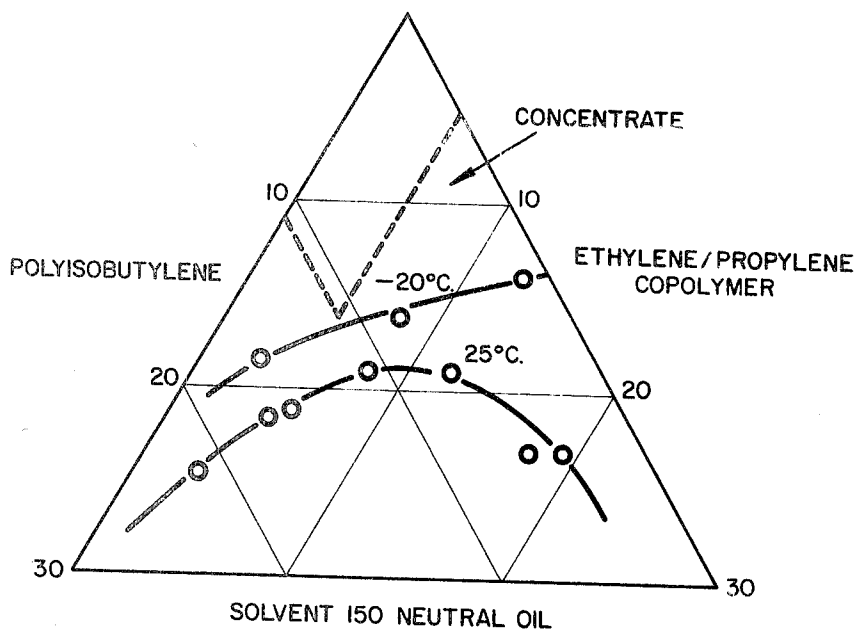


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OIL CONCENTRATE CONTAINING A COMPATIBLE MIXTURE OF
POLYISOBUTYLENE AND ETHYLENE-ALPHA OLEFIN COPOLYMER
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OIL CONCENTRATE CONTAINING A COMPATIBLE MIXTURE OF POLYISOBUTYLENE AND ETHYLENE-ALPHA OLEFIN COPOLYMER

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11 Claims

ABSTRACT OF THE DISCLOSURE

An additive concentrate for lubricating oils which comprises a compatible mixture of polyisobutylene and a polymer of ethylene and alpha-olefin in mineral oil. The polymer mixture is compatible over a wide temperature range and imparts unique and desirable viscosity characteristics to lubricating oils at both low and high temperatures.

CROSS-REFERENCES TO RELATED APPLICATIONS

This is a continuation of application Ser. No. 714,399 filed Mar. 12, 1968, now abandoned, which is a continuation-in-part of application Ser. No. 565,026, filed May 27, 1966, now abandoned, which is a continuation-in-part of application No. 540,649, filed Apr. 6, 1966, now abandoned.

BACKGROUND OF THE INVENTION**Field of the invention**

This invention relates to oil compositions that are useful primarily as engine lubricating oils and are characterized by a unique and most desirable low viscosity at low temperatures and high viscosity at higher temperatures. In a more specific aspect, the invention relates to an additive concentrate comprising a compatible mixture of polyisobutylene and ethylene-alpha olefin in mineral oil.

DESCRIPTION OF THE PRIOR ART

The desirability of providing a lubricating oil having a relatively low viscosity at low temperatures to facilitate cold starting and minimize friction and engine wear while operating at low temperatures and a high viscosity at higher temperatures to insure adequate lubrication and minimize friction and engine wear at engine operating temperatures, has been recognized for some time. The use of engines of higher horsepower and speed, and the use of closer tolerances between moving parts thereof have accentuated the demands for lubricants that will provide effective lubrication under a wide variety of conditions ranging from starting an engine at frigid temperatures to operating it at high speeds for extended periods of time and at average temperatures of several hundred ° F.

One answer of the oil industry to demands for oils to meet these requirements has been to provide the so-called double and triple branded motor oils. These are generally oils or oil blends containing at least about 1% and as much as 15% by volume of one or more high molecular weight polymers, which are well known in the industry as viscosity index improvers.

However, this solution to the problem has brought with it several other problems which are of a magnitude sufficient to have resulted in a considerable decline in the popularity of such multi-branded oils.

One such problem relates to means for accurately predicting the engine cold cranking characteristics (i.e., "engine viscosity") of an oil.

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The problem of accurately predicting the cranking characteristics of a motor oil (i.e., crankcase oil) in an engine operating at low temperatures (e.g., below about 0° F.) is well-known. It is further known that the viscosity of such an oil influences the force (torque) required to crank an engine and the engine cranking speed; and that the viscosity of any oil is temperature dependent. Thus, the viscosity of a motor oil influences the ease of starting the engine at low temperatures. As is known in the art, "engine viscosity" of a motor oil will determine the ease of engine cranking.

Engine manufacturers, oil processors, and automobile owners, among others, are vitally interested in being able to determine the engine viscosity of a motor oil without having to crank the oil under controlled conditions in actual engine. The cranking characteristics of the so-called "straight mineral" oils can, in general, be predicted adequately (i.e., without actual cranking) by using the viscosity at the temperature of interest, e.g., 0° to -20° F. The "straight mineral" oil viscosity is obtained by extrapolating low-shear viscosities obtained at 100° and 210° F. on the ASTM viscosity-temperature chart. Thus, the effectiveness of a V.I. improver, most important quality imparted to a motor oil by a V.I. improver, is currently determined by measuring the viscosity of a polymer-treated motor oil at 210° and 100° F. and extrapolating to 0° F. The measured 210° F. viscosity and the extrapolated 0° F. viscosity are used to calculate the V.I. or viscosity index of the motor oil.

This procedure, however, is not satisfactory for non-Newtonian oils, as has been amply pointed out in the literature. Most motor oils used at the present time are non-Newtonian oils, containing polymeric additives, i.e., the above-mentioned viscosity index improvers. The complex viscosity-temperature relationships which these present day motor oils exhibit preclude the use of the extrapolated viscosity technique employed to predict the engine cranking characteristics of a straight mineral motor oil. That is, the extrapolated viscosity technique is not applicable to polymer-containing motor oils or other non-Newtonian oils.

Accordingly, there is now provided a method and apparatus for predicting the engine cranking performance of a crankcase oil. The method involves the use of an engine viscosity simulator of improved characteristics predicting the relative distribution of the viscous forces and the hydrodynamic forces in a liquid system particularly, a non-Newtonian liquid system. The viscosity of a motor oil will thereby actually be measured at 0° and 210° F. This change will enhance the true contribution of the V.I. improver to the viscosity properties of the motor oil.

It has been found that commercially available V.I. improvers, e.g., polyisobutylene, polymers of methacrylic acid esters and higher fatty alcohols, copolymers of styrene and C₈-C₁₂ olefins, etc. thicken motor oils to an undesirably large degree at 0° F. Disadvantageously, within a broad molecular weight range, the boundaries of which are determined by the necessity of maintaining a reasonably shear stability, it is found that the relative thickening at 0° and 210° F. for a given polymer composition is not easily amenable to change.

Another problem attendant the provision of a suitable motor oil is that incurred when two or more additives are employed so as to favorably modify the viscosity characteristics of the oil. Thus, it was speculated that the use of two or more additives would favorably affect the viscosity of the oil at both low and high temperatures. This theory was in all instances nullified by the general knowledge, that when two different high polymers are blended, incompatibility is the rule rather than the exception. Incompatibility is manifested by non-homogeneity of the blend and this is reflected in poor physical properties and

separation of phases in the presence of a solvent. This incompatibility of certain high polymers toward each other has been observed for a long time, see, for example, Dobry-Kawenoki, *Journal of Polymer Science*, 2 90 (1947) and experiments to improve such products by blending different constituents have often been frustrated by their incompatibility. This incompatibility can be easily recognized by the fact that films obtained from mixtures are not homogeneous but turbid or opaque and possesses mechanical properties which are inferior to those films obtained from the separate constituents. Technical reviews often contain information concerning compatibility but only from the special point of view of technical interest.

In the absence of a chemical reaction, two solutions of small molecules are generally always miscible, provided they are far enough from saturation. In other words, an unsaturated solution of a material of low molecular weight can always dissolve a quantity of some other substance which is comparable with the amount which can be dissolved in the pure solvent. However, as has already been pointed out, experiments have shown that this is not true for macromolecules and that a polymer solution which is still far from its saturation point is, in general, almost totally impenetrable to another high molecular weight polymer. This phenomenon causes incompatibility and it reveals a characteristic property of macromolecules and, hence, polymer solutions.

With regard to the compatibility of two high polymers toward each other, the only well developed theoretical background on compatibility of two polymers in solution in a common solvent is that of R. L. Scott (*J. Chem. Phys.*, 17, 279 (1949)). This treatment set forth the limits of concentration and molecular weight below which two polymers would remain in a homogeneous solution. The method of Scott was widely accepted when published and later given extensive treatment by P. J. Flory (*Principles of Polymer Chemistry*, Cornell University Press, 1953, pp. 554-559). However, experience has shown that Scott's treatment (although a mathematical classic) cannot be used to predict the composition and molecular weights in the ternary system polymer-polymer-solvent. For example, G. Allen, G. Gee and J. P. Nicholson (*Polymer* 1, 56 (1960)) determined the necessary interaction parameters for the system polystyrene-polybutadiene and applied Scott's treatment to the binary mixture. They predicted on this basis that these two polymers in the bulk (minus the advantage of a solvent) would be miscible at molecular weights of $\sim 20,000$. Later, T. R. Paxton (*J. Appl. Polymer Sci.*, 7, 1499 (1963)) showed that this prediction was grossly inaccurate, just as Allen, Gee and Nicholson implied it would be. Paxton found that the two polymers in question were not compatible at molecular weights of the order of ~ 1000 even when diluted 70% with a common solvent. In a second paper, Allen, Gee and Nicholson (*Polymer* 2, 8 (1961)) discuss the limitations of the existing theory and its almost complete inability to predict quantitatively the compatibility of mixed polymers in solution. Thus, as a general rule, workers in the field have concluded that two polymers distinctly different in structure would not normally be compatible at high concentrations in a high molecular weight solvent, especially at low temperatures.

SUMMARY OF THE INVENTION

It has now been discovered that certain polymers of polyisobutylene are compatible, i.e., mutually soluble with certain polymers of ethylene and alpha-olefins in solvent such as oils, particularly ethylene-propylene copolymers and terpolymers, and that mixtures of these two polymeric compositions evidence highly unusual compatibility and viscosity properties when added to oil. Their effect is to produce a higher V.I. than is attainable with either polyisobutylene or ethylene-propylene copolymer alone. Under the system of directly determining the viscosity properties of motor oils, the 0° F. viscosity rela-

tive to the 210° F. viscosity for the mixture of polyisobutylene plus ethylene-propylene copolymer or terpolymer may be lower than with either polymer alone. This may be referred to as the delta viscosity; that is, the viscosity difference between the viscosity measured for mixtures of polyisobutylene plus ethylene-propylene copolymer in mineral oil solvent, e.g., Solvent 150 Neutral, and the viscosity calculated from the measured viscosities of either polyisobutylene or ethylene-propylene copolymer or terpolymer alone in said Solvent 150 Neutral. In connection with the compatibility of the polymers, it has been unexpectedly discovered that two polymers distinctly different in structure (i.e., polyisobutylene vs. ethylene-alpha olefin copolymer) are compatible with each other at high concentrations (e.g., 20% concentration of each) in a high molecular weight solvent (e.g., mineral oil) at high molecular weights (e.g., 20,000) and remain so to temperatures below -20° C.

In accordance with the present invention, the applicable isobutylene polymers generally have a viscosity average molecular weight of between about 20,000 and about 200,000 and preferably between about 100,000 and 150,000. The polymerization reaction and the conditions utilized are well-known in the art and the polymerization reaction per se does not constitute a part of the present invention.

The polymerization of the isobutylene comprising monomer may be carried out in a wide variety of ways. The reaction process may be carried out as either a batch or a continuous operation and with or without the use of an inert organic diluent as a reaction medium. Usually a diluent is preferred for carrying out the process. Any inert organic solvent may be used as a diluent, as for example, aliphatic hydrocarbons such as hexane, heptane, isooctane, etc., cycloaliphatic hydrocarbons such as cyclohexane, aromatic hydrocarbons, such as benzene, toluene, xylene, etc., or any mixture of such hydrocarbons, or halogenated aromatic hydrocarbons such as chlorobenzenes, chloronaphthalenes, etc.

The selection of the temperatures and the pressures utilized for the polymerization reaction will depend upon a number of factors, e.g., the purity of the monomer utilized, the activity of the catalyst system being used, the degree of polymerization desired, etc. In general, the polymerization will be carried out at temperatures within the range of from about -50° C. to about 150° C. and preferably from about -20° C. to about 100° C. Similarly, while atmospheric pressure or pressure of only a few pounds may be used, the polymerization reaction may be carried out at a wide range of pressures, as for example, through a partial vacuum to about 1,000 p.s.i. and preferably from about atmospheric to about 500 p.s.i. High pressures may, of course, be used, but generally do not appreciably alter the course of polymerization reaction.

Suitable catalyst systems include the "Friedel-Crafts" catalysts which are well-known in the art, e.g., SchilDKnecht, "Vinyl and Related Polymers" Wiley (1952), page 541. These materials include HgCl_2 , BeCl_2 , ZnCl_2 , ZnBr_2 , CdCl_2 , CaCl_2 , BF_3 , BCl_3 , BBr_3 , AlCl_3 , AlBr_3 , AlI_3 , TiCl_4 , TiBr_4 , ZrCl_4 , ZrBr_4 , SnCl_4 , SnBr_4 , SbCl_5 , MoCl_5 , BiCl_3 , FeCl_3 , UCl_4 .

It is contemplated that the above Friedel-Crafts catalysts may be employed in a catalyst system consisting essentially of said Friedel-Crafts compound and an aluminum alkyl compound wherein the molar ratio of Friedel-Crafts compound to aluminum alkyl is a minimum of one. The alkyl component of the alkyl aluminum compound preferably has from 1 to about 8 carbon atoms. One or two of the alkyl components, if desired, can be replaced by halogen atoms. Specific examples of the preferred alkyl aluminum compounds include aluminum triethyl, aluminum triisobutyl, aluminum diethyl chloride, aluminum sesquichloride, aluminum ethyl dichloride, aluminum ethyl dibromide, aluminum diethyl

bromide, aluminum ethyl diiodide, aluminum diethyl iodide, aluminum methyl dichloride, aluminum dimethyl chloride, aluminum methyl dibromide, aluminum dimethyl bromide, aluminum methyl diiodide, aluminum dimethyl iodide, aluminum trimethyl, and the like. Particularly effective catalyst systems used in the preparation of the polyisobutylene component utilized herein include boron trifluoride, titanium tetrachloride, aluminum trichloride, and a combination of stannic chloride and aluminum triethyl.

Other catalysts may also be used in preparation of the isobutylene polymer such as natural earths of the type of fuller's earth, bauxite, natural and artificial clays, active carbon and other similar well-known polymerizing agents.

The second component of the polymeric mixtures of the instant invention are oil-soluble polymers of ethylene and alpha-olefin, e.g., ethylene-propylene copolymers. These polymers will contain from about 40 to about 90 mole percent, preferably 50 to 88 mole percent, of ethylene; from about 60 to about 10 mole percent, preferably 50 to 12 mole percent, of a C_3 - C_{18} alpha-olefin and from about 0 to about 10 mole percent, e.g., 2 to 8 mole percent, of a third monomer selected from the group consisting of the hereinafter described C_4 - C_{28} alpha-olefins and polyolefins. Also, the ethylene-alpha olefin polymers useful in this invention exhibit a degree of crystallinity up to about 25%. The ethylene-alpha olefin polymer of this invention may be further characterized as having a viscosity average molecular weight within the range between about 10,000 and 250,000, preferably 50,000 to 100,000. Thus, contrary to Ser. No. 565,026, it has now been found that the ethylene-alpha olefin polymer of this invention need only be oil-soluble and have the requisite crystallinity, molecular weight and monomer content. These polymers are produced by well-known methods and the polymerization reaction per se does not constitute a part of the present invention.

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.

The ethylene-alpha olefin copolymers of this invention may be prepared, for example, by reacting from about 2 to about 98 wt. percent ethylene with about 98 to about 2 wt. percent of alpha-olefin, preferably propylene, in the presence of a soluble species of Ziegler catalyst, preferably a catalyst prepared by activating VCl_4 or $VOCl_3$ with an alkyl aluminum chloride. Into the monomeric mixture may be introduced a conventional chain transfer agent such as hydrogen fluoride, hydrogen chloride, hydrogen bromide, hydrogen iodide, hydrogen, etc. Also, if desired, the ethylene-alpha olefin polymer of this invention may be prepared by chemically, thermally, or mechanically degrading high molecular weight polymer in accordance with well-known techniques to produce a polymer having the requisite molecular weight and oil-solubility characteristics. Other methods of preparing the ethylene-alpha olefin polymer of the instant invention are given in copending application Ser. No. 657,064, filed July 31, 1967, which disclosure is incorporated herein in its entirety by express reference.

The resultant product which finds utility in the present invention has a viscosity average molecular weight (Mv.) of about 10,000 to 250,000 preferably from about 40,000 to 150,000 and most preferably from about 50,000 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 estimated on the basis of viscosity measurement at 135° F. of solutions which contained 0.5 milligram of polymer per milliliter of decalin.

A summary of typical ranges of catalyst concentrations, chain transfer agent concentrations, process variables and monomer percents in the final compositions follow. It is to be understood that due to the complexity and large number of the variable combinations possible, that some undesirable and, indeed, inoperable copolymers may result especially when the extremes of the various parameters are utilized. However, one skilled in the art should, with reasonable experimentation, be able to reproduce a copolymeric product exhibiting the physical characteristics of the ethylene-alpha-olefin copolymers and terpolymers of the present invention.

	Preferred	More preferred	Most preferred
Catalyst composition: Al/V molar ratio.....	0.5-25	1-12	2-7
Catalyst concentration in the solvent, p.p.m. by wt.....	1-1,000	5-500	10-200
Chain transfer agent concentration mole percent; based on the total moles of monomer feed.....	0.001-10	0.01-5	0.2-2.0
Process variables:			
Temperature, ° C.....	0-200	0-60	20-55
Pressures, p.s.i.g.....	0-2,000	0-300	0-100
Reaction of contact time mins.....	1-300	3-60	10-35
Percent of each component in the resulting elastomer:			
Wt. percent ethylene.....	40-90	50-88	80-88
Wt. percent propylene and/or other alpha-olefin.....	10-60	12-50	12-20

In general, the soluble catalysts which may be used in polymerizing the monomers of this invention can be formed by mixing an organo-aluminum halide with various vanadium compounds. These vanadium compounds may then be reacted with an aluminum alkyl compound in order to produce the final catalyst composition. Examples of the vanadium compounds which may be used include the vanadium oxyhalides, the vanadium tetrahalides, the vanadium oxyacetylacetonates, the alkyl vanadates, and the like. The copolymers may also be prepared with certain titanium compounds. The titanium compounds suitably employed are those that can be reacted with a selected vanadium compound to produce a reaction product which is a complex.

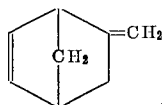
The alkyl aluminum compounds most conveniently used include those having the formula R_mAlX_n wherein R is a C_1 to C_{12} , preferably C_1 to C_8 , monovalent hydrocarbon radical, X is a halogen having an atomic number above 17, preferably chlorine or a C_1 to C_{12} , preferably C_1 to C_8 , monovalent hydrocarbon radical or hydrogen, m is an integer between 1 and 3 and the sum of m plus n is equal to 3. Specific examples of suitable R groups include methyl, ethyl, propyl, n-butyl, n-amyl, isoamyl, phenyl, tolyl, and cyclopentyl radicals.

Ethylene and a C_3 to C_{18} alpha-olefin can be copolymerized to prepare the additives of this invention. The alpha-olefin may be linear or branched where the branching occurs three or more carbon atoms from the double bond, and, while a single olefin is preferably, mixtures of these C_3 to C_{18} olefins may be employed. Suitable examples of C_3 to C_{18} alpha-olefins include: 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, the present invention also contemplates the use of a C_4 to C_{28} alpha-olefin and/or diolefin, polyolefin and the like which is copolymerized with ethylene and propylene to produce terpolymers. 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_{18} olefinic monomers may be employed.

The diolefins which are useful for copolymerization with ethylene and propylene include the bicyclic, alicyclic

or aliphatic nonconjugated diolefins containing from about 6 to about 28 carbon atoms, preferably from about 6 to 12 carbon atoms. Nonlimiting examples of suitable monomers include 1,5-cyclooctadiene, 1,5-hexadiene, dicyclopentadiene, 5-vinyl-2-norbornene, 1,5-cyclodecadiene, 2,4-dimethyl-2,7-octadiene, 3(2-methyl-1-propenyl)cyclopentene, 1,5-octadecadiene, and the like. Especially preferred is methylene-norbornene, that is:



A preferred embodiment of the instant invention is an ethylene-propylene-methylene norbornene terpolymer.

The polymer mixture of this invention is employed as an additive concentrate, i.e., a polymer blend in an inert solvent or neutral oil, in concentrations of about 0.1 to about 10 wt. percent, preferably between about 0.5 and about 5.0 wt. percent based on the oleaginous 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 oleaginous composition to which the additive concentrate is added. However, no more polymer mixture will be added than will be in solution in the oleaginous composition. Typically the additives are sold as concentrates wherein the polymeric blend is present in amounts of from about 5 to 50 wt. percent, preferably 8 to 40 wt. percent, weight percent based on the total amount of the inert solvent or neutral oil employed with the polymeric additive component. Suitable solvents and/or oils are well-known to the art and nonlimiting examples include mineral oils, hexane, heptane and the like.

Example 1

The following example is presented in order to illustrate a typical method of preparing the polyisobutylene component employed in the blends of this invention.

A series of experiments were accomplished in which isobutylene was polymerized with titanium tetrachloride and aluminum triethyl. The results are reported in Table I.

TABLE I.—POLYMERIZATION OF ISOBUTYLENE WITH AN ALUMINUM TRIETHYL-TITANIUM TETRACHLORIDE CATALYST SYSTEM

	Run			
	1	2	3	4
Catalyst:				
Ti component.....	TiCl ₄	TiCl ₄	TiCl ₄	TiCl ₄
Al/Ti ratio.....	0.05	0.5	0.5	0.5
Con. Ti halide, percent.....	1.6	1.6	0.8	0.15
Temp., °C.....	45	20	0	0
Time, hrs.....	2	0.5	1.5	1.25
Yield of polymer, percent.....	78	58	79	70
Viscosity average molecular weight (Mv×10 ⁻⁴).....	2.8	5.4	18	20.4

Example 2

The following example is presented in order to illustrate a typical method of preparing ethylene/propylene copolymers employed in the instant invention.

A series of copolymerizations of ethylene with propylene were carried out in a one gallon stirred, stainless steel autoclave operated at 60 p.s.i.g. pressure. The catalyst system used was composed of various species of vanadium compounds with diethyl aluminum chloride, which catalyst was used in amounts of approximately 0.2 wt. percent in diluent based on diluent weight. The operating conditions and the properties of the polymer produced from each run are summarized in Table II following.

TABLE II.—PREPARATION OF POLYMERS WITH ANHYDROUS HYDROGEN HALIDE

Run No.:	Temp., °C.	Residence time, min.	Monomer feed		Cat. feed, G./100 g. S.	al/V molar ratio	HCl feed ²	Rate of copolymer, g./hr.
			G./100 g. S. ¹	C ₂ , wt. percent				
A.....	38	15	7.0	22	0.008	3.0	0.40	385
B.....	38	15	8.0	20	0.006	4.0	0.15	437
C.....	38	15	9.0	34	0.004	5.0	0.27	526
Run No.:	Cat. eff., g./g.V	Conversion		Copolymer composition		Viscosity avg.		Catalyst system
		C ₂ , wt. percent	C ₃ , wt. percent	C ₂ , wt. percent	Inherent viscosity ³	mol. wt. (10 ⁻³)		
A.....	482	95	37	38.0	1.35	77	VOCl ₃ Et ₂ AlCl	
B.....	728	95	44.5	34.7	1.30	75	VOCl ₃ Et ₂ AlCl	
C.....	1,315	95	40	55.2(E)	1.67	85	VCl ₄ Et ₂ AlCl	

¹ All runs were made at 60 p.s.i.g. pressure in normal hexane solvent.

² Anhydrous HCl feed: wt. percent based on total monomer feed.

³ Decalin viscosity at 135° C.

The polymeric blend of the present invention can be employed alone in oleaginous compositions or, if desired, can be employed in combination with other viscosity index improvers in order to affect that characteristic of the base oleaginous composition. If desired, said blend may be employed in combination with other additives, for example, pour point depressants, detergent type additives corrosion inhibitors, anti-oxidants, sludge inhibitors, metal deactivators, etc.

While the disclosure has been directed to an oleaginous composition comprised of a lubricating oil, it is to be understood that the present invention also contemplates that the additives defined herein may, if desired be employed with various other oleaginous compositions such as, for example, gasoline, middle distillate fuels, transformer oils, greases, etc.

The following examples describe the invention more fully, both from a standpoint of the preparation of the polymer mixture and of their advantageous use in typical oleaginous compositions.

In accordance with the present invention, it is found that the above-described polymers of isobutylene and ethylene- α -olefin copolymers represent mutually soluble polymeric components and that mixtures of these two polymers in oil have highly unusual viscosity properties. It must be noted, however, that, in addition to using the polymers in the manner hereinbefore described, to achieve the desired properties, said polymers must be employed in certain relative weight ratios. Accordingly, the additive products which attain the objectives described above are derived exclusively from the foregoing polymers and used in such weight proportions so that the solvated individual polymeric components are miscible with each other. Compositions of said mixture; in terms of the solvent and individual components, lie approximately within the area similar to the ternary phase diagram of FIG. 1 which is incorporated herein by reference. Thus, said FIG. 1 represents an embodiment of the present invention wherein various blends of polyisobutylene-ethylene-propylene, in Solvent 150 Neutral oil are represented. As can be ap-

preciated from FIG. 1, the temperature of the blend concentrate is a factor of miscibility, however, it is well within the bounds of facile experimentation to complete ternary phase diagrams for other temperatures, as well as for different polymeric components, e.g., components of different monomeric origin, molecular weight, etc.

As is apparent, the curves of the figure represent compositional threshold values at which phase separation just begins to occur. Hence, a blend of about 10.5 weight percent ethylene/propylene copolymer with 5.5 wt. percent polyisobutylene in 84 wt. percent Solvent 150 Neutral oil (indicated by the dashed lines) would be miscible at temperatures of about -20° C. and above. Similarly a 10-10 wt. percent blend of ethylene/propylene copolymer with polyisobutylene in 80 wt. percent solvent would not be miscible at 25° C. and lower and would separate into phases.

It is to be understood that FIG. 1 is in keeping with the spirit of phase separation occurrence and that other factors, e.g., pressure, polymer purity, other blend components will affect the ternary phase behaviors but, as mentioned, the actual phase behaviors are easily ascertainable for each specific composition mixture.

Generally, however, the blends of the instant invention will range from about 3.0 to about 20.0 wt. percent of polyisobutylene and from about 2.0 to about 25.0 wt. percent of ethylene-alpha-olefin polymer, the remainder of the blend comprising neutral solvent for the components. When added to an oleaginous material, the resulting treated composition will usually contain from about 0.3 to about 2.0 wt. percent of polyisobutylene and about 0.2 to about 2.5 wt. percent of ethylene-alpha-olefin polymer. Thus, the relative amounts of polymeric constituents, without solvent, etc. will generally be from about 10 to about 90 wt. percent polyisobutylene

A sleeve is fixed within said cavity with a spindle adapted to rotate within said sleeve. The spindle comprises, in combination, a shaft, an insulator and a drum. The drum is provided with a pair of substantially symmetrical flats which create a continuously varying shear weight which simulates, to a degree heretofore unattainable, engine viscosity. The spindle is driven by means of a gear train responsive to a motor which gear train and motor also drive a tachometer for measuring rate of evolution of said spindle.

Broadly, the method of simulating the engine viscosity of a test oil comprises (a) cranking, at a substantially constant voltage, first oil sample of known viscosity (b) recording the thus-known viscosity and the corresponding cranking speed (c) repeating steps (a) and (b) using a second oil sample of known viscosity, thereby generating a positive viscosity versus speed (d) repeating step (a) using an oil of unknown viscosity (e) noting the cranking speed resulting from step (d) and reading the engine viscosity of said oil of unknown viscosity from said plot.

Using the above-mentioned engine viscosity simulator in the method referred to above, samples of polyisobutylene (molecular weight 130,000), and ethylene/propylene copolymer (molecular weight 130,000) and a mixture of said polyisobutylene in said ethylene/propylene copolymer were tested in a Solvent 150 Neutral. The resulting viscosities at various power inputs are recorded in Table III. The viscosity (cs.) at 200° F. for each sample is also recorded therein.

In order to illustrate the synergistic advantages accruing from use of the mixture of polyisobutylene and ethylene/propylene copolymer of this invention, the viscosity of same is compared with a numerical average of the polyisobutylene and ethylene/propylene copolymer-oil blends.

TABLE III.—MEASURED 0° F. VISCOSITIES (ENGINE VISCOSITY SIMULATOR) OF VARIOUS POLYMER-OIL BLENDS
[Viscosities in Poise]

Sample	Power input into engine viscosity simulator				Viscosity in cs. at 210° F.
	70 volts	80 volts	90 volts	100 volts	
2.00 wt. percent polyisobutylene plus solvent 150 neutral.....	31.5	30.0	29.0	24.5	12.46
2.05 wt. percent ethylene-propylene copolymer (Run C, Table II) plus solvent 150 neutral....	31.5	30.5	30.0	26.0	-----
1.00 wt. percent polyisobutylene plus 1.03 wt. percent ethylene-propylene copolymer (Run C, Table II) plus solvent 150 neutral....	31.5	31.0	31.0	27.5	11.93
Solvent 150 neutral.....	29.5	29.5	27.7	24.5	12.23
	19.0	19.0	19.0	19.0	-----

¹ Average.

and from about 9 to about 90 wt. percent ethylene-alpha-olefin copolymer.

Example 3

In this example the efficacy of the polyisobutylene-ethylene-propylene copolymer mixtures of this invention, with regard to their unusual viscosity-temperature properties, is illustrated by comparison with polyisobutylene and ethylenepropylene copolymers per se in oil blends.

In the comparison an engine viscosity simulator as disclosed in U.S. Ser. No. 456,343, filed May 17, 1965 (as incorporated herein by reference), now U.S. Pat. No. 3,350,922 was utilized. Said engine viscosity simulator comprises a sample holder provided with a cavity and with means for controlling the temperature thereof.

The foregoing data illustrate that a mixture of polyisobutylene and ethylene-propylene copolymer prepared using hydrogen halide exhibits a synergistic improvement when compared with either polyisobutylene or the ethylene-propylene copolymer per se or the numerical average thereof.

Example 4

This example serves to illustrate the fact that conventional polymeric V.I. improvers, other than those of the present invention, are not compatible for blending. The data in Table IV illustrates systems in which two conventional V.I. improvers were employed and the amounts utilized thereof. In each instance it is noteworthy that the components used were not compatible.

TABLE IV

Component A	Wt. percent, Component A	Component B	Wt. percent, Component B	Compatibility
High mol. wt. polymer (methylmethacrylate/C ₁₀ oxoacrylate).....	10	High mol. wt. polymer polyisobutylene...	10	Incompatible.
Alkylated polystyrene.....	10	Polyisobutylene.....	10	Do.
Do.....	10	Mixed alcohol methacrylate.....	10	Do.
Vinyl acetate-fumarateester.....	10	Do.....	10	Do.
Do.....	10	Polyisobutylene.....	10	Do.

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Example 5

An ethylene-propylene-methylene-norbornene copolymer is prepared in accordance with conventional procedures. The resulting terpolymer is blended with an isobutylene polymer prepared in accordance with Example 1. The resultant blend evidences utility as a viscosity improver for lubricating oils.

Example 6

Ethylene and propylene were continuously polymerized in the presence of n-heptane solvent, $\text{VOCl}_3 \cdot \text{Al}_2\text{Et}_3\text{Cl}_3$, and hydrogen. The polymerization reaction was carried out in a two-liter 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 fed 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 bone-dry 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 aluminum 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 V.

TABLE V

Temperature, ° C.	55
Solvent volume, liters @ 1 atm., 25° C.	1.5
Monomer feed composition:	
Volume percent propylene	75
Volume percent ethylene	25
Monomer feed rate, liters/min.	3.0
Hydrogen feed rate, cc./min. @ 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, min.	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. The copolymer recovered had the properties shown in Table VI.

TABLE VI

Mole percent ethylene	85.6
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. percent polyisobutylene (20,000 Staudinger mol. wt.) required to thicken Reference Oil 150 to a viscosity of 12±5 cs. at 210° F./wt. percent ethylene-propylene copolymer required to thicken Reference Oil 150 to the same viscosity.

In accordance with the present invention, the ethylene-propylene copolymer prepared in this example was blended with various amounts of the polyisobutylene of Example

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3 in Solvent 150 Neutral Oil. A ternary phase diagram essentially similar to FIG. 1 was obtained.

Variations of the present invention can be made without departing from the scope and spirit of the invention. Accordingly, the invention is restricted solely by the appended claims.

What is claimed is:

1. A compatible composition, which comprises a major proportion of a hydrocarbon solvent and from about 3.0 to about 20.0 wt. percent of polyisobutylene having a molecular weight within the range between about 20,000 and 200,000 and from about 2.0 to about 25.0 wt. percent of a second polymer comprised of 40 to 90 mole percent ethylene and 10 to 60 mole percent C_3 - C_{18} alpha-olefin; said second polymer being further characterized as having a viscosity average molecular weight within the range between about 10,000 and 250,000 and a crystallinity of less than 25%.

2. The composition of claim 1 wherein said hydrocarbon solvent is a mineral oil.

3. The composition of claim 2 wherein said alpha-olefin is propylene.

4. The composition of claim 3 wherein said second polymer contains 0-10 mole percent of a third monomer selected from the group consisting of C_4 - C_{28} alpha-olefins, C_6 - C_{28} nonconjugated diolefins and combinations thereof.

5. The composition of claim 4 wherein said third monomer is methylene-norbornene.

6. The composition of claim 3 wherein said second polymer comprises 50 to 88 mole percent ethylene and 12 to 50 mole percent propylene.

7. The composition of claim 6 wherein said second polymer has a viscosity average molecular weight within the range between about 50,000 and 100,000.

8. The composition of claim 7 wherein said second polymer comprises 80 to 88 mole percent ethylene and 12 to 20 mole percent propylene.

9. A mineral oil having incorporated therein the compatible composition of claim 1 in an amount sufficient to give a polyisobutylene content within the range between about 0.3 and 2.0 wt. percent and an ethylene-alpha olefin polymer content within the range between about 0.2 and 2.5 wt. percent.

10. A composition containing a major proportion of a mineral oil, from about 0.3 to about 2.0 wt. percent of polyisobutylene having a molecular weight within the range between about 20,000 and 200,000 and from about 0.2 to about 2.5 wt. percent of a polymer comprised of 40 to 90 mole percent ethylene and 10 to 60 mole percent C_3 - C_{18} alpha-olefin; said second polymer being further characterized as having a viscosity average molecular weight within the range between about 10,000 and 250,000 and a crystallinity of less than 25%.

11. The composition of claim 10 wherein said alpha-olefin is propylene.

References Cited

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