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(54) ETHYLENE/ALPHA-OLEFIN POLYMERS AND LUBRICATING OILS CONTAINING THEM

(71) We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with certain polymers prepared from ethylene and at least one other alpha-olefin, and lubricating oils containing them, and is an improvement in our modification of the invention of patent application 60785/70 (Serial No. 1,239,083) which is a divisional of patent application 31921/68 (Serial No. 1,239,082).

An important property of a lubricant composition is the rate at which its viscosity changes as a function of temperature. The relationship between the viscosity and temperature is commonly expressed in the art as the viscosity index (V.I.). Lubricant compositions which change little in viscosity with variations in temperature have a greater viscosity index than do compositions whose viscosity is materially affected by changes in temperature. In this connection, the viscosity index of a lubricant composition has in the past been determined by measuring the viscosity of the oil at 210°F. and 100°F. and extrapolating to 0°F. The measured 210°F. viscosity and the extrapolated 0°F. viscosity are used to calculate the viscosity index of the oil.

In the case of motor oils which contain polymeric viscosity index improvers, the extrapolated 0°F. viscosity is usually much lower than its measured value since motor oils containing polymeric additives are non-New-

tonian. Many of the well-known viscosity index improvers such as polyisobutylene and polymethacrylates, impart a high viscosity index (based on extrapolated 0°F. viscosity) to an oil but in actual practice these additives are found to thicken the motor oil to an undesirably large degree at 0°F. It is now recognized that viscosity index alone is not a true measure of an oil's effectiveness in facilitating cold starting and minimizing friction and engine wear. Accordingly, the direct determination of the low temperature (0°F.) viscosity of a motor oil under engine conditions by use of a suitable device such as the engine viscosity simulator disclosed in U.S. Patent No. 3,350,922, is necessary in order to evaluate the viscosity characteristics imparted by a viscosity index improver.

Beside the attainment of V.I. improvement and good low temperature viscosity characteristics, consideration must also be given to the solubility of the polymer additive in the base composition, as well as the additive stability against breakdown under shear stresses encountered in its application. In the synthesis of polymeric V.I. agents to date, it has generally been found that solubility and shear stability are inversely proportional to the molecular weight of the polymer. Since the greatest V.I. effect has been obtained from polymers of the highest molecular weight, effectiveness has, disadvantageously, been sacrificed in order to ensure proper stability in respect to resistance against shear stresses and to attain the desired solubility of the additives. Thus, the V.I. improving characteristic of additives has been undesirably restricted by limitation of one of the aforementioned characteristics. Another feature of V.I. improvers is the amount of additive necessarily utilized in order

to attain the desired V.I. improvement. This measure of effectiveness of an additive, as reflected by the amounts utilized, may be referred to as the thickening potency of the additive. It is readily apparent, therefore, that in addition to effective V.I. improvement with accompanying shear stability, solubility, etc., it is highly desirable to prepare a V.I. improver which has a thickening potency such that smaller amounts of additive as compared to amounts conventionally employed can be utilized to attain the desired improvements.

Many of the commercialized viscosity index improvers such as the polyisobutenes, polymethacrylates, fumaric acid ester copolymers, polyacrylates and polyalkylstyrenes are deficient in that they thicken motor oils to an undesirably large degree at low temperatures and/or exhibit substantial shear breakdown and/or are deficient in one or more of the other aforementioned viscosity index improver characteristics.

Other polymers suggested as useful oil additives include ethylene/alpha-olefin polymers such as ethylene-propylene copolymers. In general, these oil additives are low molecular weight ethylene/alpha-olefin copolymers which are used to depress the pour point of heating oils. Heretofore, however ethylene/alpha-olefin polymers have not found wide acceptance as lubricant viscosity index improvers. These ethylene based polymers, particularly copolymers of ethylene and propylene, would not appear to be acceptable commercial viscosity index improvers since they would be expected to produce hazy oils and exhibit poor low temperature solubility since they do not contain the oil-solubilizing long alkyl side chains possessed by conventional viscosity index improvers. Indeed, as discussed more fully hereinafter, the production of relatively haze-free oil compositions containing ethylene-propylene copolymers has been found to be extremely difficult. Of course, a motor oil containing a significant amount of visual haze is unacceptable from the view point of consumer appeal and poor performance due to the presence of oil-insolubles which could cause problems such as filter plugging, oil screen plugging and polymer drop out as sludge especially in centrifugal pumps.

In accordance with this invention, an essentially haze-free oil composition useful as a lubricant contains as a V.I. improver an oil-soluble polymer comprising ethylene and a C_3 to C_{18} alpha-olefin, said polymer being characterized by the following combination of parameters: (a) an average ethylene content within the range of between 60 and 80 mole %, wherein said polymer contains no more than 1.3% by weight of a polymer fraction which is insoluble in normal decane at 45°C.; (b) a degree of crystallinity less than 25%; (c) an M_w/M_n (i.e. weight average molecular weight/number average molecular

weight) ratio less than 4.0; and (d) a viscosity average molecular weight of between 10,000 and 200,000. The polymers of the invention besides exhibiting low haze when added to lubricating oils, are found to have the unusual combination of properties including excellent V.I. improving characteristics, high thickening potency and excellent shear stability. Such combination of properties render the polymers of this invention especially useful in lubricating oils of both the mineral and synthetic type.

The alpha-olefins which are of interest and used in the preparation of the V.I. improvers of this invention are those monomers containing from 3 to 18 carbon atoms per molecule. The alpha-olefins may be linear or branched where the branching occurs three or more carbon atoms from the double bond, and, while a single olefin is preferable, mixtures of these C_3 to C_{18} olefins may be employed. It is most preferred, however, that the ethylene monomer be copolymerized with propylene. Suitable examples of C_3 to C_{18} alpha-olefins include, among others, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 4-methyl-1-pentene, 4-methyl-1-hexene, 5-methyl-1-hexene, 4,4-dimethyl-1-pentene, 4-methyl-1-heptene, 5-methyl-1-heptene, 6-methyl-1-heptene, 4,4-dimethyl-1-hexene, 5,6,5-trimethyl-1-heptene and mixtures thereof.

While ethylene-propylene copolymers are preferred for the purposes of this invention, when propylene is employed as the comonomer, i.e., with ethylene, it is also possible to use a third monomer which may be one or more of the aforescribed C_4 to C_{18} alpha-olefins and/or C_6 to C_{18} non-conjugated diolefins. These unsaturated monomers are also preferably linear, but may be branched where the branching occurs three or more carbon atoms from the double bond, and, while a single olefinic monomer is preferable, mixtures of these olefinic monomers may also be employed. The amount of the third monomer contained in the polymer may range from 0 to about 10 mole %, e.g. 0.5 to 5.0 mole %.

The diolefins which are useful for copolymerization with ethylene and propylene include the bicyclic, alicyclic or aliphatic nonconjugated diolefins containing from 6 to 28 carbon atoms, preferably from 6 to 12 carbon atoms. Examples of suitable monomers are 1,5-cyclooctadiene, 1,4-hexadiene, dicyclopentadiene, methylene-norbornene, 5-vinyl-2-norbornene, 1,5-cyclodecadiene, 2,4-dimethyl-2,7-octadiene, 3(2-methyl-1-propenyl) cyclopentene, and 1,5-octadecadiene.

The polymers of the invention contain from 60 to 80 mole % of ethylene and 20 to 40 mole % of the aforescribed C_3 to C_{18} alpha-olefin. It is preferred, however, that the polymer contain from 72 to 80 mole % ethylene

and 20 to 28 mole % C_3 - C_{11} alpha-olefin, preferably propylene. The preferred compositional range is based upon the finding that polymers containing more than 80 mole % ethylene contribute substantial amounts of haze to oils when blended therewith while polymers containing less than about 72 mole % ethylene will give a greater increase in the low temperature (0°F.) viscosity of an oil containing same under engine cranking conditions.

As indicated above, in order for a material to be a commercially acceptable motor oil additive, it must produce an essentially haze-free oil composition when incorporated therein. The aforescribed polymer of this invention will produce an oil composition having good haze properties well within acceptable limits. The haze-forming tendencies of ethylene-alpha-olefin Ziegler polymers, especially ethylene-propylene copolymers, is related to their compositional distribution and molecular weight distribution. This is particularly true in the case of ethylene-propylene copolymers. It has been found that the polymers having more than 1.3 wt. % of a fraction which is insoluble in normal decane at 45°C. will produce significant amounts of haze in oils. Accordingly, the polymer of the invention will not contain more than 1.3 wt. % of this insoluble fraction. Preferably, the polymer of the invention will contain less than 0.5 wt. %, more preferably essentially none of a polymer fraction which is insoluble in normal decane at 45°C. The presence of this undesired normal decane-insoluble fraction indicates that the compositional distribution (and in some instances also the molecular weight distribution) of the polymer is relatively broad and that the polymers contains a fraction which has a high ethylene content, i.e. an ethylene content greater than the average ethylene content of the total polymer. It is the high ethylene fraction which is insoluble in normal decane at 45°C. Generally, the normal decane-insoluble fraction will have an ethylene content above 82 mole %. In this connection, a precise method of determining the amount of polymer fraction which is insoluble in normal decane at 45°C. is given hereinafter in Example 1 where a normal decane solution containing a specified amount of polymer (i.e., 0.758 gram of polymer in 100 millilitres of normal decane) is subjected to defined conditions of separation.

The ethylene content of the aforescribed polymers was measured in the following manner. A series of copolymer standards were prepared using C_2 labelled ethylene. The ethylene content of these polymers was conventionally measured by a radioactive counting method. The polymers were burnt to CO_2 which was trapped in alcoholic ethanolamine and counted in solution. A sample of polyethylene was also synthesized and counted to determine the acti-

vity of the starting monomer. An infrared method was then standardized using the samples of known ethylene content. The absorbance ratio at 8.6 microns (methyl groups) and 13.9 microns (methylene sequences) was determined on a Beckman 5A Infrared Spectrometer and correlated with the C_2 ethylene values.

The ethylene-alpha-olefin polymers of this invention will have a viscosity average molecular weight (M_v) of 10,000 to 200,000, preferably 30,000 to 100,000. Unless otherwise specified, the term "molecular weight" as used herein means molecular weight based on viscosity measurement. The molecular weights indicated herein and in the claims thereof were determined by viscosity measurements in decalin at 135°C. and calculated by the formula

$$\eta = (K' \times 10^{-4}) M_v^{0.74}$$

in which η represents intrinsic viscosity and K' varies from 2.22 for a polymer containing no ethylene, i.e., a homopolymer of propylene, to 5.86 for a homopolymer of ethylene. In this connection, $K' = 1.15K$ wherein K relates η and M_v according to the method outlined by G. Moraglio in *Chimica 1' Industria* 41, 984 (1959).

The polymers of this invention have a degree of crystallinity up to 25%, preferably 3 to 18%, and a surprisingly narrow molecular weight distribution. The surprisingly narrow molecular weight distribution of the polymers of this invention is evidenced by the fact that the number average molecular weight, M_n , and the weight-average molecular weight, M_w , of the ethylene-alpha-olefin polymers are similar in value. As is generally known, only when there is one molecular species, all molecules of which have the same molecular weight, will the values of M_n and M_w be equal. The narrow molecular weight distribution of the polymers of this invention may be characterized by the ratio M_w/M_n wherein said ratio is less than 4.0, preferably less than 2.6, e.g., 2.2.

The determination of the ratio M_w/M_n was made by the gel permeation chromatography (GPC) technique. The procedure used was as follows: Four polystyrene gel separation columns containing average gel pore sizes of 10^6 , 10^5 , 10^4 and 10^3 Å, respectively, were connected in series for the fractionation of the polymer. The solvent employed was trichlorobenzene, and the separations were conducted at 135°C. using a flow rate of 1 ml./min. The samples were introduced into the system as 0.5 wt. % solutions using an injection time of 60 seconds. A correlation between elution volume (expressed as "counts" with one count equal to 5 ml.) and molecular weight relevant to these operating conditions was obtained from the peak elution

volumes of a series of narrow polystyrene fractions of known molecular weight. The calibration standards obtained from Pressure Chemical Co., Pittsburgh, Pa. covered the molecular weight range from 4,800 to 2,145,000. The standard molecular weights were converted to equivalent chain length values ($\text{\AA}$) and the correlation between equivalent chain length and count number (elution volume) was employed in the analysis of ethylene-alpha-olefin, e.g., propylene, distribution curves.

The treatment of the raw GPC data (in the form of continuously plotted curves) for the ethylene-alpha-olefin samples essentially followed classical molecular weight distribution techniques. For a given sample the height of the distribution curve above the base line was measured (in any convenient units) at regular elution volume intervals over the entire distribution. The interval employed was $\frac{1}{2}$ count ($2\frac{1}{2}$ ml.). The height at a given count was taken as a measure of the weight fraction of the sample having an equivalent chain length corresponding to that particular elution volume. The measured heights were then normalized to yield the corresponding weight fractions which were used to compute the number average equivalent chain length and the weight average equivalent chain length.

With regard to the degree of crystallinity of the copolymers utilized in the present invention, it was found that two independent techniques employed to determine same led to unexpectedly good experimental agreement. The two methods utilized were x-ray diffraction and differential thermal analysis.

Accordingly, differential thermal analysis and X-ray diffraction patterns indicate a degree of crystallinity up to 25%. It is preferred, however, that the degree of crystallinity be within the range of from about 3 to about 18%.

The polymers of this invention are prepared by employing Ziegler polymerization techniques which will produce a polymer within the scope of the defined parameters. Many Ziegler catalyst systems investigated, however, have produced polymers falling outside the scope of the polymer definition and the resultant polymers imparted visible haze to oil compositions containing same.

Thus, while theoretically various Ziegler catalyst combinations such as described in U.S. Patent No. 3,051,690 should be suitable, to date only vanadium oxychloride and ethyl aluminum sesquichloride when used in combination with hydrogen have been found to directly yield a polymer having the requisite characteristics described above, particularly with respect to their relative freedom from haze formation as indicated by the character-

istic of less than 1.3% by weight of a polymer fraction which is insoluble in normal decane at 45°C.

Thus, the preferred process for preparing the polymers of the present invention is to polymerize ethylene with an alpha-olefin, especially propylene, in the presence of the combination of vanadium oxychloride and ethyl aluminum sesquichloride, using hydrogen and a solvent medium. Hydrogen may be introduced incrementally or substantially at a single charge at various stages of the polymerization process, and can be mixed with an inert gas such as nitrogen or with a gaseous monomer and sparged through the reaction mixture, or retained as a blanket over it. It is preferred, however, to mix the hydrogen with the monomer feed.

As noted above, various well-known Ziegler catalyst systems were found to give unacceptable polymers as to haze formation, crystallinity, molecular weight distribution and wide compositional distribution. It is possible, however, in some instances to use selected Ziegler catalysts which may yield a polymer departing only somewhat from the characteristics of the present invention, and then use a complementary separation technique such as solvent fractionation to isolate the polymer of the invention from the total polymer thus formed. Even in this case only a rather narrow group of Ziegler catalysts appear suitable. By way of illustration, the present polymer product can be prepared by polymerizing ethylene and propylene in the presence of hydrogen and a vanadium tetrachloride-ethyl aluminum sesquichloride catalyst system and by dissolving the polymer thus produced in normal decane at 95°C. The solution is then cooled to about 45°C. and then centrifuged to remove the high ethylene content insoluble fraction and produce a soluble polymer fraction within the scope of the present invention. It should be noted, however, the mere removal of the normal decane-insoluble fraction from typical Ziegler ethylene-propylene copolymers will not produce the present polymer product since the soluble polymer may still lack the requisite narrow molecular weight distribution, ethylene content and/or crystallinity.

The soluble Ziegler catalyst thus preferred is formed by mixing an alkyl-aluminum halide such as ethyl aluminum sesquichloride with vanadium compounds such as vanadium oxychloride (VOCl_3).

The monomers used in this invention should be polymerized in the presence of various solvents. They include aliphatic, naphthenic, aromatic and halogenated hydrocarbon solvents, mineral oils, or an excess of the higher alpha-olefin such as propylene may be used. Specific examples of solvents include n-hexane, hept-

tane, propane, cyclohexane, toluene, xylenes, tetrachloroethylene, decalin and chlorobenzene, preferably, n-hexane.

A summary of typical ranges of monomer

concentrations, catalyst concentrations, hydrogen concentrations, and process variables employed in the process of this invention follows.

	Broad	Preferred	Most Preferred
Catalyst Composition Al/V molar ratio	1 to 50 (essential)	2 to 30	3 to 15
Catalyst Concentration in the feed, catalyst/ total monomer weight ratio	2×10^{-4} to 2×10^{-2} (essential)	8×10^{-4} to 1×10^{-2}	1×10^{-3} to 8×10^{-3}
Hydrogen Concentration, mole % based on the total moles of monomer feed	0.01 to 20 (essential)	0.01 to 10	0.025 to 5.0
Process Variables			
Temperature, °C.	-20 to 100	10 to 90	30 to 70
Pressures, atm.	0.5 to 100	0.75 to 50	1 to 15
Reaction or contact time, minutes	1 to 180	3 to 120	5 to 40
Monomer Feed Composition			
Ethylene/alpha-olefin weight ratio	1 to 10 (essential)	.5 to 5	.9 to 4

- 10 When the polymeric additives of the present invention are employed as a minor proportion by weight in lubricating oils such as crankcase oils, hydraulic oils, automatic transmission oils, industrial oils, greases, and the like, they may be added in proportions of 0.01 to 30.0%, preferably 0.1 to 10.0, and more preferably 0.3 to 2.5 by weight, based on oil.
- 15 The proportions giving the best results will vary somewhat according to the nature of the lubricating oil base stock and the specific purpose for which the lubricant is to serve in a given case. Typically, such additives are sold as concentrates wherein the additive is present in amounts of from 5 to 50 wt. %, preferably 6 to 25 wt. %, based on the total amount of the hydrocarbon, e.g. mineral oils, hexane, heptane and the like, employed for the additive.

- 20 In the oil compositions containing the polymers of this invention, hydrocarbon mineral oil may be employed as the base material, such as paraffin base, naphthene base or mixed paraffin base distillate or residual oils. Paraf-

fin base distillate lubricating oil fractions are used in the formulation of premium grade motor oil such as contemplated in this invention. The well-known synthetic lubricating bases of the ester or ether type may also be used as the lubricating base oil. Broadly speaking, a mineral or synthetic lubricating oil having an SUS viscosity at 100°F. between about 50 and 1000 may be used in the formulation of the improved lubricants of this invention. Usually the viscosity range falls between 70 and 300 SUS at 100°F.

Specific examples of synthetic base oils include, among others, esters of monobasic acids (e.g., ester of C_8 Oxo alcohol with C_8 Oxo acid, ester of C_{12} Oxo alcohol with octanoic acid, etc.), esters of dibasic acids (e.g., di-2-ethyl hexyl sebacate, di-nonyl adipate, etc.), esters of glycols (e.g., C_{12} Oxo acid diester of tetraethylene glycol, etc.), complex esters (e.g., the complex ester formed by reacting one mole of sebacic acid with two moles of tetramethylene glycol and two moles of 2-ethyl-hexanoic acid, complex ester

formed by reacting one mole of tetraethylene glycol with two moles of sebacic acid and two moles of 2-ethyl hexanol, complex ester formed by reacting together one mole of azelaic acid, one mole of tetraethylene glycol, one mole of C_8 Oxo alcohol, and one mole of C_8 Oxo acid), esters of phosphoric acid (e.g., the ester formed by contacting three moles of the monomethyl ether of ethylene glycol with one mole of phosphorus oxychloride, etc.), halocarbon oils (e.g., the polymer of chlorotrifluoroethylene containing 12 recurring units of chlorotrifluoroethylene), alkyl silicates (e.g., polymethyl siloxanes, polyalkyl siloxane, ethyl polysiloxanes, methylphenyl polysiloxanes, ethylphenol polysiloxanes, etc.), sulfite esters (e.g., ester formed by reacting one mole of sulfur oxychloride with two moles of the methyl ether of ethylene glycol, etc.), carbonates (e.g., the carbonate formed by reacting C_8 Oxo alcohol with ethyl carbonate to form a half ester and reacting this half ester with tetraethylene glycol), mercaptals (e.g., the mercaptal formed by reacting 2-ethyl hexyl mercaptan with formaldehyde, formals (e.g., the mercaptal formed by reacting C_{13} Oxo alcohol with formaldehyde), polyglycol type synthetic oils (e.g., the compound formed by condensing butyl alcohol with 14 units of propylene oxide, etc.), or mixtures of any of the above (or with mineral, animal or vegetable oils) in any proportions may also be used.

The polymers of the invention can be employed alone in lubricant compositions, or if desired, can be employed in combination with other viscosity index improvers in order to affect that characteristic of the base lubricant composition. If desired, the polymers may be employed in combination with other additives, for example, pour point depressants; detergent type additives, such as barium nonyl phenol sulfide, calcium tertiary-amylphenol sulfide, nickel oleate, barium octadecylate, calcium phenol stearate, zinc di-isopropyl salicylate, aluminum naphthenate, calcium cetyl phosphates, barium di-tertiary-amyl-phenyl sulfide, calcium petroleum sulfonate, zinc methylcyclohexyl thiophosphate and calcium dichlorostearate.

The present invention also contemplates that the polymers described herein can be subjected to such after-treatment as may be desired to fit them for particular uses or to impart desired ancillary properties. It is to be understood, therefore, that polymers of the invention can be subjected to chemical modifying treatments, such as halogenation, halogenation followed by dehalogenation, sulfohalogenation by treatment with sulfur chloride, or mixtures of chlorine and sulfur dioxide, sulfonation, as well as any other reaction to which hydrocarbon polymers may be subjected. In addition, it is also contemplated that the polymers of the invention can be

blended with other polymers so as to impart various desired properties thereto.

The drawing is a graphic representation of the molecular weight distribution of three different ethylene-propylene copolymers. The aforementioned gel permeation chromatography (GPC) technique was used in determining these molecular weight distribution curves. Other properties of these polymers and their methods of preparation are given below in Example 2.

EXAMPLE 1

As has been pointed out, polymeric additives which impart significant amounts of visible haze to oils are unacceptable for use in motor oils. Ziegler polymers prepared from ethylene and lower alpha-olefins, especially propylene, would be expected to form substantial amounts of haze in motor oils since these polymers are essentially linear, relatively high in molecular weight and do not contain oil-solubilizing long alkyl side chains such as the commercially available viscosity index improvers. In fact, a large number of polymerizations have been carried out using various Ziegler catalysts in conjunction with a number of chain transfer agents. In the vast majority of these polymerizations, the products produced were unsuitable or required fractionation to produce the low haze-forming polymer of the invention.

The technique and apparatus which was used herein for measuring haze is described in U.S. Patent No. 3,358,148. Briefly, the haze measurement is obtained by passing a light beam through a sample and measuring the amount of light transmitted by means of a conventional light meter. The light transmitted through the oil sample is greatest for those oils having the lowest degree of haze. The actual haze measurement was made by placing a standard or reference oil containing none of the polymer to be evaluated in the sample tube, passing a light beam there-through and adjusting the light meter reading to a reference level. The haze-forming characteristics of a polymer were determined herein by blending sufficient polymer into the reference oil to give an oil blend having a viscosity at 210°F. of $12 \pm .5$ cs. In this example, 0.9% by weight of the test polymers (based on oil) were blended with the reference oil. The polymer-oil blend was then tested in the apparatus in the same manner as the reference sample and the meter reading was observed. In this test, an oil blend having a haze less than 13 units would be considered acceptable for commercial use.

In this example, ethylene-propylene copolymers having similar average ethylene contents and average molecular weights were compared in haze-forming characteristics. The copolymers were prepared in the presence of hydrogen and a catalyst system consisting of

(A) vanadium oxy trichloride-ethyl aluminum sesquichloride or (B) vanadium tetrachloride-ethyl aluminum sesquichloride or (C) vanadium tetrachloride-diethyl aluminum chloride. 5 The specific process conditions employed are set forth below in Table I. The process con-

dition used for each catalyst system differed somewhat so that polymers having essentially the same average composition and average molecular weight could be made from each catalyst system. 10

TABLE I
Feed Components,
Pounds/100 Pounds of Hexane Solvent

Polymer	Residence Time* Minutes	Ethylene	Propylene	Vanadium Catalyst	Hydrogen Parts per Million Parts Ethylene	Catalyst Used	Catalyst Al/V Molar Ratio
A	17	3.50	1.80	0.0094	53	$\text{VOCl}_3\text{--Et}_2\text{Al}_2\text{Cl}_3$	10
B	14.5	3.50	1.60	0.005	76	$\text{VCl}_4\text{--Et}_2\text{Al}_2\text{Cl}_3$	6
C	14.5	3.50	1.80	0.005	50	$\text{VCl}_4\text{--Et}_2\text{AlCl}$	5

*3 gallon stainless steel reactor maintained at 55°C. and 50 psig.

15 The resulting polymers were evaluated in the aforescribed haze test. In addition, the polymers were fractionated in the following manner by conventional fractional precipitation using the temperature effect on solubility: 0.758 gram of polymer were dissolved in 100 ml. of normal decane at 95°C. and cooled to

a temperature of 45°C. over a period of about 30. minutes. The polymer was then centrifuged at 45°C. and 2000 rpm for 12 hours to remove the insoluble fraction which was recovered and weighed. The results are given below in Table II. 20 25

TABLE II

Haze-Forming Characteristics of Ethylene-Propylene Copolymers

Unfractionated Polymer	Catalyst Used to Prepare Polymer		
	$\text{VOCl}_3\text{---Et}_2\text{Al}_2\text{Cl}_3$	$\text{VCl}_4\text{---Et}_2\text{Al}_2\text{Cl}_3$	$\text{VCl}_4\text{---Et}_2\text{AlCl}$
	Polymer A	Polymer B	Polymer C
Mole % Ethylene	76	77	77
Inherent Viscosity in decalin @ 135°C., dl/g	1.6	1.5	1.2
Haze Units*	6	14	93
Fraction of Polymer Soluble in n-decane @ 45°C.			
Wt. % Soluble	100.00	98.65	96.79
Haze Units*	5	3	28
Fraction of Polymer Insoluble in n-decane @ 45°C.			
Wt. % Insoluble	0.00	1.35	3.21
Mole % Ethylene	—	81	84
Inherent Viscosity in decalin @ 135°C., dl/g	—	1.7	1.5

*Polymer evaluated for haze in a reference oil which is Solvent 150 Neutral which is a solvent extracted, neutral, paraffinic type oil having a viscosity of 150 SuS at 100°F.

Referring to the above Table, it is seen that although the polymers were essentially of the same average composition and average molecular weight (inherent viscosity) the polymers were substantially different in haze-forming characteristics when blended with the oil. For example, oil compositions containing Polymer A were very low in haze whereas oil compositions containing Polymer B were not good in terms of haze, and oil compositions containing Polymer C were completely unacceptable from the standpoint of haze. Table II also shows that Polymer B was further processed to produce a low haze-forming polymer (3 haze units) within the scope of the invention by removing the polymer fraction which was insoluble in normal decane at 45°C. However, Polymer C was not sufficiently improved with respect to haze-

forming characteristics by removal of the polymer fraction insoluble in normal decane at 45°C, since the soluble polymer fraction had a molecular weight distribution greater than the limits of the polymer of this invention.

EXAMPLE 2

The molecular weight distribution curves presented in the drawing show that Polymer I is unimodal and has a narrow molecular weight distribution whereas Polymer II is bimodal and Polymer III has a very broad molecular weight distribution.

Polymer I corresponds to Polymer A of Example 1. Polymer III was prepared using anhydrous hydrochloric acid as a chain transfer agent whereas Polymer II was prepared without the use of a chain transfer agent. The actual polymerization conditions are shown below in Table III.

TABLE III
Feed Components
Grams/100 Grams of Hexane Solvent

	Residence Time, Minutes	Monomers	Catalyst	Chain Transfer Agent	Catalyst used	Catalyst Al/V Molar Ratio
Polymer II	15 ⁽¹⁾	7.0 ⁽²⁾	0.008	0.40	VOCl ₃ -Et ₂ AlCl	3
Polymer III	5 ⁽³⁾	7.0 ⁽²⁾	0.02	None	VOCl ₃ -Et ₂ AlCl	3

⁽¹⁾ One gallon stirred glass reactor maintained at 38°C. and 5 psig.

⁽²⁾ Monomer feed consisted of 22 mole % ethylene and 78 mole % propylene.

⁽³⁾ One gallon stirred stainless reactor maintained at 42°C. and 15 psig.

The molecular weight distribution ($\overline{M}_w/\overline{M}_n$), thickening efficiency and sonic breakdown characteristics of Polymers I, II and III are shown below in Table IV.

With respect to the sonic breakdown, this is a standard measurement for determining the shear stability of polymer-oil compositions, the lower percentage reflecting which compositions have the greatest resistance to shear breakdown and, hence, which are the most stable under automotive lubricating conditions. In this method the sample under test is blended with an approved base stock to a viscosity at 210°F. of 15.0 ± 0.5 centistokes.

A portion of the blend is subjected to sonic shearing forces at a specific power input and a constant temperature for 15 minutes. Viscosities are determined on the blend both before and after the treatment; the decrease in viscosity after the treatment is a measure of the molecular breakdown of the polymer under test. It is customary to examine the blend of a standard sample of known behaviour each time a test is made, and to use this as a reference to establish the correct value of the sample under test. The corrected value is reported as a percent sonic breakdown which is calculated from the formula:

$$\frac{(\text{Viscosity of blend before test} - \text{Viscosity of blend after test})}{(\text{Viscosity of blend before test} - \text{Viscosity of base oil})} (100)$$

20

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TABLE IV

	Thickening Efficiency	$\overline{Mw}/\overline{Mn}$	% Sonic Breakdown
Polymer I	2.2	2.2	8
Polymer II	1.6	34.4	18
Polymer III	1.6	27.2	54

As seen from the foregoing results, Polymers II and III which are polymodal and/or have broad molecular weight distributions are substantially less resistant to shear degradation than Polymer I which has a narrow molecular weight distribution. This is the case even though Polymer I (which is a polymer of the invention) has the highest thickening efficiency. Since shear stability is inversely proportional to thickening efficiency, this example illustrates the importance of molecular weight distribution on shear stability.

In specification 60785/70 (Serial No. 1,239,083) there is described and claimed an oil composition comprising a major proportion by weight of a lubricating oil and a minor proportion by weight of an oil-soluble polymer comprising ethylene and a C_8-C_{18} alpha-olefin, said polymer having the following combination of parameters:

- (a) an ethylene content within the range between 70 and 91 mole %,
- (b) a degree of crystallinity less than 25%,
- (c) an $\overline{Mw}/\overline{Mn}$ ratio less than 4.0, and
- (d) a viscosity average molecular weight of between about 10,000 and 200,000.

In said specification there is also described and claimed an oil concentrate comprising a hydrocarbon solvent and 5 to 50 weight % based on solvent of an oil-soluble polymer comprising ethylene and a C_8-C_{18} alpha-olefin, said polymer having the following combination of parameters:

- (a) an ethylene content within the range between 70 and 91 mole %,
- (b) a degree of crystallinity less than 25%,
- (c) an $\overline{Mw}/\overline{Mn}$ ratio less than 4.0, and
- (d) a viscosity average molecular weight of between about 10,000 and 200,000.

We make no claim to such oil compositions and concentrates.

WHAT WE CLAIM IS (subject to the foregoing disclaimer):

1. A polymer comprising ethylene and a C_8-C_{18} alpha-olefine having the following combination of parameters:
 - (a) an ethylene content within the range of

between 60 and 80 mole %, wherein said polymer contains no more than 1.3% by weight of a polymer fraction which is insoluble in normal decane at 45°C,

- (b) a degree of crystallinity less than 25%,
- (c) an $\overline{Mw}/\overline{Mn}$ ratio less than 4.0, and
- (d) a viscosity average molecular weight of between 10,000 and 200,000.

2. A polymer according to claim 1 wherein the $\overline{Mw}/\overline{Mn}$ ratio is less than 2.6.

3. A polymer according to any one of the preceding claims wherein said polymer has a viscosity average molecular weight of between 30,000 and 100,000.

4. A polymer according to any one of the preceding claims wherein said polymer has an ethylene content of between 72 and 80 mole % and an $\overline{Mw}/\overline{Mn}$ ratio less than 2.6.

5. A polymer according to any one of the preceding claims which contains no more than 0.5% by weight of a polymer fraction which is insoluble in normal decane at 45°C.

6. A polymer according to any one of the preceding claims wherein which contains no fraction which is insoluble in normal decane at 45°C.

7. A polymer according to any one of the preceding claims wherein said alpha-olefin is propylene.

8. A polymer according to claim 7 wherein said polymer also contains up to 10 mole % of a C_8-C_{18} alpha-olefin, or a C_8-C_{28} non-conjugated diolefin or a mixture thereof.

9. A polymer according to claim 1 substantially as hereinbefore described with reference to either of the Examples.

10. A low haze oil composition comprising a major proportion by weight of a lubricating oil and a minor proportion by weight of an oil-soluble polymer according to any one of the preceding claims.

11. A composition according to claim 10 which contains 0.01 to 30% by weight, based on the oil, of said oil-soluble polymer.

12. A composition according to claim 11 wherein said polymer is present in a concentration of from 0.3 to 2.5% by weight based on the oil.

TABLE IV

	Thickening Efficiency	$\overline{M}_w/\overline{M}_n$	% Sonic Breakdown
Polymer I	2.2	2.2	8
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Polymer III	1.6	27.2	54

As seen from the foregoing results, Polymers II and III which are polymodal and/or have broad molecular weight distributions are substantially less resistant to shear degradation than Polymer I which has a narrow molecular weight distribution. This is the case even though Polymer I (which is a polymer of the invention) has the highest thickening efficiency. Since shear stability is inversely proportional to thickening efficiency, this example illustrates the importance of molecular weight distribution on shear stability.

In specification 60785/70 (Serial No. 1,239,083) there is described and claimed an oil composition comprising a major proportion by weight of a lubricating oil and a minor proportion by weight of an oil-soluble polymer comprising ethylene and a C_3-C_{18} alpha-olefin, said polymer having the following combination of parameters:

- (a) an ethylene content within the range between 70 and 91 mole %,
- (b) a degree of crystallinity less than 25%,
- (c) an $\overline{M}_w/\overline{M}_n$ ratio less than 4.0, and
- (d) a viscosity average molecular weight of between about 10,000 and 200,000.

In said specification there is also described and claimed an oil concentrate comprising a hydrocarbon solvent and 5 to 50 weight % based on solvent of an oil-soluble polymer comprising ethylene and a C_3-C_{18} alpha-olefin, said polymer having the following combination of parameters:

- (a) an ethylene content within the range between 70 and 91 mole %,
- (b) a degree of crystallinity less than 25%,
- (c) an $\overline{M}_w/\overline{M}_n$ ratio less than 4.0, and
- (d) a viscosity average molecular weight of between about 10,000 and 200,000.

We make no claim to such oil compositions and concentrates.

WHAT WE CLAIM IS (subject to the foregoing disclaimer):

1. A polymer comprising ethylene and a C_3-C_{18} alpha-olefine having the following combination of parameters:
 - (a) an ethylene content within the range of

between 60 and 80 mole %, wherein said polymer contains no more than 1.3% by weight of a polymer fraction which is insoluble in normal decane at 45°C.,

- (b) a degree of crystallinity less than 25%,
- (c) an $\overline{M}_w/\overline{M}_n$ ratio less than 4.0, and
- (d) a viscosity average molecular weight of between 10,000 and 200,000.

2. A polymer according to claim 1 wherein the $\overline{M}_w/\overline{M}_n$ ratio is less than 2.6.

3. A polymer according to any one of the preceding claims wherein said polymer has a viscosity average molecular weight of between 30,000 and 100,000.

4. A polymer according to any one of the preceding claims wherein said polymer has an ethylene content of between 72 and 80 mole % and an $\overline{M}_w/\overline{M}_n$ ratio less than 2.6.

5. A polymer according to any one of the preceding claims which contains no more than 0.5% by weight of a polymer fraction which is insoluble in normal decane at 45°C.

6. A polymer according to any one of the preceding claims wherein which contains no fraction which is insoluble in normal decane at 45°C.

7. A polymer according to any one of the preceding claims wherein said alpha-olefin is propylene.

8. A polymer according to claim 7 wherein said polymer also contains up to 10 mole % of a C_4-C_{18} alpha-olefin, or a C_6-C_{28} non-conjugated diolefin or a mixture thereof.

9. A polymer according to claim 1 substantially as hereinbefore described with reference to either of the Examples.

10. A low haze oil composition comprising a major proportion by weight of a lubricating oil and a minor proportion by weight of an oil-soluble polymer according to any one of the preceding claims.

11. A composition according to claim 10 which contains 0.01 to 30% by weight, based on the oil, of said oil-soluble polymer.

12. A composition according to claim 11 wherein said polymer is present in a concentration of from 0.3 to 2.5% by weight based on the oil.



13. An oil concentrate comprising a hydrocarbon solvent and 5 to 50 weight %, based on solvent, of the polymer according to any one of claims 1 to 9.

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