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(54) LUBRICANT CONTAINING ETHYLENE-ALPHA OLEFIN POLYMER

(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 oils containing certain polymers prepared from ethylene and at least one other alpha-olefin.

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 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. One of the major requirements of lubricating oils is their satisfactory viscosity-temperature characteristics. These characteristics are necessary in order that the oils will not lose their fluidity but will show an equally good performance within a relatively wide temperature range to which they may be exposed in service. The wider the possible temperature variations, the smaller should be the change in viscosity with temperature.

In refining natural petroleum oils or in preparing synthetic oils, it is economically feasible to improve their viscosity index only up to a certain maximum inasmuch as further treatment has only an additional negligible effect on viscosity index characteristics. Further marked improvement can be effected, however, by adding to said com-

positions various types of additives for viscosity index improvement. In raising the viscosity index of lubricant compositions by additives, recourse has been made to the introduction of long-chained compounds of the nature of linear polymers; generally the highest V.I. increase being obtained from polymers of the greatest chain length. While such polymeric products have been generally satisfactory in V.I. improvement, there has been, prior to the present invention, a limit to V.I. improvement without incurring concomitant limiting factors.

For example, apart from the attainment of V.I. improvement, 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,

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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.

In accordance with this invention oil compositions comprise 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 $\overline{Mw}/\overline{Mn}$ ratio less than 4.0, and
- (d) a viscosity average molecular weight of between 10,000 and 200,000.

The polymers contained in lubricating oils are found to have an unusual combination of properties including excellent V.I. improving characteristics, high thickening potency, low haze characteristics and superior shear stability. Such combination of properties renders the polymers especially useful in lubricating oil of both the mineral and synthetic type. In general, these ethylene-alpha-olefin polymers may be described as crystalline-amorphous, low molecular weight with a narrow molecular weight distribution, essentially unbranched random polymers with relatively small regions of ethylene or alpha-olefin, homopolymers sequences, i.e., a degree of crystallinity less than 25%.

A process for preparing these polymers is described and claimed in our co-pending Patent Application No. 31921/68 (Serial No. 1,239,082).

The C_3 to C_{18} 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.

When propylene is employed as the comonomer, i.e., with ethylene, one may also use a C_4 to C_{28} alpha-olefin. 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 C_4 to C_{28} olefinic monomers may be employed.

The monomers may be polymerized in the presence of various solvents, e.g. aliphatic, naphthenic, aromatic and halogenated hydrocarbon solvents, mineral oils, or an excess of the higher alpha-olefin such as propylene may be used.

The polymers used as additives in the oil compositions of this invention may be obtained by the use of hydrogen gas and a specific Ziegler-type catalyst, e.g. a mixture of an organo-aluminium halide and a vanadium oxy halide. Further details of the method of polymerisation are described in our Patent Application No. 31921/68 (Serial No. 1,239,082).

The ethylene-alpha-olefin polymers used in the oil compositions of this invention will have a viscosity average molecular weight

($\overline{Mv}$) 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 hereof were determined by viscosity measurements in decalin at 135°C and calculated by the

formula $[\eta] = (K^1 \times 10^{-4}) \overline{Mv}^{0.74}$ in which $[\eta]$ represents intrinsic viscosity and K^1 varied 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, $K^1 = 1.15K$ wherein K

relates η and $\overline{Mv}$ according to the method outlined by G. Moraglio in *Chimica l'Industria* 41, 984 (1959).

The polymers used in the compositions of this invention may be further described as containing from 70 to 91 mole %, preferably 78—88 mole %, of ethylene and from 9 to 30 mole %, preferably 12 to 22 mole %, of the aforescribed alpha-olefin and when propylene is used as the C_3 to C_{18} alpha-olefin, 0 to 10 mole %, e.g., 0.5—5.0 mole %, of the C_4 — C_{28} alpha-olefin.

The polymers used in the composition of this invention have a degree of crystallinity less than 25% and a surprisingly narrow molecular weight distribution. The surprisingly narrow molecular weight distribution of the polymers is shown by the fact that

the number average molecular weight, $\overline{Mn}$, and the weight-average molecular weight,

$\overline{Mw}$, of the ethylene-alpha-olefin polymers are nearly equal 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

Mn and Mw be equal. The narrow molecular weight distribution of the polymers of this invention may be characterized by the ratio

- 5 Mw/Mn wherein said ratio is less than about 4.0:1, preferably less than 2.6:1, e.g., 1.4:1 to 2.2:1.

10 The determination of the ratio Mw/Mn 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 sec. 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 (Å) 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.

15 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.

20 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 of less than 25% and generally a degree of crystallinity within the range of 1 to 20% in the copolymers used in the oils of this invention. In order for the copolymers to exhibit superior properties, the degree of crystallinity should reside within the range of from 3 to 18%.

In the lubricating oil compositions in 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. Paraffin base distillate lubricating oil fractions are used in the formulation of premium grade motor oil such as contemplated in this invention. Broadly speaking, a mineral 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. The well-known synthetic lubricating bases of the ester or ether type may also be used as the lubricating base oil.

The copolymers or terpolymers are employed as additives in the oil compositions of this invention in concentrations of less than 50%, preferably 0.1 to 10 wt.%, preferably between 0.5 and 5.0 wt.% based on the composition being treated, so as to accomplish the desired objects. It is to be understood that such ranges are flexible and will be determined by the particular character of the composition, e.g. lubricating oil, to which the additive is added. Typically such additives are sold as concentrates wherein the additive is present in amounts of from 5 to 50 wt.%, preferably 10 to 25 wt.%, based on the total amount of the hydrocarbon solvent, e.g. mineral oils, hexane, heptane and the like, employed for the additive.

The copolymers or the terpolymers can be employed alone in lubricant compositions of the present invention, 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, said copolymers or terpolymers may be employed in combination with other additives, for example, pour point depressants, detergent type additives, corrosion inhibitors, anti-oxidants, sludge inhibitors, and metal deactivators.

EXAMPLE 1

Ethylene and propylene were continuously polymerized in the presence of n-heptane solvent, VOCl_3 , $\text{Al}_2\text{Et}_2\text{Cl}_3$, and hydrogen. The polymerization reaction was carried out in a two-litre glass reactor equipped with a monomer inlet tube, catalyst inlet, co-catalyst inlet, solvent inlet, reflux

condenser, stirrer, product recovery outlet and a temperature control jacket. Provision was made to continuously control the rate of addition of monomer, hydrogen, solvent, catalyst and co-catalyst. The reaction was carried out continuously under conditions of constant volume and pressure (i.e., 1 atm.) by controlling the rate of feed introduction and product removal. The ethylene and propylene monomers were purified by contact with hot (e.g., 150°C) copper oxide and molecular sieves. Purification of the solvent, i.e., n-heptane, was effected by passage through a bed of alumina and silica gel. Similarly, the hydrogen gas was dried by passage through a silica gel bed. The entire system was maintained oxygen and moisture-free by blanketing with nitrogen. A solution of vanadium oxychloride (VOCl_3) in n-heptane corresponding to a 0.03 molar solution was introduced through the catalyst inlet while a solution of ethyl aluminium sesquichloride ($\text{Al}_2\text{Et}_3\text{Cl}_3$) in n-heptane corresponding to a 0.12 molar solution was introduced through the co-catalyst inlet. The reactor operating conditions were as shown in Table I.

TABLE I

Temperature, °C.	55
Solvent Volume, litres @ 1 atm., 25°C.	1.5
Monomer Feed Composition	
Volume % propylene	75
Volume % ethylene	25
Monomer Feed Rate, litres/minute	3.0
Hydrogen Feed Rate,	
cc./minute @ 1 atm., 25°C	30
VOCl_3 Catalyst Solution Feed Rate,	
cc./min.	1.0
Catalyst Composition, Al/V molar ratio	5.0
Reactor Residence Time, minutes	20

A sample of the product stream was removed and a polymeric product was recovered by steam distilling off the solvent and vacuum drying the product at 50°C. 0.7 weight % of the polymer was dissolved in a lubricating oil in order to determine the V.I. and thickening efficiency of the resulting oil composition. The copolymer recovered had the properties shown in Table II.

TABLE II

Mole % Ethylene	77.0
Inherent Viscosity	
@ 135°C decalin, dl/g	2.01
V.I. ⁽¹⁾	135
Thickening Efficiency ⁽²⁾	2.7

⁽¹⁾ Viscosity Index as determined by ASTM D-567 in Reference Oil 150 which is a solvent extracted, neutral, paraffinic-type oil of about 46.53 SUS at 210°F and 189.9 SUS at 100°F.

⁽²⁾ Thickening Efficiency is the ratio of Wt.% polyisobutylene (20,000 Staudinger

mol. wt.) required to thicken Reference Oil 150 to a viscosity of 12 ± 5 cs at 210°F/Wt.% ethylene-propylene copolymer required to thicken Reference Oil 150 to the same viscosity.

EXAMPLE 2

This example serves to illustrate the correlation between the degree of crystallinity of a copolymer used in the oil compositions of this invention and its potency as a V.I. improver. In this example, a number of ethylene-propylene copolymers were prepared in accordance with the procedure of Example 1 except that the ethylene-propylene feed ratios were controlled to give various polymer compositions which were examined for their degrees of crystallinity by X-ray diffraction. The procedure utilized was similar to that of Weidinger and Hermans, *Makromolekular Chem.*, 50, 98 (1961). The method of determining the crystalline fraction in the ethylene-propylene polymer consisted of: (1) obtaining a diffractogram of the ethylene-propylene copolymer sample, (2) measuring the amorphous and crystalline areas of the diffractogram and (3) calculating the percent crystallinity from these two measurements.

The method is based upon taking a series of diffractograms of ethylene-propylene-copolymer samples that vary in crystallinity. The data is normalized to the same absorbance. A plot of the normalized crystalline area versus the normalized amorphous gives a linear relations between the two quantities. This allows the calculation of the crystalline fraction in any other sample from the observed crystalline and amorphous areas.

1.0 weight % of the polymer was dissolved in the same oil as used in Example 1 to determine the V.I. and thickening efficiency of the resulting oil composition. The V.I. of each of these ethylene-propylene copolymer samples were compared at equal viscosity average molecular weight (equal thickening power) and the resulting data in terms of percent crystallinity and V.I. are presented in Table III.

TABLE III

Sample No.	Mole % Ethylene	Thickening Power	% Crystallinity	V.I.
1	72	2.0	2.64	131
2	77	2.0	11.47	136
3	78	2.0	13.87	140
4	80	2.0	19.75	136
5	81	2.0	24.82	131
6	82	*	*	*

* Insoluble in oil.

It can be seen from the foregoing that

the polymer crystallinity has an important effect on the V.I. properties of the polymer.

WHAT WE CLAIM IS:—

1. 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 10,000 and 200,000.
2. A composition according to claim 1 wherein said polymer has an ethylene content of between 78 and 88 mole %.
3. A composition according to either of claims 1 and 2 wherein the ratio $\overline{M}_w/\overline{M}_n$ is less than 2.6:1.
4. A composition according to any one of the preceding claims wherein said polymer has a viscosity average molecular weight of between 30,000 and 100,000.
5. A composition according to any one of the preceding claims wherein said alpha-olefin is propylene.
6. A composition according to claim 5 wherein said polymer contains up to 10 mole % of a third monomer which is a C_4-C_{20} alpha-olefin.
7. A composition according to any one of the preceding claims wherein the degree of crystallinity is between 1 and 20%.
8. A composition according to claim 7 wherein said degree of crystallinity is between 3 and 18%.
9. A composition according to any one of the preceding claims wherein said lubricating oil has a viscosity of between 50 SUS and 1000 SUS at 100°F.
10. A composition according to any one of the preceding claims which contains 0.1 to 10 weight %, based on the total composition of said polymer.
11. A composition according to claim 1 wherein the amount of polymer is 0.5 to 5.0 weight % based on the total composition.
12. An oil concentrate comprising a hydrocarbon solvent and 5 to 50 weight % based on solvent of the polymer as defined in any one of claims 1—8.
13. An oil composition according to claim 1 substantially as hereinbefore described with reference to the Examples.

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4. A composition according to any one of the preceding claims wherein said polymer has a viscosity average molecular weight of between 30,000 and 100,000.
5. A composition according to any one of the preceding claims wherein said alpha-olefin is propylene.

6. A composition according to claim 5 wherein said polymer contains up to 10 mole % of a third monomer which is a C_4-C_{28} alpha-olefin.
7. A composition according to any one of the preceding claims wherein the degree of crystallinity is between 1 and 20%.
8. A composition according to claim 7 wherein said degree of crystallinity is between 3 and 18%.
9. A composition according to any one of the preceding claims wherein said lubricating oil has a viscosity of between 50 SUS and 1000 SUS at 100°F.
10. A composition according to any one of the preceding claims which contains 0.1 to 10 weight %, based on the total composition of said polymer.
11. A composition according to claim 1 wherein the amount of polymer is 0.5 to 5.0 weight % based on the total composition.
12. An oil concentrate comprising a hydrocarbon solvent and 5 to 50 weight % based on solvent of the polymer as defined in any one of claims 1—8.
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