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3,756,954

DEGRADED ETHYLENE-PROPYLENE INTER-POLYMERS USEFUL AS VISCOSITY MODIFIERS FOR LUBRICANTS

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10 Claims

ABSTRACT OF THE DISCLOSURE

Interpolymers (especially copolymers) of ethylene and propylene are oxidized and degraded by heating above 100° C. with an oxygen-containing gas, usually air, in the presence of an aliphatic amine. The degraded polymers are characterized by causing substantially no increase in the low-temperature fluidity of a fuel oil, and are useful as viscosity modifiers for lubricants.

This invention relates to new compositions of matter suitable for use as viscosity modifiers in lubricating oils. More particularly, it relates to oil-soluble compositions characterized by causing substantially no increase in the fluidity of a fuel oil at -20° C. when dissolved in said fuel oil at a concentration of 0.02% by weight, said compositions being prepared by oxidizing and degrading an ethylene-propylene interpolymer having a molecular weight of at least about 1000 by contacting the same with an oxygen-containing gas, in the presence of a minor amount of at least one aliphatic amine, at a temperature of at least about 100° C. for a period of time sufficient to effect a substantial reduction in the molecular weight of said interpolymer.

The use of viscosity modifiers in lubricating oils has been known for some time. These materials are chosen for their ability to inhibit thickening of the lubricant at low temperatures and thinning at high temperatures. For many years, the "viscosity index" was used to measure this ability. The viscosity index was determined from the viscosity of the oil at 100° F. and 210° F., and increased in numeral value with increased effectiveness of the additive as a viscosity modifier. However, the viscosity index did not accurately reflect the behavior of the viscosity modifier at extremely low temperatures. An SAE 10W oil (including multi-grade oils such as 10W-30 and 10W-40) has for some time been required to have a viscosity at 0° F. of 24 poises or less. Formerly, 0° viscosity values determined by extrapolation from viscosities at higher temperatures were accepted, but it was found that these values were not accurate and the motor oil specifications now require that the 0° viscosity be determined experimentally by means of the Cold Crank Simulator Test (ASTM D2602). The high-temperature requirements of lubricants are reflected by a required minimum viscosity at 210° F. of 58 SUS for SAE 30 (including 10W-30) oils, and of 70 SUS for SAE 40 (including 10W-40) oils.

The use of olefin polymers, including ethylene-propylene interpolymers, as viscosity modifiers is also known. Such polymers are also used as low-temperature fluidity modifiers and pour point depressants in fuel oils; particularly valuable in this regard are certain oxidized, degraded polymers such as those described in U.S. Pat. 3,374,073. However, for some time there appeared to be no correlation between the effectiveness of a polymer as a fuel oil fluidity modifier and its effectiveness at low temperatures in lubricating oils. It was frequently found that although the polymer might inhibit thickening to some extent above the pour point in a motor oil, it not only did not lower the pour point but actually inhibited the effective-

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tiveness of pour point depressants separately added for that purpose.

A principal object of the present invention, therefore, is to provide new compositions for use as lubricant additives.

A further object is to provide viscosity-modifying lubricant additives suitable for use in multi-grade motor oils.

Another object is to provide viscosity-modifying additives which are compatible with pour point depressants when used in lubricating oils.

Another object is to provide improved lubricant compositions having a decreased tendency to thicken at low temperatures and thin at high temperatures, and having a low pour point.

Other objects will in part be obvious and will in part appear hereinafter.

The present invention is based partly on the discovery that there is, in fact, an inverse correlation between the efficiency of an ethylene-propylene interpolymer as a low temperature fluidity modifier in a fuel oil and its ability (as well as that of the lubricant as a whole) to respond positively to a pour point depressant in a lubricating oil. In other words, polymers which are effective as fuel oil fluidity modifiers are generally unresponsive to pour point depressants in lubricants, and render the lubricant similarly unresponsive when dissolved therein; and conversely, the polymers of the present invention, which serve as excellent viscosity modifiers in lubricating oils and are responsive (thus rendering the lubricant also responsive) to the action of a pour point depressant, are generally ineffective as fluidity modifiers in fuel oils. According to the invention, this ineffectiveness is primarily shown by a failure to substantially increase the fluidity of a fuel oil at -20° C. when dissolved therein at a concentration of 0.02% by weight. The principal ways of measuring fluidity are the Enjay Cold Flow Test and the Enjay Fluidity Test. In the first of these, a measured quantity of fuel is placed in a can which is stored in a cold box at the test temperature (in this instance, -20° C.) for 16-24 hours. A tube is then carefully inserted in to the fuel oil so as to avoid agitation thereof and a vacuum of 12 inches of mercury is applied to the system. The amount of fuel discharged outside of the cold box is measured as a function of time, and the flow rate and overall percentage of fuel removed from the can are determined.

In the Enjay Fluidity Test, 40 ml. of the fuel being tested is placed in a vessel to which is fastened a graduated cap with a capillary opening therein. The entire unit is cooled to the test temperature (-20° C.) and is then inverted, allowing the fuel oil to flow through the capillary. After 3 minutes, the volume of fuel which has passed through is measured.

As an alternative to the Enjay Cold Flow and Fluidity Tests, the effect of an additive on the low temperature fluidity of a fuel oil may be gauged roughly by its effect on the pour point thereof. Generally, the compositions of this invention will cause little or no lowering of the pour point: at most, about a 10° F. change therein will be noted.

The oxidized, degraded interpolymers (hereinafter sometimes referred to merely as "the degraded interpolymers") of this invention are derived principally from ethylene and propylene. They may include minor amounts, i.e., up to about 10% based on the amounts of monomeric ethylene and propylene units in the interpolymer, of polymerized units derived from other monomers. Examples of such other monomers include polymerizable mono-olefins having at least 4 carbon atoms such as 1-butene, 1-pentene, 2-butene, 3-hexene, 4-methyl-1-pentene, 1-decene, 1-nonene, 2-methylpropene, and 1-dodecene. They also include polymerizable polyenes, especially dienes; e.g.,

conjugated dienes such as butadiene, isoprene, piperylene, 1,3-hexadiene, 1,3-octadiene, 2,4-decadiene, etc., and non-conjugated dienes such as 3,3-dimethyl-1,5-hexadiene, 1,9-decadiene, dicyclopentadiene, 1,19-eicosadiene, 1,4-pentadiene, 1,5-hexadiene, 5-ethylidenenorbornene, etc. The non-conjugated dienes are especially useful. For the most part, such other monomers contain about 4-12 carbon atoms although they may contain as many as 25 carbon atoms.

Copolymers containing about 20-70% (by weight) propylene units and about 30-80% ethylene units, and terpolymers containing about 25-50% propylene, about 50-70% ethylene and about 1-10% non-conjugated diene units, are especially useful for the purposes of this invention, with the copolymers being preferred.

The interpolymers from which the degraded, polymers are derived usually have weight average molecular weights of at least 1000 and usually about 50,000-800,000, although polymers of higher molecular weight may sometimes be used. Those having molecular weights of about 80,000-600,000 are especially useful.

The degraded interpolymers are prepared most conveniently by heating an interpolymer such as illustrated above, or a fluid solution of such interpolymer in an inert solvent, with oxygen or air in the presence of a minor amount of an aliphatic amine as described hereinafter. A

is at least about 100° C., usually at least 140° C., and may be as high as 200° C., 300° C. or even higher.

Degradation of the interpolymer is characterized by a substantial reduction of its molecular weight. The mechanism by which the interpolymer is degraded is not precisely known, nor is the chemical composition of the degraded product. It is known, however, from infrared analysis that the product contains oxygen in the form of carboxylic acid, ester and carbonyl groups. An interpolymer as described above which has been degraded to the extent that its molecular weight is at least about 5% less than the molecular weight of the interpolymer before degradation is useful for the purposes of this invention. An interpolymer having a weight average molecular weight of about 3000-200,000, preferably 3000-5000, is preferred.

The preparation of the compositions of this invention is illustrated by a procedure in which solution in mineral oil of (1) various ethylene-propylene copolymers, or interpolymers with diene intermonomers, and (2) a commercially available C₁₁₋₁₄ tertiary alkyl primary amine mixture are blown with air at 150-160° C. for various periods of time. Reactants, concentrations, reaction conditions and the like are listed in Table I, all percentages being by weight. Following degradation, the oil solutions of the interpolymers are filtered, occasionally with the addition of a diarylamine oxidation inhibitor for filtration.

TABLE I

	Interpolymer		Percent		
	Percent ethylene (approx.)	Termonomer	Mooney viscosity	Interpolymer in soln.	Amine in soln.
Example:					
1.....	49	-----	154	15	0.5
2.....	53.7	-----	36	10	0.38
3.....	66	-----	42	15	0.5
4.....	60.8	-----	63	15	0.5
5.....	51	Dicyclopentadiene.....	45	15	0.5
6.....	65	do.....	57	15	0.48
7.....	65	5-ethylidenenorbornene.....		15	0.5

¹ 210° F.

² 0.8-1.5% (based on polymer) of a diarylamine antioxidant added before filtration.

³ 212° F.

mixture of oxygen and an inert gas such as nitrogen or carbon dioxide may be used. The inert gas then functions as a carrier of oxygen and often provides a convenient means of introducing oxygen into the reaction mixture.

The oxygen or air may be introduced by bubbling it through the polymer solution. However, it is frequently preferred to merely blow air over the surface of the solution while subjecting it to vigorous shearing agitation.

The inert solvent used in preparing the fluid solution of the interpolymer is preferably a liquid hydrocarbon such as naphtha, hexane, cyclohexane, dodecane, mineral oil, biphenyl, xylene, or toluene, an ether such as diphenyl oxide, or a similar non-polar solvent. The amount of the solvent is not critical so long as a sufficient amount is used to result in the fluid solution of the interpolymer. Such solution usually contains about 60-95% of the solvent.

In accordance with this invention, the mixture being degraded also contains a minor amount of at least one aliphatic amine. The amine serves as a color stabilizer under the conditions of the reaction. Its use is critical to the invention since it apparently inhibits destructive oxidation leading to highly colored by-products while allowing oxidation and degradation of the polymer to the extent required. The amine should, of course, be nonvolatile at the degradation temperature. It may be primary (e.g., t-octylamine) secondary (e.g., diamylamine) or tertiary (e.g., tributylamine and azomethines of primary amines). Tertiary alkyl primary amines, including commercially available mixtures of C₁₁₋₁₄ amines of this type, are preferred. The amount of amine used is usually about 1-5%, based on the weight of the polymer being degraded.

The temperature at which the interpolymer is degraded

The compositions of this invention can be employed in a variety of lubricating compositions based on diverse oils of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. The lubricating compositions contemplated include principally crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines including automobile and truck engines, two-cycle engine lubricants, aviation piston engines, marine and railroad diesel engines, and the like. However, automatic transmission fluids, trans-axle lubricants, gear lubricants, metal-working lubricants, hydraulic fluids, and other lubricating oil and grease compositions can benefit from the incorporation of the present compositions.

Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as solvent-refined or acid-refined mineral lubricating oils of the paraffinic, naphthenic, or mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils. Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, etc.); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzene, dinonylbenzenes, di-(2-ethylhexyl)benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyls, etc.); and the like. Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol ether hav-

ing an average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃-C₈ fatty acid esters, or the C₁₃ Oxo acid diester of tetraethylene glycol. Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, pentaerythritol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didodecyl phthalate, diicosyl sebacate, the 2-ethyl-hexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid, and the like. Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants (e.g.,

tetraethyl silicate,
tetraisopropyl silicate,
tetra-(2-ethyl-hexyl) silicate,
tetra-(4-methyl-2-tetraethyl) silicate,
tetra-(p-tert-butylphenyl) silicate,
hexyl-(4-methyl-2-pentoxy)-disiloxane,
poly(methyl)-siloxanes,
poly(methylphenyl)-siloxanes, etc.).

Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decane phosphonic acid, etc.), polymeric tetrahydrofurans, and the like.

In general, about 0.05-20.0 parts (by weight) of the composition of this invention (excluding diluent) is dissolved in 100 parts of oil to produce a satisfactory lubricant. The invention also contemplates the use of other additives in combination with the products of this invention. Such additives include, for example, detergents and dispersants of the ash-containing or ashless type, oxidation inhibiting agents, pour point depressing agents, extreme pressure agents, color stabilizers and anti-foam agents.

The ash-containing detergents are exemplified by oil-soluble neutral and basic salts of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, or organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage such as those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a molecular weight of 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium and barium.

The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the basic salts involve heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature above 50° C. and filtering the resulting mass. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-

propanol, octyl alcohol, Cellosolve, carbitol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; and amines such as aniline, phenylenediamine, phenothiazine, phenyl-β-naphthylamine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent, a phenolic promoter compound, and a small amount of water and carbonating the mixture at an elevated temperature such as 60-200° C.

Ashless detergents and dispersants are illustrated by the interpolymers of an oil-solubilizing monomer, e.g., decyl methacrylate, vinyl decyl ether, or high molecular weight olefin, with a monomer containing polar substituents, e.g., aminoalkyl acrylate or poly(oxyethylene)-substituted acrylate; the amine salts, amides, and imides of oil-soluble monocarboxylic or dicarboxylic acids such as stearic acid, oleic acid, tall oil acid, and high molecular weight alkyl or alkenyl-substituted succinic acid. Especially useful as ashless detergents are the acylated polyamines and similar nitrogen compounds containing at least about 54 carbon atoms as described in U.S. Pat. 3,272,746; reaction products of such compounds with other reagents including boron compounds, phosphorus compounds, epoxides, aldehydes, organic acids and the like; and esters of high molecular weight carboxylic acids as described in U.S. Pats. 3,381,022 and 3,542,678.

Extreme pressure agents and corrosion-inhibiting and oxidation-inhibiting agents are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulfides and polysulfides such as benzyl disulfide, bis(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized sperm oil, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, and sulfurized terpene; phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate; phosphorus esters including principally dihydrocarbon and trihydrocarbon phosphites such as dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentyl phenyl phosphite, dipentyl phenyl phosphite, tridecyl phosphite, distearyl phosphite, dimethyl naphthyl phosphite, oleyl 4-pentylphenyl phosphite, polypropylene (molecular weight 500)-substituted phenyl phosphite, diisobutyl-substituted phenyl phosphite; metal thiocarbamates, such as zinc dioctyldithiocarbamate, and barium heptylphenyl dithiocarbamate; Group II metal phosphorodithioates such as zinc dicyclohexylphosphorodithioate, zinc dioctylphosphorodithioate, barium di(heptylphenyl)-phosphorodithioate, cadmium dinonylphosphorodithioate, and the zinc salt of a phosphorodithioic acid produced by the reaction of phosphorus pentasulfide with an equimolar mixture of isopropyl alcohol and n-hexyl alcohol.

Typical of lubricating compositions included in this invention are solutions in mineral oil of a product of any of Examples 1-7 and other additives, as follows (all parts being by weight and exclusive of solvent):

	Parts
Mineral oil	95.24
Product of this invention	1.0
Pentaerythritol ester of polyisobutenyl succinic acid	1.88
Basic calcium petroleum sulfonate	0.97
Zinc salt of a mixture of diisobutyl- and di-(primary amyl) phosphorodithioic acid	0.74
Terpolymer of vinyl acetate ethyl vinyl ether and (C ₁₂₋₁₄ dialkyl) fumarate	0.17
Silicone anti-foam agent	0.006

These compositions are characterized by low pour point and 0° F. viscosity. By contrast, the polymers of Examples 1-7, when dissolved in fuel oil at a concentration of 0.02% by weight (exclusive of solvent), have substantially no effect on the fluidity thereof at -20° C.

What is claimed is:

1. A lubricating composition comprising a major amount of a lubricating oil and a minor amount effective

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to improve viscosity of an oil-soluble composition of matter which causes substantially no increase in the fluidity of a fuel oil at -20°C . when dissolved in said fuel oil at a concentration of 0.02% by weight, said oil-soluble composition being prepared by oxidizing and degrading an ethylene-propylene interpolymers containing about 20 to 70% propylene units and 30 to 80% ethylene units by weight having a molecular weight of about 1000-800,000 by contacting the same with an oxygen-containing gas, in the presence of a minor color stabilizing amount of at least one alkyl amine, at a temperature of at least about 100°C . for a period of time sufficient to effect a reduction of at least about 5% in the molecular weight of said interpolymers.

2. A lubricating composition according to claim 1 wherein the interpolymers contains only ethylene and propylene units.

3. A lubricating composition according to claim 2 wherein the interpolymers contains about 20-70% propylene units and about 30-80% ethylene units.

4. A lubricating composition according to claim 3 wherein the amine is a mixture of C_{11-14} tertiary alkyl primary amines.

5. A lubricating composition according to claim 4 wherein the interpolymers before degradation has a molecular weight of about 50,000-800,000.

6. A lubricating composition according to claim 4 wherein the interpolymers after degradation has a molecular weight of about 3000-200,000.

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7. A lubricating composition according to claim 1 wherein the interpolymers is a terpolymer containing about 25-50% propylene units, about 50-75% ethylene units and about 1-10% of units derived from a non-conjugated diene.

8. A lubricating composition according to claim 7 wherein the amine is a mixture of C_{11-14} tertiary alkyl primary amines.

9. A lubricating composition according to claim 8 wherein the terpolymer before degradation has a molecular weight of about 50,000-800,000.

10. A lubricating composition according to claim 8 wherein the terpolymer after degradation has a molecular weight of about 3000-200,000.

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