular chain length modifier such as zinc chloride, dialkyl zinc such as diethyl zinc and the like helps to direct the reaction to the desired molecular weight distribution. The partial pressure of hydrogen can broadly be between about 0.1 and about 150 p.s.i. and preferably between about 0.5 and about 25 for a continuous polymerization and between about 0.5 and about 10 for a semi-continuous or batch reaction. The temperature at which the polymerization reaction is conducted can suitably be between about 100° F. and

about 250° F. and preferably between about 220° F. and about 250° F.

A suitable solvent for the reaction mixture is desirable since the resulting polymer is highly viscous and can be substantially non-flowable at room temperature. Suitable solvents include hydrocarbon solvents such as butane, pentane, hexane, heptane, and the like, naphtha, gasoline fractions, kerosene, gas oil fractions, furnace oil fractions, light lubricating oils, heavy lubricating oils and the like. Organic hydrocarbon solvents such as benzene, toluene, the xylenes and the like and chlorinated hydrocarbon solvents are less preferred. The most preferred solvents are those light solvents which can be easily distilled from the product polymer or mineral oils which can be incorporated in the finished oil together with the polymer. Since a solvent is not necessary, it can be used in amounts from zero percent to about 75 percent, and when used it is preferably used in an amount of about 25 to about 50 percent.

Variables which affect the weight average molecular weight, the number average molecular weight or the molecular weight distribution include the reaction temperature, the partial pressure of hydrogen, the amount of catalyst, the titanium/aluminum ratio in the catalyst, the titanium compound used, the olefin to catalyst ratio, the olefin concentration and the like. Furthermore, it is essential that certain deleterious impurities, particularly those containing oxygen such as air, water and the like be excluded from the reactor if the poly(1-olefins) of the specified characteristics are to be obtained. Even minute amounts of oxygen significantly broaden the distribution. In contrast with this requirement, it is well known that it is advantageous to add minute amounts of oxygen or oxygen containing compound to the alpha-olefin polymerization reaction in order to substantially increase the yield of product per amount of catalyst used as well as the isotacticity. Therefore, minute amounts of oxygen are generally beneficial in alpha-olefin polymerizations.

The polymer made by the Ziegler-Natta type catalyst contains substantially completely a head-to-tail alignment of the repeating units in the molecules forming the polymer. We have found that the purple titanium trichloride makes an isotactic poly(1-olefin) which is superior to the atactic poly(1-olefin) made by the use of brown titanium trichloride as a lubricating oil additive hereunder. However, any suitable Ziegler-Natta catalyst system can be used provided that all conditions and variables are properly correlated to produce the necessary molecular weights and distribution.

We have found that the poly(1-olefin) having the critical relationship of molecular weights, M_w and M_n , and molecular weight distribution M_w/M_n is particularly useful for improving the viscosity characteristics of mineral lubricating oils. The expressions weight average molecular weight M_w , number average molecular weight M_n and molecular weight distribution M_w/M_n are well known and useful in the field of high molecular weight polymers. A useful description of these expressions is found in Chapter 1 of *The Structure of Polymers* by M. L. Miller, Reinhold Publishing Corporation (1966). In our work these expressions were determined by gel permeation chromatography using an instrument that was calibrated using known standard poly(1-hexene) fractions.

The following examples are set out to illustrate our invention and to provide a better understanding of its details and advantages. In the examples, except where specifically indicated, all reactants, solvents and catalysts were of ultra-high purity for the reaction. For example, the heptane solvent was purified to about 10 parts per billion oxygen.

EXAMPLE 1

A high molecular weight polymer of 1-hexene was made in a 0.5 liter stirred reactor by a continuous process. 1-hexene was introduced into the reactor at the rate of 900

ml. per hour. A catalyst was prepared by reacting a 1.3 weight percent solution of triethyl aluminum in heptane with a 0.17 weight percent solution of $(\text{TiCl}_3)_3 \cdot \text{AlCl}_3$ (obtained from Stauffer Chemical Company and designated as titanium trichloride AA-purple crystalline) in heptane in a stirred reactor at 100° F. under 10 p.s.i.g. of nitrogen. The catalyst stream contained a molar ratio of aluminum triethyl to titanium trichloride, TiCl_3 , of two to one and was introduced into the polymerization reactor at the rate of 900 ml. per hour. The reactor was maintained at 240° F. and was pressured with hydrogen to a pressure of 52 p.s.i.g. A product stream was continuously removed from the reactor at the rate of 1,500 ml. per hour which provided an average residence time for the 1-hexene in the reactor of 20 minutes.

The stream that was removed from the reactor was a mixture of poly(1-hexene), unreacted 1-hexene, heptane and trace amounts of the catalyst. The catalyst was killed by mixing a 10 percent aqueous sodium hydroxide solution with the hydrocarbon stream. The water solution was separated from the hydrocarbon solution by decantation. The hydrocarbon solution was then water-washed, dried and filtered. The hydrocarbon solution was next mixed with sufficient light neutral oil having a 210° F. viscosity of 4.15 centistokes (cs.) to form a 50 weight percent solution of poly(1-hexene) in the oil after the 1-hexene and heptane were stripped off to a flash point of 380° F.

The poly(1-hexene) was recovered in a 70 percent yield based on the 1-hexene fed to the reactor. It was determined to possess a weight average molecular weight M_w of 92,000, a number average molecular weight of 11,000 and a molecular weight distribution of 8.5.

This polyhexene-oil mixture, two different lube oil base stocks and an additive mixture were mixed together to form a compounded oil containing 4.9 weight percent polyhexene, 39.9 percent light neutral oil having a 210° F. viscosity of 4.15 cs., 45.9 percent of a medium neutral oil having a 210° F. viscosity of 5.32 cs. and 9.3 percent of the additive mixture. These additives were commercially used materials and were added to provide a fully compounded lube oil suitable for actual use so that the testing and evaluation would be fully meaningful. The mixture contained a dispersant, a detergent, a pour point depressant and an anti-foam agent.

The viscosity index of the light neutral oil was 98 and that of the medium neutral oil was 116. The 210° F. viscosity of the resulting fully compounded oil-polymer mixture was 14.3 cs. which classifies it as an SAE 40 grade oil. Its 100° F. viscosity was 94.0 cs. which gave it a viscosity index of 170 by ASTM D34-43. The oil-polymer mixture was found to have a 0° F. viscosity of 2,300 centipoises (cp.) by ASTM D2602-70 which classifies it as an SAE 10W-40 grade oil.

The pour point was found to be -25° F. The shear stability of the oil-polymer mixture was determined by ASTM D2603. It was found that the 210° F. viscosity was reduced to 13.20 cs. after 10 minutes representing a loss of 1.1 cs. An equivalent oil containing 2.9 percent of a commercially used polyacrylate viscosity modifier had a 2.4 cs. viscosity loss from 13.92 cs. to 11.54 cs. in the same test.

EXAMPLE 2

Another poly(1-hexene) material was made in the same manner as used in Example 1. A 1-hexene-heptane solution was introduced into the 0.5 liter reactor at the rate of 800 ml. per hour based on 1-hexene and 400 ml. per hour based on heptane. A catalyst was prepared by reacting a 2.7 weight percent solution of triethyl aluminum in heptane with a 0.5 weight percent slurry of $(\text{TiCl}_3)_3 \cdot \text{AlCl}_3$ in heptane in a stirred reactor at 120° F. under 8 p.s.i.g. of hydrogen. The catalyst stream contained a molar ratio of aluminum triethyl to titanium trichloride, TiCl_3 , of two to one and was introduced into the polymerization reactor at the rate of 1,200 ml. per hour. The reactor was

maintained at 240° F. and was pressured with hydrogen to a pressure of 40 p.s.i.g. A product stream was continuously removed from the reactor at the rate of 2,000 ml. per hour which provided an average residence time in the reactor for the 1-hexene of 15 minutes.

The product was recovered in 80 percent yield as a 40 percent solution of the poly(1-hexene) in the same light neutral oil as used in Example 1. It was determined to have a weight average molecular weight M_w of 120,000 and the distribution factor was determined to be 7.3 from its sonic shear and 0° F. viscosity data.

This poly(1-hexene)-oil mixture was mixed with the same light neutral and medium neutral base stocks as used in Example 1 as well as an additive mixture. The fully compounded lube oil mixture contained 4.8 weight percent of the poly(1-hexene), 37.2 percent of a light neutral oil having a 210° F. viscosity of 4.15 cs., 50.1 percent of a medium neutral oil having a 210° F. viscosity of 5.32 cs. and 7.9 percent of the additive mixture. This oil was compared in a road simulator test with an oil in actual commercial use containing a polyacrylate polymer for viscosity modification. This polyacrylate compounded lube oil contained 7.8 weight percent of a concentrate containing 37.2 weight percent of the polyacrylate in an oil solution, 15.0 percent of a medium neutral oil having a 210° F. viscosity of 7.0 cs., 69.8 percent of a medium neutral oil having a 210° F. viscosity of 5.32 cs. and 7.4 percent of a similar additive mixture.

Each oil was placed in one of two identical 1968 Chevrolet V-8 automobiles. They were operated side-by-side on dynamometers in a test laboratory and were controlled by a magnetic tape which was made by a car driven for 2,000 miles over a balanced city-suburban route. This test represented identical usage for 2,000 miles equally simulating acceleration, braking, various constant speeds, air temperature, hill climbing and the like. The oils were tested at intervals. Table I lists the comparative viscosity data of these two oils that resulted from this engine shear test:

TABLE I

	Miles				
	0	250	500	1,000	2,000
Poly(1-hexene): Viscosity at—					
100° F. SUS	432	451	431	425	463
210° F. SUS ^a	74.9	75.4	73.4	72.3	75.2
Polyacrylate: Viscosity at—					
100° F. SUS	389	368	368	359	360
210° F. SUS ^b	73.0	70.4	70.4	68.1	67.1

^a Sonic shear test, ASTM D2603 gave 4.0 SUS loss.

^b Sonic shear test, ASTM D2603 gave 6.2 SUS loss.

These results are plotted in the drawing. It is observed that the commercial, polyacrylate-modified oil fails specification due to the continuous decrease in viscosity during the entire 2,000 miles of the test. In surprising contrast with this, the polyhexene-modified oil maintains its viscosity grade and even shows an unexpected increase in its 210° F. viscosity after about 1,000 miles of actual engine use.

EXAMPLE 3

A high molecular weight poly(1-hexene) was made in a 30 gallon stirred reactor. While a hydrogen blanket was maintained in the reactor, 65 pounds of a light neutral oil, one pound of a six weight percent solution of triethyl aluminum in a 22 to 28 carbon alpha-olefin wax and 0.05 pound of $(\text{TiCl}_3)_3 \cdot \text{AlCl}_3$ were added to the reactor. After the reactor was heated to 2400° F. under a constant blanket of hydrogen at a pressure of 19 p.s.i.g., 1-hexene was pumped into the reactor at 1.35 pounds per minute for 75 minutes. The mixture was stirred at the same temperature and hydrogen pressure for an additional hour. The contents were removed from the reactor and quenched with 20 percent sodium hydroxide, washed, dried, filtered and stripped to a 380° F. flash point. The yield of poly(1-hexene) was 95 percent based on 1-hexene

charged to the reactor. The product was 38.6 percent poly(1-hexene) in the light neutral oil having a viscosity of 39.9 SUS at 210° F. It was used to make a series of fully formulated motor oils as set out in Table II.

TABLE II

Base oil 210° F., SUS	Poly(1- hexene), wt. percent	Finished oil 210° F., SUS	Shear loss ^a SUS	CCS, ^b cp.	SAE grade after shear
37-----	3.1	77	7	1,080	5W-40
40-----	3.3	95	10	2,100	10W-50
44-----	1.7	76	6	2,150	10W-40

^a Loss on shear after 10 minute exposure in sonic shear test, ASTM D2603.

^b Cold cranking simulator.

EXAMPLE 4

A 50 gallon glass-lined reactor was charged with 178.4 pounds of n-heptane, then sealed, evacuated and purged with nitrogen. The reactor was kept sealed and 542.3 grams of (TiCl₃)₃·AlCl₃ was introduced followed by 768.9 grams of triethyl aluminum as a 30 percent solution in n-heptane. After the reactor atmosphere was purged with hydrogen and heated to 140° F. under 10 p.s.i.g. of hydrogen, an additional 1,966 grams of a 30 percent solution of triethyl aluminum in n-heptane was charged. After standing for one hour at these conditions, 54.6 pounds of

oil. The viscosity index was calculated as 137 by ASTM D567 and 166 by ASTM D2270. After 10 minutes in the ultrasonic oscillator (ASTM D2603) the viscosity loss was 0.86 centistoke at 210° F. and 6.7 centistokes at 100° F. giving a viscosity index loss of 1 and 3 by D567 and D2270, respectively. The oil remained an SAE 10W-40 grade oil after the sonic shear test.

EXAMPLES 5 TO 28

A series of 1-hexene polymers were made by the general procedures of Examples 1 or 3 but with variations in the conditions under which the polymer was made in order to obtain polymers with different average molecular weights and molecular weight distributions so that they could be evaluated as viscosity modifiers in mineral oil formulations. The results of these evaluations are set forth in Table III. The 210° F. viscosities in Table III were determined according to ASTM D445 and the 0° F. viscosities by the cold cranking simulator (CCS) in accordance with ASTM D2602-70. The loss on shear was determined by ASTM D2603. Where it is indicated that the oil failed the CCS viscosity test, failure resulted from the formulated oil leaving the test section and climbing the rotor shaft of the cold cranking simulator. Those polymers made with a distribution factor of 1.5 included a fractionation step.

TABLE III

Example	SAE grade	Polymer, wt. percent	Base oil, cs. at 210° F.	Oil mixture, cs. at 210° F.	Shear loss, cs.	CCS, cp.	M _w	M _n	M _w /M _n
5-----	5W-20	1.5	3.2	5.7	0.75	550	190,000	23,000	8.3
6-----	10W-30	3.0	5.3	10.6	0.70	2,100	37,000	10,000	3.7
7-----	10W-30	3.0	5.3	10.1	0.50	2,250	76,000	9,000	8.5
8-----	10W-30	3.0	4.15	10.4	0.80	1,350	155,000	18,500	8.4
9-----	10W-30	2.5	4.15	11.2	1.60	1,410	190,000	23,000	8.3
10-----	10W-30	4.0	4.15	11.3	0.60	1,675	61,000	17,000	3.6
11-----	20W-40	2.7	6.00	14.1	1.15	4,360	155,000	18,500	8.4
12-----	20W-40	2.2	6.00	14.2	1.20	4,200	190,000	23,000	8.3
13-----	5W-30	3.3	3.2	11.0	1.4	840	190,000	23,000	8.3
14-----	10W-40	1.5	5.3	16.3	2.1	2,000	610,000	170,000	3.6
15-----	-----	2.5	5.3	15.0	2.3	Failed	260,000	19,000	13.7
16-----	20W-40	5.0	5.3	13.4	0.6	2,570	76,000	9,000	8.5
17-----	10W-40	7.0	4.2	14.2	0.6	2,245	76,000	9,000	8.5
18-----	10W-40	4.6	4.2	14.0	1.1	1,775	155,000	18,500	8.4
19-----	10W-40	3.9	5.3	14.2	1.2	2,250	155,000	18,500	8.4
20-----	10W-40	3.8	4.2	14.9	2.0	1,720	190,000	23,000	8.3
21-----	10W-40	2.8	5.3	15.1	1.7	2,170	190,000	23,000	8.3
22-----	20W-50	4.0	6.0	18.1	1.3	5,750	155,000	18,500	8.4
23-----	20W-50	3.4	6.0	18.2	1.4	5,660	190,000	23,000	8.3
24-----	5W-40	4.5	3.2	14.7	1.8	1,065	190,000	23,000	8.3
25-----	10W-50	4.1	5.0	18.5	1.9	2,300	190,000	23,000	8.3
26-----	10W-50	4.0	5.3	18.3	1.7	2,400	175,000	18,000	9.7
27-----	10W-50	2.0	5.3	21.5	2.1	2,160	610,000	170,000	3.6
28-----	10W-50	4.0	4.2	24.0	1.7	2,125	270,000	75,000	3.6

1-decene was charged to the reactor and the temperature was raised to 146° F. at 10 p.s.i.g. of hydrogen.

After standing for one hour at these conditions, one liter of 30 percent aqueous sodium hydroxide was added to quench the catalyst. A portion of the hydrocarbon phase was separated from the aqueous phase, washed, dried and diluted with 7.35 pounds of light neutral oil having a 210° F. viscosity of 4.15 cs. and stripped of volatiles. The resulting concentrate contained 55 weight percent of the poly(1-decene) and 45 percent of the light neutral oil. The poly(1-decene) was determined to have a weight average molecular weight M_w of 270,000, a number average molecular weight M_n of 37,000, and a molecular weight distribution M_w/M_n of 7.3.

A compounded oil was formulated which contained 9.5 weight percent of this concentrate (about 5.23 percent polydecene), 82.8 percent of a medium neutral base oil having a 210° F. viscosity of 5.32 centistokes and about 7.7 percent of a dispersant, pour depressant and antifoam additive mixture. This oil possessed a 210° F. viscosity of 13.82 centistokes, a 100° F. viscosity of 92.2 centistokes and a 0° F. viscosity of 2,050 centipoises by the cold cranking simulator. This oil was an SAE 10W-40 grade

EXAMPLES 29 AND 30

In Table IV the results of adding a polyisobutylene, which is commercially used for modifying the viscosity characteristics of oils, to a light neutral oil having a 210° F. viscosity of 4.15 cs. are set out.

TABLE IV

Example	Additive	Amount, wt. percent	Viscosity		Loss on shear
			210° F., cs.	CCS, cp.	
29-----	Polyisobutylene--	8.5	13.84	Failed--	0.7
30-----	do-----	9.3	15.03	do-----	0.8

It is noted in Table IV that the polyisobutylene mixture fails the cold cranking simulator or 0° F. test by leaving the test area and climbing the rotor shaft.

It is to be understood that the above disclosure is by way of specific example and that numerous modifications and variations are available to those of ordinary skill in the art without departing from the true spirit and scope of our invention. The novel polymers and method for making them are covered in our application for letters patent filed on even date herewith.

We claim:

1. A shear stable, multiviscosity grade lubricating oil composition comprising mineral oil, and as a viscosity improver a minor amount of an alpha-olefin polymer produced from one alpha-olefin monomer having from five to 12 carbon atoms or produced from a mixture of alpha-olefin monomers having from three to 12 carbon atoms with monomers having from five to 12 carbon atoms comprising at least about 20 mol percent of the mixture and with substantially all of the alternate carbon atoms in each linear polymer chain having dependent therefrom the same alkyl group having from three to ten carbon atoms when said linear alpha-olefin polymer is produced from one alpha-olefin monomer or randomly different alkyl groups having from one to 10 carbon atoms when said linear alpha-olefin polymer is produced from said mixture of alpha-olefin monomers.

said alpha-olefin polymer characterized by a weight average molecular weight M_w between about 50,000 (M/84) and about 1,000,000 (M/84), a number average molecular weight M_n between about 4,000 (M/84) and about 1,000,000 (M/84) where M is the molecular weight of the alpha-olefin monomer or average molecular weight of the mixture of alpha-olefin monomers.

a distribution factor M_w/M_n of between one and about 12, the upper limit of said distribution factor being about 12 when M_w is about 50,000 (M/84) and about two when M_w is about 1,000,000 (M/84) with the upper limit of said distribution factor proportionately decreasing from about 12 to about two as M_w increases from about 50,000 (M/84) to about 1,000,000 (M/84), and

said lubricating oil composition comprising from about 0.5 (M/84) weight percent to about 10 (M/84) percent of said alpha-olefin polymer in an amount sufficient to provide a multiviscosity grade difference of at least three in SAE viscosity classification J300a.

2. A shear stable, multiviscosity grade lubricating oil composition in accordance with claim 1 in which said alpha-olefin polymer is characterized by a weight average molecular weight M_w between about 100,000 (M/84) and about 1,000,000 (M/84), a number average molecular weight M_n between about 12,000 (M/84) and about 1,000,000 (M/84), and a distribution factor M_w/M_n of between one and about nine, the upper limit of said distribution factor being about nine when M_w is about 100,000 (M/84) and about two when M_w is about 1,000,000 (M/84) with the upper limit of said distribution factor proportionately decreasing from about nine to about two as M_w increases from about 100,000 (M/84) to about 1,000,000 (M/84), and said alpha-olefin polymer present in an amount sufficient to provide a multiviscosity grade difference of at least four in accordance with SAE viscosity classification J300a.

3. A shear stable, multiviscosity grade lubricating oil composition in accordance with claim 1 in which said alpha-olefin polymer is characterized by a weight average molecular weight M_w between about 150,000 (M/84) and about 1,000,000 (M/84), a number average molecular weight M_n between about 35,000 (M/84) and about 1,000,000 (M/84), and a distribution factor M_w/M_n of between one and about six, the upper limit of said distribution factor being about six when M_w is about 150,000 (M/84) and about two when M_w is about 1,000,000 (M/84) with the upper limit of said distribution factor proportionately decreasing from about six to about two as M_w increases from about 150,000 (M/84) to about 1,000,000 (M/84), and said alpha-olefin polymer present in an amount sufficient to provide a multiviscosity grade difference of at least five in accordance with SAE viscosity classification J300a.

4. A shear stable, multiviscosity grade lubricating oil composition in accordance with claim 1 in which said

alpha-olefin polymer is characterized by a weight average molecular weight M_w between about 200,000 (M/84) and about 1,000,000 (M/84), a number average molecular weight M_n between about 90,000 (M/84) and about 1,000,000 (M/84), and a distribution factor M_w/M_n of between one and about three, the upper limit of said distribution factor being about three when M_w is about 200,000 (M/84) and about 1.5 when M_w is about 1,000,000 (M/84) with the upper limit of said distribution factor proportionately decreasing from about three to about 1.5 as M_w increases from about 200,000 (M/84) to about 1,000,000 (M/84), and said alpha-olefin present in an amount sufficient to provide a multiviscosity grade difference of at least six in accordance with SAE viscosity classification J300a.

5. A shear stable, multiviscosity grade lubricating oil composition in accordance with claim 1 in which each alternate carbon atom of the alpha-olefin polymer has dependent therefrom an alkyl group having from two to eight carbon atoms.

6. A shear stable, multiviscosity grade lubricating oil composition in accordance with claim 5 in which said lubricating oil composition comprises from about 1.0 (M/84) percent to about 6.0 (M/84) percent of said alpha-olefin polymer.

7. A shear stable, multiviscosity grade lubricating oil composition in accordance with claim 1 in which the said linear alpha-olefin polymer has a substantially isotactic structure.

8. A shear stable, multiviscosity grade lubricating oil composition in accordance with claim 1 in which each alternate carbon atom of the alpha-olefin polymer has dependent therefrom an alkyl group having four carbon atoms.

9. A shear stable, multiviscosity grade lubricating oil composition in accordance with claim 8 in which said lubricating oil composition comprises from about 1.0 percent to about 3.5 percent of said alpha-olefin polymer.

10. A shear stable, multiviscosity grade lubricating oil composition in accordance with claim 9 in which the said linear alpha-olefin polymer has a substantially isotactic structure.

11. A shear stable, multiviscosity grade lubricating oil composition in accordance with claim 2 in which each alternate carbon atom of the alpha-olefin polymer has dependent therefrom an alkyl group having from two to eight carbon atoms.

12. A shear stable, multiviscosity grade lubricating oil composition in accordance with claim 11 in which said lubricating oil composition comprises from about 1.0 (M/84) percent to about 6.0 (M/84) percent of said alpha-olefin polymer.

13. A shear stable, multiviscosity grade lubricating oil composition in accordance with claim 12 in which each alternate carbon atom of the alpha-olefin polymer has dependent therefrom an alkyl group having four carbon atoms.

14. A shear stable, multiviscosity grade lubricating oil composition in accordance with claim 13 in which said lubricating oil composition comprises from about 1.0 percent to about 3.5 percent of said alpha-olefin polymer.

15. A shear stable, multiviscosity grade lubricating oil composition in accordance with claim 14 in which the said linear alpha-olefin polymer has a substantially isotactic structure.

16. A shear stable, multiviscosity grade lubricating oil in accordance with claim 3 in which each alternate carbon atom of the alpha-olefin polymer has dependent therefrom an alkyl group having from two to eight carbon atoms.

17. A shear stable, multiviscosity grade lubricating oil in accordance with claim 16 in which each alternate carbon atom of the alpha-olefin polymer has dependent therefrom an alkyl group having four carbon atoms.

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18. A shear stable, multiviscosity grade lubricating oil in accordance with claim 17 in which said lubricating oil composition comprises from about 1.0 percent to about 3.5 percent of said alpha-olefin polymer.

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