

Description

The present invention relates to additives for improving the flow properties and viscometric properties of certain oleaginous compositions and to oleaginous compositions containing said additives. More particularly, the present invention relates to additives for improving the low temperature flow properties and viscometric properties such as viscosity index of lubricating oil compositions and to lubricating oil compositions containing said additives. Still more particularly, the present invention relates to improved lubricating oil compositions including such additives and exhibiting improved low temperature flow properties and viscometric properties. The present invention also relates to methods for improving the flow properties and viscometric properties of oleaginous composition, particularly engine crankcase lubricant compositions.

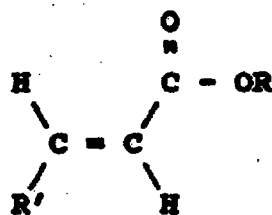
A wide variety of compounds for use as lubricating oil or fuel oil additives are known in this art. These include compounds variously referred to as pour point depressants, viscosity index improving compositions, wax crystal modifiers, and the like. In particular, Cashman et al., U.S. Patent No. 2,825,717, discloses the preparation of certain lubricating oil additives by the copolymerization of polycarboxylic acid esters with other polymerizable monomeric materials, including vinyl compounds such as vinyl acetate. The preferred unsaturated polycarboxylic acid esters therein are fumaric acid esters produced from C_1 through C_{18} aliphatic alcohols.

Bartlett, U.S. Patent No. 2,818,602, discloses pour point depressing and/or viscosity index improving materials obtained by polymerizing certain specified alkyl fumarate esters. In particular this patentee discloses the use of polymerized fumarate esters of C_{12} to C_{14} alcohols for such purposes. This patent specifically discloses that the C_{12} alcohol was more effective than the C_{14} alcohol, although both polymerized esters exhibited pour point depressing properties.

Rossi et al., U.S. Patent No. 4,089,589, discloses the use of specified mixtures of lubricating oil pour point depressants which include polyesters consisting of a polymeric ester of acrylic acid or methacrylic acid and a monohydric alcohol containing from 10 to 18 carbon atoms, and/or interpolymers of a vinyl alcohol ester of a C_2 to C_{18} alkanolic acid (e.g., vinyl acetate) and a di(C_6 - C_{18} alkyl) fumarate as one of the components thereof for improving the viscosity index of high wax content lubricating oils which also include viscosity index improving ethylene copolymers. Also, Wyman, U.S. Patent No. 3,250,715, discloses terpolymers of dialkyl fumarates, vinyl esters, and alkyl vinyl ethers for improving the pour point of lubricating oils, and most particularly in which the dialkyl fumarates are prepared for various C_{10} through C_{18} alcohols including tetradecyl alcohol alone as well as alcohol mixtures averaging from 12 to 14 carbon atoms.

There has also been disclosed in EP-A-153176 and EP-A-153177, the use in various middle distillate fuel compositions for lowering the pour point and controlling the size of wax crystals in these composition additives which specifically include polymers and copolymers of specific dialkyl fumarate vinyl acetate copolymers. Most specifically, these patent applications disclose the use of such additives in which the average number of carbon atoms in the alkyl groups in the polymer or copolymer must be from 12 to 14. In addition these additives are also disclosed as being useful in combination with the polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof, as well as with various other additives. Furthermore, British Patent No. 2,023,645 discloses, for use in treating distillate fuel oils, various three-component systems which include as a first component flow improvers having an ethylene backbone, such as various ethylene polymers including ethylene polymerized with various mono- or diesters (e.g., vinyl acetate; and C_{13} fumarates), as a second component a lube oil pour depressant such as various oil soluble esters and/or higher olefin polymers (e.g., dialkyl fumarate, vinyl acetate copolymers), and as a third component various polar oil-soluble compounds (e.g., phenates, sulfonates, phosphates, and carboxylates).

It is also disclosed in Lewtas's U.S. Patent Nos. 4,661,121 and 4,661,122 that the size of wax crystals forming in fuels boiling in the range of 120°C to 500°C can be controlled by an additive which includes the polymers and copolymers of mono- and di-n-alkyl esters of mono-ethylenically unsaturated C_4 to C_8 mono- or dicarboxylic acids, in which the average number of carbon atoms in the n-alkyl groups is from 14 to 18. These patents show a preference for copolymers of di-n-alkyl fumarates and vinyl acetate, and specifically state that the fumarates can be made from single alcohols or mixtures of alcohols, and when mixtures are used they are mixed prior to esterification. Furthermore, these patents disclose the use of various ethylene unsaturated ester copolymer flow improvers as co-additives therewith, but do not specify that these additives are produced from alcohol mixtures. In EP-A-316108 there is disclosed as a dewaxing aid a copolymer of dialkyl fumarate and vinyl acetate in which a large proportion of the alkyl groups are C_{20} to C_{24} alkyl groups. In EP-A-269714 there is disclosed a dual component flow improver additive composition for oleaginous compositions which comprises (i) low molecular weight polymers and interpolymers (e.g., copolymers) of unsaturated mono- or dicarboxy esters having the formula



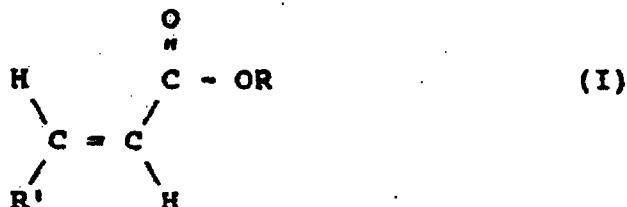
in which R' is either hydrogen or a COOR radical, and R is a C₁₄ alkyl group; and (ii) low molecular weight lubricating oil flow improver (LOFI) comprising non-ethylene containing polymers which are soluble or dispersible in these lubricating oils, preferably interpolymers of dialkyl fumarates and vinyl esters in which the fumarates are esterified with mixtures of C₆ through C₂₀ alcohols.

Various oil-soluble hydrocarbon polymeric materials such as ethylene-alpha-olefin copolymers, e. g., ethylene-propylene copolymers, are known to be useful as viscosity index improvers for oleaginous compositions such as lubricating oils.

While these various types of additive compositions have met with various degrees of success in the particular environments in which they are employed it has been observed that various lubricating oil compositions, such as those containing certain viscosity improving additives such as copolymers of ethylene and propylene, as well as those lubricating oil compositions containing lubricating oil flow improvers, nevertheless experience difficulty in passing recently adopted, more stringent, low temperature, slow cool performance tests designed to measure the low temperature pumpability of crankcase lubricating oils. It is therefore an object of the present invention to provide oleaginous compositions, particularly lubricating oil compositions, which exhibit enhanced low temperature pumpability and viscometric properties.

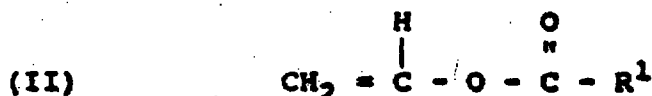
SUMMARY OF THE INVENTION

In accordance with the present invention there is provided an oleaginous composition, particularly a lubricating oil composition, exhibiting improved low temperature flow properties and viscometric properties which comprises lubricating oil and (i) from 0.19 to 1.5 wt % of a first additive or component which is a lubricating oil flow improver (LOFI) comprising low molecular weight, i.e. number average molecular weight ($\bar{M}_n$) of not greater than 40,000, polymers and interpolymers (e.g., copolymers) of unsaturated mono- or dicarboxy esters having the formula:



in which R' is either hydrogen or a COOR radical, and R is a C₁₄ alkyl group; and (ii) from 0.01 to 10 wt % of a second additive or component which is an oil soluble hydrocarbon polymeric viscosity index improver, preferably an ethylene-alpha-olefin copolymer.

In a preferred embodiment of the present invention, the first additive, i.e., lubricating oil flow improver, comprises a low molecular weight ($\bar{M}_n$) interpolymers of at least one of the carboxy ester monomers of formula (I) above interpolymers with a variety of different comonomers such as a polymerizable vinyl ester monomeric compound having the formula:



in which R¹ is an alkyl group containing from about 1 to 18 carbon atoms, preferably from about 1 to 6 carbon atoms, and most preferably 1 carbon atom. The preferred ester monomer of formula (II) is vinyl acetate.

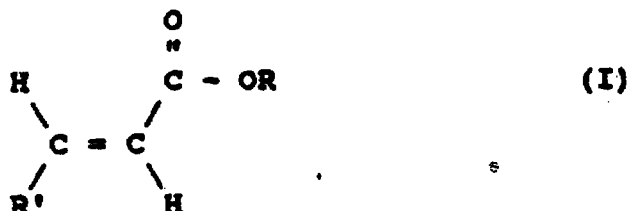
The second additive, i.e., the viscosity index improver, comprises an oil soluble hydrocarbon polymer, pre-

ferably an ethylene-alpha-olefin copolymer, and more preferably an ethylene-propylene copolymer.

DETAILED DESCRIPTION

The oleaginous compositions of the present invention comprise (i) oleaginous material, preferably lubricating oil, generally in a major amount; (ii) first additive comprised of polymers or interpolymers of unsaturated carboxy esters; and (iii) second additive comprised of a hydrocarbon polymeric viscosity index improver.

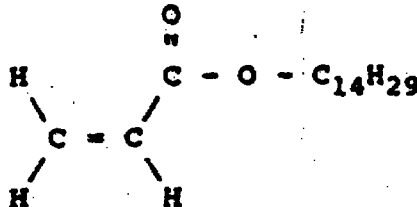
The first additive of the present invention is a lubricating oil flow improver and is comprised of a polymer or interpolymer represented by the formula



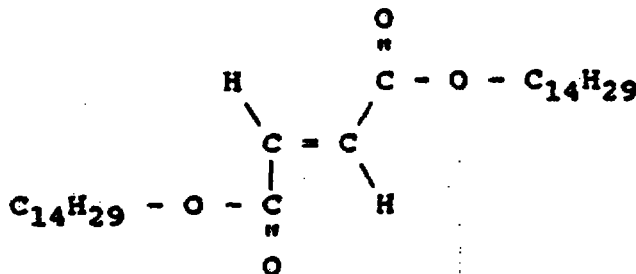
in which R' is either hydrogen or the COOR radical, and in which R is a C₁₄ alkyl group. The production of these ester and diester polymers includes an esterification reaction between unsaturated mono- or dicarboxylic acids or their corresponding anhydrides, as well as the polymerization of the esterified monomers and C₁₄ alcohols, and is well known in the art, as specifically disclosed beginning at column 2, line 35 of Cashman et al., U.S. Patent No. 2,825,717.

While the alkyl group represented by R may be straight chain or slightly branched, the straight chain alkyl group is preferred.

Some illustrative examples of compounds of formula I include



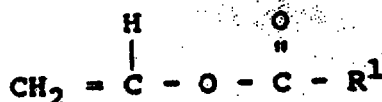
and



The first additive or component may be a homopolymer, e.g., a homopolymer derived from monomers of formula I, or an interpolymer as defined hereinafter.

The first additive or component preferably includes the interpolymers of the diester monomers of formula (I), wherein R' is COOR, with certain specified polymerizable monomeric compounds, namely vinyl esters, alpha-olefins, or styrenes such as styrene itself. One of these copolymerizable compounds is a monomer of formula

(II)



In which R¹ is an alkyl group containing from 1 to about 18 carbon atoms, preferably from 1 to about 6 carbon atoms, and most preferably 1 carbon atom, preferably vinyl acetate, which is interpolymerized with the diester of formula I in a reaction which is carried out in the presence of free radical initiators, such as peroxide catalyst.

The first component is characterized by a low molecular weight, i.e., a number average molecular weight (M_n) of not greater than about 40,000, and typically ranging from 1,500 to 40,000, and preferably from 2,500 to 15,000.

Alternatively, such molecular weights of the first component lubricating oil flow improvers of the present invention are more conveniently expressed by the specific viscosity exhibited by such polymers. Accordingly, such specific viscosities will typically range from 0.11 to 2.2, preferably from 0.2 to 0.9, and most preferably from 0.2 to 0.7.

Such specific viscosities are determined in accordance with the following equation:

$$\text{Specific Viscosity} = \frac{K - \text{vis of Solution}}{K - \text{vis of Solvent}} - 1$$

wherein "K-vis of Solution" is the kinematic viscosity at 40°C (104°F) of a 2.0 mass/volume percent solution of the polymer (a.i. basis) in mixed xylenes (solvent) available commercially, using Ubbelohde-type viscometers with a viscometer constant of about 0.003 mm²/s (cSt), second; and the "K-vis of Solvent" is the corresponding kinematic viscosity of the solvent alone at the same temperature. All specific viscosities reported herein are determined by the above method.

When interpolymers of monomer components depicted by formulas (I) and (II) are employed as the first component, the mole ratio employed for the polymerization of such monomers can typically vary from 1.3:1 to 0.5:1, preferably from 1.2:1 to 0.5:1, and most preferably from 1.2:1 to 1:1.

The particular dicarboxylic acid or anhydride monomer which is preferred will depend on the identity of its comonomer. Thus, when the comonomer is a vinyl ester, the preferred dicarboxylic acid is fumaric acid.

Furthermore, whether it is preferable to esterify the dicarboxylic acid or anhydride monomer first and then interpolymerize, or to first interpolymerize the free acid or anhydride monomer and then esterify, depends on the particular identity of the dicarboxylic monomer and its comonomer.

Thus, for example, it is conventional to first esterify the fumaric acid monomer or any other dicarboxylic monomer, prior to interpolymerization with a vinyl ester.

Moreover, while it is preferred to achieve complete esterification of all of the carboxyl groups of the dicarboxylic monomer, it is permissible to achieve only partial esterification, of typically not less than about 70, and preferably not less than about 80, mole % of the available esterifiable carboxyl groups.

Accordingly, esterification is conducted with a C₁₄ alcohol, which alcohol can be slightly branched or straight chain, preferably straight chains, and most preferably straight chain alkyl. Thus, the alcohol used for esterification is selected from the C₁₄ aliphatic alcohols. Primary alcohols are preferred over secondary and tertiary alcohols, and straight and lightly branched chain alcohols are preferred over highly branched alcohols.

As indicated hereinafore, the dicarboxylic monomer of formula I can be interpolymerized with a variety of different comonomers. The first of these comonomers, as indicated hereinafore, is a vinyl ester represented by formula II, with the preferred ester monomer of formula II being vinyl acetate. The preferred interpolymer of this class of lubricating oil flow improvers is C₁₄ dialkyl fumarate/vinyl acetate copolymer.

The interpolymers can be prepared by conventional free radical polymerization techniques, starting with a mixture of all of the constituent monomers which is essentially free of polymer. Thus the polymers are random interpolymers and are not graft or block interpolymers. Conventional free radical polymerization catalysts, such as azobis-(isobutyronitrile), tert-butyl hydroperoxide, and benzoyl peroxide, can be used. Such polymerization techniques can be conducted neat in the absence of solvent or in bulk.

Polymerization of the ester monomers is preferably carried out in an inert hydrocarbon solvent, such as hexane or heptane, or low viscosity lubricating oils. Polymerization is carried out in an oxygen-free reactor. The desired atmosphere can be maintained by carrying out the polymerization in a nitrogen atmosphere as is known in the art. Temperatures of 65 to 150°C, depending on the choice of initiator, can be used. Polymerization is carried out at either atmospheric or super-atmospheric pressure and on either a batch or a continuous basis. Polymerization can be stopped when the described degree of polymerization is reached by known techniques, such as adding inhibitors to the reaction mixture, or can be allowed to go to completion.

The second type of comonomer employed for interpolymerization with the unsaturated dicarboxyl monomer is an alpha-olefin. Straight chain alpha-olefins are preferred over branched chain alpha-olefins. Moreover,

if branching occurs, it is preferred that it occur at the beta-carbon, and that such branching contain not more than about 5, and preferably not more than about 2, carbons. Suitable alpha-olefins typically contain between about 6 and 46, e.g., between about 10 and 22, and preferably about 18 carbon atoms per molecule. Mixtures of olefins may be used, e.g., a C₁₀-C₂₄ mixture.

Representative olefins include 1-hexene, 1-heptene, 1-nonene, 1-decene, 1-hexadecene, 1-octadecene, 1-eicosene, 1-heneicosene, 1-docosene, 1-tricontene, 1-tetracontene, 2-methyloctadecene, 2-ethyleicosene, and mixtures thereof.

The mole ratio of alpha-olefin to unsaturated dicarboxyl monomer employed in the reaction mixture will typically range from 1.2:1 to 0.8:1, preferably from 1.1:1 to 0.9:1, and most preferably about 1:1.

The third preferred comonomer for interpolymerization with the unsaturated dicarboxy monomer is a styrene compound such as styrene.

In forming this preferred unesterified intermediate polymer, the molar ratio of styrene to unsaturated dicarboxy-containing monomer (e.g., maleic anhydride) can typically vary from 3:1 to 1:1, preferably from 2:1 to 1:1, and most preferably from 1.5:1 to 1:1.

Most preferably, equal molar amounts of styrene and unsaturated carboxy containing monomer are employed. In addition, minor amounts of other miscellaneous interpolymerizable comonomers can be included in the reaction mixture. By minor amount is typically meant less than about 1, preferably less than about 0.3 mole of miscellaneous monomers per mole of carboxy containing monomer. Similar considerations, vis-a-vis miscellaneous monomers, apply with respect to use of the alpha-olefins as a comonomer for interpolymerization with the dicarboxy monomer.

Various methods of polymerizing styrene or the alpha-olefins and the dicarboxy-containing monomers are known in the art and need not be discussed in detail herein. Such methods include neat and bulk polymerization techniques.

The polymerization reaction for use of either the styrene or alpha-olefin comonomers with the dicarboxy monomer is typically conducted to produce an unesterified interpolymer having a number average molecular weight of less than about 25,000, preferably less than about 15,000, as determined by membrane osmometry. Upon esterification, such molecular weights will be as described generally above as well as the corresponding specific viscosities.

The resulting interpolymer is then esterified with the C₁₄ alcohol of the type described above with respect to esterification of the dicarboxy monomer.

The esterification reaction can be accomplished simply by heating the dicarboxy-containing polymer and the C₁₄ alcohol under conditions typical for effecting esterification. Such conditions usually include, for example, a temperature of at least about 80°C, preferably from 100°C to 150°C, provided that the temperature be below the decomposition point of the reaction mixture, and the water of esterification is removed as the reaction proceeds. Such conditions may optionally include the use of an excess of the alcohol reactant so as to facilitate esterification, the use of a solvent or diluent such as mineral oil, toluene, benzene, xylene or the like, and the use of an esterification catalyst such as toluene sulfonic acid, sulfuric acid, phosphoric acid, or the like. These conditions and variations thereof are well known in the art.

The first additive or component compositions of this invention are oil-soluble, dissolvable in oil with the aid of a suitable solvent, or are stably dispersible materials. Oil-soluble, dissolvable, or stably dispersible as that terminology is used herein does not necessarily indicate that the materials are soluble, dissolvable, miscible, or capable of being suspended in oil in all proportions. It does mean, however, that the first additive composition, for instance, is soluble or stably dispersible in oil to an extent sufficient to exert its intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular first additive composition hereof, if desired.

The lubricating oil compositions of the present invention contain an amount of said first additive or component composition which is effective to improve the flow properties, particularly low temperature flow properties, of the lubricating oil composition, i.e., a lubricating oil flow improving effective amount. Generally, this effective amount may vary somewhat depending on the particular type of oil. Accordingly, while any effective amount of the first additive composition can be incorporated into the final, e.g., fully formulated, lubricating oil composition, it is contemplated that such effective amount be sufficient to provide said lube oil composition with an amount of the first additive composition of from 0.19 to 1.5, preferably from 0.19 to 1.0, and more preferably from 0.19 to 0.5 wt. percent, based on the weight of said lubricating composition.

The second additive or component of the instant invention is a viscosity index improver or modifier comprised of a hydrocarbon polymer.

These oil-soluble hydrocarbon polymeric viscosity index (V.I.) improver additives contemplated to be compounded into the lubricating oil in accordance with this invention are generally high molecular weight hydrocarbon polymers. The V.I. improvers may also be derivatized to include other properties or functions, such as

the addition of dispersancy properties.

These oil soluble V.I. polymers will generally have number average molecular weights of from 20,000 to 1,000,000, preferably from 40,000 to 300,000, as determined by gel permeation chromatography or membrane osmometry.

Examples of suitable hydrocarbon polymers include homopolymers and interpolymers of two or more monomers of C_2 to C_{30} , e.g., C_2 to C_8 olefins, preferably ethylene and C_3 to C_{30} olefins, including both alpha-olefins and internal olefins, particularly preferred being the copolymers of ethylene and propylene. Other polymers can be used such as polyisobutylenes, homopolymers and interpolymers of C_6 and higher alpha-olefins, atactic polypropylene, hydrogenated polymers and copolymers and terpolymers of styrene, e.g., with isoprene and/or butadiene.

More specifically, other hydrocarbon polymers suitable as viscosity index improvers in the present invention include those which may be described as hydrogenated or partially hydrogenated homopolymers, and random, tapered, star or block interpolymers (including terpolymers, tetrapolymers, etc.) of conjugated dienes and/or monovinyl aromatic compounds with, optionally, alpha-olefins or lower alkenes, e.g., C_3 to C_{18} alpha-olefins or lower alkenes. The conjugated dienes include isoprene, butadiene, 2,3-dimethylbutadiene, piperylene and/or mixtures thereof, such as isoprene and butadiene. The monovinyl aromatic compounds include any of the following, or mixtures thereof, vinyl di- or polyaromatic compounds, e.g., vinyl naphthalene, but are preferably monovinyl monoaromatic compounds, such as styrene or alkylated styrenes substituted at the alpha-carbon atoms of the styrene, such as alpha-methylstyrene, or at ring carbons, such as o-, m-, p-methylstyrene, ethylstyrene, propylstyrene, isopropylstyrene, butylstyrene, isobutylstyrene, tert-butylstyrene (e.g., p-tert-butylstyrene). Also included are vinylxylenes, methylethyl styrenes and ethylvinylstyrenes. Alpha-olefins and lower alkenes optionally included in these random, tapered and block copolymers preferably include ethylene, propylene, butene, ethylene-propylene copolymers, isobutylene, and polymers and copolymers thereof. As is also known in the art, these random, tapered and block copolymers may include relatively small amounts, that is less than about 5 moles, of other copolymerizable monomers such as vinyl pyridines, vinyl lactams, methacrylates, vinyl chloride, vinylidene chloride, vinyl acetate, vinyl stearate, and the like.

Specific examples include random polymers of butadiene and/or isoprene and polymers of isoprene and/or butadiene and styrene. Typical block copolymers include polystyrene-polyisoprene, polystyrene-polybutadiene, polystyrene-polyethylene, polystyrene-ethylene propylene copolymer, polyvinyl cyclohexane-hydrogenated polyisoprene, and polyvinyl cyclohexane-hydrogenated polybutadiene. Tapered polymers include those of the foregoing monomers prepared by methods known in the art. Star-shaped polymers typically comprise a nucleus and polymeric arms linked to said nucleus, the arms being comprised of homopolymer or interpolymers of said conjugated diene and/or monovinyl aromatic monomers. Typically, at least about 80% of the aliphatic unsaturation and about 20% of the aromatic unsaturation of the star-shaped polymer is reduced by hydrogenation.

Representative examples of patents which disclose such hydrogenated polymers or interpolymers include U.S. Patent Nos. 3,312,621; 3,318,813; 3,630,905; 3,668,125; 3,763,044; 3,795,615; 3,835,053; 3,838,049; 3,965,019; 4,358,565; and 4,557,849.

The polymer may be degraded in molecular weight, for example by mastication, extrusion, oxidation or thermal degradation, and it may be oxidized and contain oxygen. Also included are derivatized polymers such as post-grafted interpolymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol, or amine, e.g., an alkylene polyamine or hydroxy amine, e.g., see U.S. Patent Nos. 4,089,794; 4,160,739; 4,137,185; or copolymers of ethylene and propylene reacted or grafted with nitrogen compounds such as shown in U.S. Patent Nos. 4,068,056; 4,068,058; 4,146,489; and 4,149,984.

Suitable hydrocarbon polymers are ethylene interpolymers containing from 15 to 90 wt. % ethylene, preferably 30 to 80 wt. % of ethylene and 10 to 85 wt. %, preferably 20 to 70 wt. % of one or more C_3 to C_8 , alpha-olefins. While not essential, such interpolymers preferably have a degree of crystallinity of less than 10 wt. %, as determined by X-ray and differential scanning calorimetry. Copolymers of ethylene and propylene are most preferred. Other alpha-olefins suitable in place of propylene to form the copolymer, or to be used in combination with ethylene and propylene, to form a terpolymer, tetrapolymer, etc., include 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, etc.; also branched chain alpha-olefins, such as 4-methyl-1-pentene, 4-methyl-1-hexene, 5-methylpentene-1, 4,4-dimethyl-1-pentene, and 6-methyl-heptene-1, etc., and mixtures thereof.

Terpolymers, tetrapolymers, etc., of ethylene, said C_{3-8} alpha-olefin, and a non-conjugated diolefin or mixtures of such diolefins may also be used. The amount of the non-conjugated diolefin generally ranges from about 0.5 to 20 mole percent, preferably from about 1 to about 7 mole percent, based on the total amount of ethylene and alpha-olefin present.

The second additive or component compositions of this invention are oil-soluble, dissolvable in oil with the

aid of a suitable solvent, or are stably dispersible materials. Oil-soluble, dissolvable, or stably dispersible as that terminology is used herein does not necessarily indicate that the materials are soluble, dissolvable, miscible, or capable of being suspended in oil in all proportions. It does mean, however, that the second additive composition, for instance, is soluble or stably dispersible in oil to an extent sufficient to exert its intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular first additive composition hereof, if desired.

The lubricating oil compositions of the present invention contain an amount of said second additive or component composition which is effective to improve the viscometric properties, particularly viscosity index of the lubricating oil composition, e.g., a viscosity index improving effective amount. Generally, this effective amount may vary somewhat depending upon the particular type of oil. Accordingly, while any effective amount of the second additive composition can be incorporated into the final, e.g., fully formulated, lubricating oil composition, it is contemplated that such effective amount be sufficient to provide said lube oil composition with an amount of the second additive composition of from 0.01 to 10, preferably from 0.05 to 5, and more preferably from 0.1 to 2.5 (most preferably to 3.0) wt. percent, based on the weight of said lubricating composition.

The additive compositions of the present invention can be incorporated into the lubricating oil in any convenient way. Thus, they can be added directly to the oil by dispersing, or dissolving the same in the oil at the desired level of concentration. Such blending can occur at elevated temperatures. Alternatively, the additive compositions may be blended with a base oil to form a concentrate, and the concentrate then blended with lubricating oil base stock to obtain the final composition. Such concentrates will typically contain the first additive composition in amounts of from 0.5 to 6, preferably from 0.5 to 5 percent by weight, based on the concentrate weight, and the second additive composition in amounts of from 0.5 to 20, preferably from 0.5 to 12 percent by weight, based on the concentrate weight.

It is to be noted that the amounts of the additive compositions of this invention present in the fully formulated oil compositions or concentrates are on an active ingredient basis (a.i.).

The lubricating oil base stock for the additive compositions of the present invention typically is adapted to perform a selected function by the incorporation of other additives therein to form lubricating oil compositions designated as formulations.

Representative other additives typically present in such formulations include corrosion inhibitors, oxidation inhibitors, friction modifiers, dispersants, anti-foaming agents, anti-wear agents, detergents, rust inhibitors.

Corrosion inhibitors, also known as anti-corrosive agents, reduce the degradation of the metallic parts contacted by the lubricating oil composition. Illustrative of corrosion inhibitors are phosphosulfurized hydrocarbons and the products obtained by reaction of a phosphosulfurized hydrocarbon with an alkaline earth metal oxide or hydroxide, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of carbon dioxide. Phosphosulfurized hydrocarbons are prepared by reacting a suitable hydrocarbon such as a terpene, a heavy petroleum fraction of a C_2 to C_6 olefin polymer such as polyisobutylene, with from 5 to 30 wt. percent of a sulfide of phosphorus for 1/2 to 15 hours, at a temperature in the range of 65,56° to 315,56°C (150° to 600°F). Neutralization of the phosphosulfurized hydrocarbon may be effected in the manner taught in U.S. Patent No. 1,969,324.

Oxidation inhibitors reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces, and by viscosity growth. Such oxidation inhibitors include alkaline earth metal salts of alkyl phenolthioesters having preferably C_6 to C_{12} alkyl side chains, e.g., calcium nonylphenol sulfide, barium t-octylphenyl sulfide, dioctylphenylamine, phenylalpha-naphthylamine, phosphosulfurized or sulfurized hydrocarbons.

Friction modifiers serve to impart the proper friction characteristics to lubricating oil compositions such as automatic transmission fluids.

Representative examples of suitable friction modifiers are found in U.S. Patent No. 3,933,659 which discloses fatty acid esters and amides; U.S. Patent No. 4,176,074 which describes molybdenum complexes of polyisobutenyl succinic anhydride-amino alkanols; U.S. Patent No. 4,105,571 which discloses glycerol esters of dimerized fatty acids; U.S. Patent No. 3,779,928 which discloses alkane phosphonic acid salts; U.S. Patent No. 3,778,375 which discloses reaction products of a phosphonate with an oleamide; U.S. Patent No. 3,852,205 which discloses 5-carboxyalkylene hydrocarbyl succinimide, S-carboxyalkylene hydrocarbyl succinamic acid and mixtures thereof; U.S. Patent No. 3,879,306 which discloses N-(hydroxyalkyl)alkenyl-succinamic acids or succinimides; U.S. Patent No. 3,932,290 which discloses reaction products of di- (lower alkyl) phosphites and epoxides; and U.S. Patent No. 4,028,258 which discloses the alkylene oxide adduct of phosphosulfurized N-(hydroxyalkyl) alkenyl succinimides. The most preferred friction modifiers are succinate esters, or metal salts thereof, of hydrocarbyl substituted succinic acids or anhydrides and thiobisalkanols such as described in U.S. Patent No. 4,344,853.

Dispersants maintain oil insolubles, resulting from oxidation during use, in suspension in the fluid thus pre-

venting sludge flocculation and precipitation or deposition on metal parts. Suitable dispersants include high molecular weight alkyl succinates, the reaction product of oil-soluble polyisobutylene succinic anhydride with ethylene amines such as tetraethylene pentamine and borated salts thereof.

Foam control can be provided by an antifoamant of the polysiloxane type, e.g., silicone oil and polydimethyl siloxane.

Anti-wear agents, as their name implies, reduce wear of metal parts. Representatives of conventional anti-wear agents are zinc dialkyldithiophosphate and zinc diaryldithiophosphate.

Detergents and metal rust inhibitors include the metal salts of sulphonic acids, alkyl phenols, sulfurized alkyl phenols, alkyl salicylates, naphthenates and other oil soluble mono- and di-carboxylic acids. Highly basic (viz, overbased) metal salts, such as highly basic alkaline earth/metal sulfonates (especially Ca and Mg salts) are frequently used as detergents. Representative examples of such materials, and their methods of preparation, are found in EP-A-208560, the disclosure of which is hereby incorporated by reference.

Some of these numerous additives can provide a multiplicity of effects, e.g., a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

Compositions when containing these conventional additives are typically blended into the base oil in amounts which are effective to provide their normal attendant function. Representative effective amounts of such additives are illustrated as follows:

Additive	Active Ingredient By	
	Volume	Weight
Corrosion Inhibitor	0.01-1	0.01-1.5
Oxidation Inhibitor	0.01-1	0.01-1.5
Dispersant	0.1-7	0.1-8
Anti-Foaming Agents	0.001-0.1	0.001-0.15
Anti-Wear Agents	0.001-1	0.001-1.5
Friction Modifiers	0.01-1	0.01-1.5
Detergents/Rust Inhibitors	0.01-2.5	0.01-3
Mineral Oil Base	Balance	Balance

When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the dual additive composition (in concentrate amounts hereinabove described), together with one or more of said other additives (said concentrate when constituting an additive mixture being referred to herein as an additive-package) whereby several additives can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The concentrate or additive-package will typically be formulated to contain the first and second additive compositions of the instant invention and optional additional additives in proper amounts to provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount of base lubricant. Thus, the additive composition of the present invention can be added to small amounts of base oil or other compatible solvents along with other desirable additives to form additive-packages containing active ingredients in collective amounts of typically from 2.5 to 90%, and preferably from 5 to 75%, and most preferably from about 8 to about 50% by weight additives in the appropriate proportions with the remainder being base oil.

The final formulations may employ typically about 10 wt. % of the additive-package with the remainder being base oil.

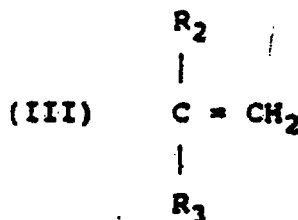
All of said weight and volume percents expressed herein are based on active ingredient (a.i.) content of the additive, and/or upon the total weight of any additive-package, or formulation which will be the sum of the a.i. weight of each additive plus the weight of total oil or diluent.

Neither the oleaginous compositions nor the additive concentrates of the instant invention contain, i.e., are free of, the second component lubricating oil flow improvers described in EP-A-296714. These second component lubricating oil flow improvers are comprised of:

- (i) polymers of ethylenically unsaturated dicarboxylic acids or their anhydrides having the carboxyl or anhydride groups located on vicinal carbons and having 4 to 10 carbons in the unesterified monomer molecule, esterified with a mixture of C₁ to C₂₀ aliphatic alcohols, preferably mixtures of alcohols in the C₄ to C₂₀ average carbon number range, more preferably in the C₈ to C₁₈ carbon range;
- (ii) interpolymers of (a) ethylenically unsaturated dicarboxylic acids or their anhydrides having the carboxyl

or anhydride groups located on vicinal carbons and having 4 to 10 carbons in the unesterified monomer molecule, esterified with a mixture of C_1 to C_{20} aliphatic alcohols, preferably mixtures of alcohols in the C_4 to C_{20} average carbon number range, more preferably in the C_8 to C_{18} carbon range, and (b) vinyl esters, alpha-olefins or styrene;

(iii) polymers of unsaturated monoesters, preferably polymers of long side chain unsaturated mono-esters, and interpolymers of long and short side chain unsaturated monoesters. The unsaturated esters are generally acrylate or 2-alkylacrylate mono-esters represented by the formula:



wherein R_2 is hydrogen or a C_1 to C_6 alkyl group; and R_3 is a $COOR_4$ group wherein R_4 is a C_1 to C_{20} , preferably a C_{10} to C_{18} alkyl group. A 2-alkylacrylate is one wherein R_2 is alkyl. The hydrocarbyl groups constituting R_4 represent the hydrocarbyl residues of mixtures of alcohols from which the same are prepared, which alcohols are preferably saturated, although some degree of unsaturation is permissible when mixtures of alcohols are employed, e.g., less than about 2 mole % of the alcohols in the mixture can be unsaturated. Straight chain or lightly branched alcohols are preferred over highly branched alcohols. The mixture of alcohols employed are those containing from C_1 to about C_{20} carbons which can be employed in such proportions that the average number of carbons in the alcohol residue of the monomer molecule is preferably between about 10 and about 18. Furthermore, it is preferred that at least 60 mole %, most preferably at least 80 mole % of the alcohols present in such mixture contain between 10 and 18 carbon atoms. Illustrative non-limiting examples of (i) are polymers of dialkyl fumarates wherein the fumarates are esterified with mixtures of C_6 through C_{20} alcohols. An illustrative non-limiting example of (ii) are interpolymers of dialkyl fumarates and vinyl esters, preferably vinyl acetate, in which the fumarates are esterified with mixtures of C_6 through C_{20} alcohols.

The following examples are given as specific illustrations of the claimed invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples. All parts and percentages in the examples, as well as in the remainder of the specification, are by weight unless otherwise specified.

The following Comparative Examples fall outside the scope of the instant invention and are presented for comparative purposes only.

COMPARATIVE EXAMPLE 1

A fully formulated 15W-40 lubricating base oil (designated Base Oil A) was prepared containing mineral oil base stock oil (i.e., a mixture of 150N and 750N); no lubricating oil flow improver (LOFI); a conventional detergent/inhibitor package containing ashless dispersant, anti-oxidant, anti-wear additive, and overbased sulfonate; and 0.85 wt. % (a.i.) of a V.I. improver comprised of ethylene-propylene copolymer having a Thickening Efficiency of about 2.0, a ratio of weight average molecular weight to number average molecular weight greater than 2, and an ethylene content of about 48 wt. %.

COMPARATIVE EXAMPLE 2

Comparative Example 1 was repeated except that the base oil contained 0.19 wt. % (a.i.) of lubricating oil flow improver composition falling outside the scope of the instant invention - LOFI B (di- C_{10} alkyl fumarate-vinyl acetate copolymer wherein the fumarate was derived from a C_{10} alkanol and the fumarate: vinyl acetate mole ratio employed in the synthesis of said LOFI B composition was 1:0.8). With the exception of the presence of LOFI B, the types and amounts of other additives were the same as in Comparative Example 1.

COMPARATIVE EXAMPLE 3

Comparative Example 2 was repeated except that the lubricating oil flow improver, LOFI B, of Comparative

Example 2 was replaced with 0.19 wt. % (a.i.) of another lubricating oil flow improver falling outside the scope of the instant invention - LOFI C (di-C₁₂ alkyl fumaratevinyl acetate copolymer wherein the fumarate: vinyl acetate mole ratio employed in the synthesis of LOFI C composition was 1:0.8). With the exception of the lubricating oil flow improver, the types and amounts of other additives were the same as in Comparative Example 2.

COMPARATIVE EXAMPLE 4

Comparative Example 2 was repeated except that the lubricating oil flow improver, LOFI B, of Comparative Example 2 was replaced with 0.19 wt. % (a.i.) of another lubricating oil flow improver falling outside the scope of the instant invention - LOFI D (di-C₁₆ alkyl fumaratevinyl acetate copolymer wherein the fumarate: vinyl acetate mole ratio employed in the synthesis of said LOFI D composition was 1:0.8). With the exception of the lubricating oil flow improver, the types and amounts of other additives were the same as in Comparative Example 2.

COMPARATIVE EXAMPLE 5

Comparative Example 2 was repeated except that the lubricating oil flow improver, LOFI B, of Comparative Example 2 was replaced with 0.19 wt. % (a.i.) of another lubricating oil flow improver falling outside the scope of the instant invention - LOFI E (di-C₁₈ alkyl fumaratevinyl acetate copolymer wherein the fumarate: vinyl acetate mole ratio employed in the synthesis of said LOFI E composition was 1:0.8). With the exception of the lubricating oil flow improver, the types and amounts of other additives were the same as in Comparative Example 2.

The following Examples illustrate the compositions of the instant invention.

EXAMPLE 6

A fully formulated 15W-40 lubricating base oil (designated Base Oil A) was prepared containing mineral oil base stock oil (i.e., a mixture of 150N and 750N); about 0.19 wt. % (a.i.) of first additive composition of the instant invention - LOFI A (di-C₁₄ alkyl fumarate - vinyl acetate copolymer wherein the di-alkyl fumarate was derived from C₁₄ alcohol and wherein the fumarate: vinyl acetate mole ratio employed in the synthesis of said first additive composition was 1:0.8); about 0.85 wt. % (a.i.) of the second additive composition comprised of V.I. improver comprised of ethylene-propylene copolymer having a Thickening Efficiency of about 2.0, a ratio of weight average molecular weight to number average molecular weight greater than 2, and an ethylene content of about 48 wt. %; and a conventional detergent/inhibitor package containing ashless dispersant, anti-oxidant, anti-wear additive, and overbased sulfonate.

Thickening Efficiency (T.E.) is defined as the ratio of the weight percent of a polyisobutylene (sold as an oil solution by Exxon Chemical Co. as Paratone N), having a Staudinger Molecular Weight of 20,000, required to thicken a solvent-extracted neutral mineral lubricating oil, having a viscosity of 150 SUS at 37.8°C, a viscosity index of 105 and an ASTM pour point of -17.8°C (0°F) (Solvent 150 Neutral) to a viscosity of 12.4 mm²/s (centistokes) at 98.9°C, to the weight percent of a test copolymer required to thicken the same oil to the same viscosity at the same temperature. T.E. is related to $\bar{M}_n$ and is a convenient, useful measurement for formulation of lubricating oils of various grades.

EXAMPLE 7

Example 6 was repeated, except that a different 15W-40 mineral oil base stock was employed. The base oil, fully formulated in accordance with Example 6, was designated Base oil B and contained the same types and amounts of additives as Base Oil A of Example 6.

EXAMPLE 8

Example 6 was repeated except that a different 15W-40 mineral oil base stock was employed. The base oil, fully formulated in accordance with Example 6, was designated Base Oil C and contained the same types and amounts of additives as Base Oil A of Example 6.

EXAMPLE 9

Example 6 was repeated except that a different 15W-40 mineral oil base stock was employed. The base

oil, fully formulated in accordance with Example 6, was designated Base Oil D, and contained the same types and amounts of additives as Base Oil A of Example 6.

EXAMPLE 10

Example 6 was repeated, except that a different 15W-40 mineral oil base stock was employed. The base oil, fully formulated in accordance with Example 6, was designated Base Oil E and contained the same types and amounts of additives as Base Oil A of Example 6.

EXAMPLE 11

Example 6 was repeated, except that a different 15W-40 mineral oil base stock was employed. The base oil, fully formulated in accordance with Example 6, was designated Base Oil F and contained the same types and amounts of additives as Base Oil A of Example 6.

EXAMPLE 12

Example 6 was repeated, except that a different 15W-40 mineral oil base stock was employed. The base oil, fully formulated in accordance with Example 6, was designated Base Oil G and contained the same types and amounts of additives as Base Oil A of Example 6.

The flow properties of Comparative Examples 1-5 and of Examples 6-12 were tested by the Mini Rotory Viscometer (MRV) procedure, and the results are summarized in TABLE I. The analysis of the flow properties was conducted by testing the lubricating oil formulations in a Mini Rotory Viscometer after subjecting each sample to a temperature profile controlled in accordance with ASTM D4684 over about a 40 to 44 hour cooling cycle. More specifically, this test is used by the SAE (J300 Specification-JUN87) for determining the low temperature pumpability of a crankcase oil. In the test procedure itself, the temperature is gradually lowered to -20°C, and then at that temperature the yield stress (YS) is measured in pascals, and the apparent viscosity (VIS) is measured in pascal seconds. The latter is required because this is a two-phase system, so that a true viscosity measurement cannot be made. Thus, in accordance with SAE requirements for 15W-40 oils, the target values of less than 35 pascals (YS) and not greater than 300 pascal seconds (VIS) are considered acceptable in order to provide a pumpable composition at -20°C, i.e., to maintain fluidity. For purposes of the instant application a sample is considered to "fail" if either the YS is greater than 35 pascals or the viscosity is greater than 300 pascal seconds.

TABLE I

Example or Comparative Example No.	Base Oil	Type	Carbon No. of Alcohol	Amount (wt. %)	Test Results		
					V.I.		VLS (Pascal Seconds)
					Improver Amount (wt. %)	YS (Pascals)	
Comp. Ex. 1	A	-	-	0	0.85	Solid	Solid
Comp. Ex. 2	A	B	C ₁₀	0.19	0.85	Solid	Solid
Comp. Ex. 3	A	C	C ₁₂	0.19	0.85	Solid	Solid
Comp. Ex. 4	A	D	C ₁₆	0.19	0.85	< 140	366
Comp. Ex. 5	A	E	C ₁₈	0.19	0.85	Solid	Solid
Example 6	A	A	C ₁₄	0.19	0.85	< 35	199
Example 7	B	A	C ₁₄	0.19	0.85	< 35	294
Example 8	C	A	C ₁₄	0.19	0.85	< 35	267
Example 9	D	A	C ₁₄	0.19	0.85	< 35	385

Base oils A - G are all obtained from South American crudes.

TABLE I (CONTINUED)

<u>LOFI</u>				<u>Test Results</u>			
Example or Comparative Example No.	Base Oil	Type	Carbon No. of Alcohol	Amount (wt. %)	V.I.		VIS (Pascal Seconds)
					Improver Amount (wt. %)	YS (Pascals)	
Example 10	E	A	C ₁₄	0.19	0.85	< 35	206
Example 11	F	A	C ₁₄	0.19	0.85	< 35	183
Example 12	G	A	C ₁₄	0.19	0.85	< 35	201
Targets for SAE 15W-40 oil							300 max.

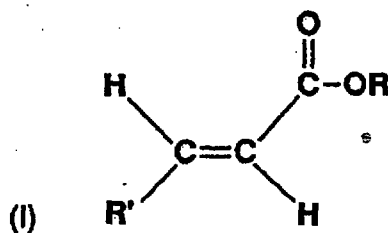
As illustrated by the data in TABLE I, the combination of the first and second additive compositions of the present invention provide lube oil formulations (Examples 6-12) which meet, with the exception of the composition of Example 9, the target for SAE 15W-40 oil with a variety of different base oils. As discussed hereinafore, different types of oils may generally require different amounts of first and/or second additives of the instant invention, i.e., lubricating oil flow improvers and viscosity index improvers or modifiers. Thus, while the amounts of the instant additives utilized in the compositions of Examples 6-12 were effective in improving the low temperature flow properties and viscometric properties of oils A-C and E-G, they were not adequate to improve the viscometric properties of oil D (Example 9) sufficiently to meet the SAE requirements for 15W-40 oil. In contrast, using lubricating oil flow improvers other than those of the instant invention (Comparative Examples 2-5), or using no lubricating oil flow improvers at all (Comparative Example 1) results in lube oil formulations which fail to meet the target for SAE 15W-40 oil. It is to be noted that LOFIs B-E of Comparative Examples 2-5 differ from LOFI A of Examples 6-12 in that the di-alkyl fumarate is derived from an alcohol different from the C₁₄ alcohol of LOFI A.

Although the invention herein has been described with reference to particular embodiments, it is to be un-

derstood that these embodiments are merely illustrative of the principles and applications of the present invention.

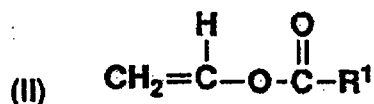
Claims

1. A lubricating oil composition comprising lubricating oil, a lubricating oil flow improver and a hydrocarbon polymeric viscosity index improver and having
 - (i) as the lubricating oil flow improver, from 0.19 to 1.5 wt % of an additive consisting essentially of at least one polymer or interpolymer of unsaturated carboxy ester represented by the formula



wherein R' is selected from the group consisting of hydrogen and COOR, and R is a C₁₄ alkyl group, the polymer or interpolymer having a number average molecular weight of not greater than 40,000; and

- (ii) from 0.01 to 10 wt % of the hydrocarbon polymeric viscosity index improver.
2. The lubricating oil composition of claim 1 wherein (i) is a homopolymer of carboxy ester of formula (I) wherein R' is COOR.
3. The lubricating oil composition of claim 1 wherein (i) is interpolymer of carboxy ester of formula (I) and at least one comonomer selected from the group consisting of vinyl esters, alpha-olefins, and styrenes.
4. The lubricating oil composition of claim 3 wherein (i) is interpolymer of carboxy ester of formula (I) and vinyl ester represented by the formula



Wherein R¹ comprises an alkyl group containing from 1 to 18 carbon atoms

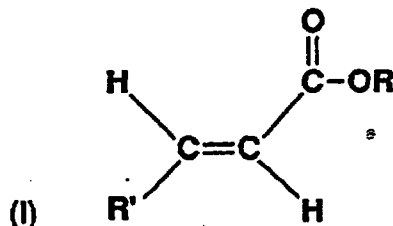
5. The lubricating oil composition of claim 4 wherein said vinyl ester comprises vinyl acetate.
6. The lubricating oil composition of any of claims 1 to 5 wherein said hydrocarbon polymeric viscosity index improver (ii) has a number average molecular weight of from 20,000 to 1,000,000.
7. The lubricating oil composition of any of claims 1 to 6 wherein said hydrocarbon polymeric viscosity index improver (ii) comprises compound selected from the group consisting of polymers and interpolymers of C₂ to C₃₀ olefins.
8. The lubricating oil composition of claim 7 wherein (ii) comprises an interpolymer of ethylene and propylene.
9. The lubricating oil composition of claim 8 wherein said ethylene-propylene interpolymer further includes diene.
10. The lubricating oil composition of claim 9 wherein said diene is 5-ethylidene-2-norbornene.
11. The lubricating oil composition of claim 6 wherein said viscosity index improver (ii) comprises a compound



derstood that these embodiments are merely illustrative of the principles and applications of the present invention.

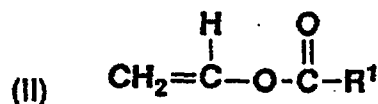
Claims

1. A lubricating oil composition comprising lubricating oil, a lubricating oil flow improver and a hydrocarbon polymeric viscosity index improver and having
(i) as the lubricating oil flow improver, from 0.19 to 1.5 wt % of an additive consisting essentially of at least one polymer or interpolymer of unsaturated carboxy ester represented by the formula



wherein R' is selected from the group consisting of hydrogen and COOR, and R is a C₁₄ alkyl group, the polymer or interpolymer having a number average molecular weight of not greater than 40,000; and
(ii) from 0.01 to 10 wt % of the hydrocarbon polymeric viscosity index improver.

2. The lubricating oil composition of claim 1 wherein (i) is a homopolymer of carboxy ester of formula (I) wherein R' is COOR.
3. The lubricating oil composition of claim 1 wherein (i) is interpolymer of carboxy ester of formula (I) and at least one comonomer selected from the group consisting of vinyl esters, alpha-olefins, and styrenes.
4. The lubricating oil composition of claim 3 wherein (i) is interpolymer of carboxy ester of formula (I) and vinyl ester represented by the formula



Wherein R¹ comprises an alkyl group containing from 1 to 18 carbon atoms

5. The lubricating oil composition of claim 4 wherein said vinyl ester comprises vinyl acetate.
6. The lubricating oil composition of any of claims 1 to 5 wherein said hydrocarbon polymeric viscosity index improver (ii) has a number average molecular weight of from 20,000 to 1,000,000.
7. The lubricating oil composition of any of claims 1 to 6 wherein said hydrocarbon polymeric viscosity index improver (ii) comprises compound selected from the group consisting of polymers and interpolymers of C₂ to C₃₀ olefins.
8. The lubricating oil composition of claim 7 wherein (ii) comprises an interpolymer of ethylene and propylene.
9. The lubricating oil composition of claim 8 wherein said ethylene-propylene interpolymer further includes diene.
10. The lubricating oil composition of claim 9 wherein said diene is 5-ethylidene-2-norbornene.
11. The lubricating oil composition of claim 6 wherein said viscosity index improver (ii) comprises a compound



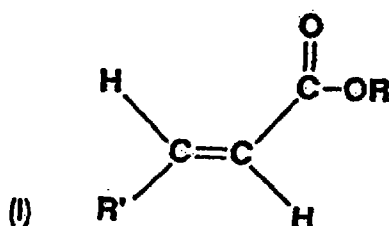
selected from the group consisting of the hydrogenated and partially hydrogenated homopolymers and interpolymers of conjugated dienes and /or monovinyl aromatic compounds.

- 5 12. A concentrate for blending with a lubricating oil base stock to prepare a composition as claimed in any of claims 1 to 11, in which concentrate (i) is present in an amount comprising from 0.5 to 6 wt % thereof; and (ii) is present in an amount comprising from 0.5 to 20 weight percent thereof.

10 Patentansprüche

1. Schmierölzusammensetzung mit einem Gehalt an Schmieröl, einem Schmieröfließverbesserer und einem Kohlenwasserstoffpolymer als Viskositätsindexverbesserer und enthaltend

(i) als Schmieröfließverbesserer 0,19 bis 1,5 Gew.% eines Additivs bestehend im wesentlichen aus mindestens einem Polymer oder Interpolymer von ungesättigtem Carboxyester entsprechend der Formel



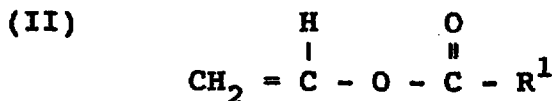
worin R' ausgewählt ist aus der Gruppe bestehend aus Wasserstoff und COOR, und R eine C₁₄-Alkylgruppe ist, wobei das Polymer oder Interpolymer ein zahlenmäßiges durchschnittliches Molekulargewicht von nicht mehr als 40 000 hat; und

(ii) als Viskositätsindexverbesserer 0,01 bis 10 Gew.% des Kohlenwasserstoffpolymers.

2. Schmierölzusammensetzung nach Anspruch 1, in welcher (i) ein Homopolymer von Carboxyester der Formel (I) ist, worin R' COOR ist.

3. Schmierölzusammensetzung nach Anspruch 1, in welcher (i) ein Interpolymer von Carboxyester der Formel (I) und mindestens einem Comonomer ist, das ausgewählt ist aus der Gruppe bestehend aus Vinylestern, α-Olefinen, und Styrolen.

4. Schmierölzusammensetzung nach Anspruch 3, in welcher (i) ein Interpolymer von Carboxyester der Formel (I) und Vinylester entsprechend der Formel



ist, worin R¹ eine Alkylgruppe umfaßt, die 1 bis 18 Kohlenstoffatome aufweist.

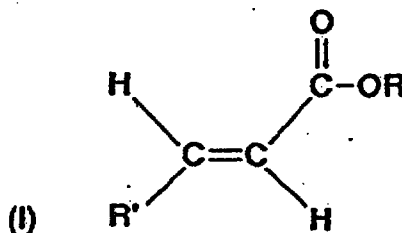
5. Schmierölzusammensetzung nach Anspruch 4, in welcher der Vinylester Vinylacetat umfaßt.
6. Schmierölzusammensetzung einem der Ansprüche 1 bis 5, in welcher das viskositätsindexverbessernde Kohlenwasserstoffpolymer (ii) oder der kohlenwasserstoffpolymere Viskositätsindexverbesserer (ii) ein zahlenmäßiges durchschnittliches Molekulargewicht von 20 000 bis 1 000 000 hat.
7. Schmierölzusammensetzung nach einem der Ansprüche 1 bis 6, in welcher das viskositätsindexverbessernde Kohlenwasserstoffpolymer (ii) eine Verbindung ausgewählt aus der Gruppe bestehend von Polymeren und Interpolymeren von C₂ bis C₃₀ Olefinen umfaßt.



8. Schmierölzusammensetzung nach Anspruch 7, in welcher (II) ein Interpolymer von Ethylen und Propylen umfaßt.
9. Schmierölzusammensetzung nach Anspruch 8, in welcher das Ethylenpropyleninterpolymer außerdem Dien enthält.
10. Schmierölzusammensetzung nach Anspruch 9, in welcher das Dien 5-Ethyliden-2-norbornen ist.
11. Schmierölzusammensetzung nach Anspruch 6, in welcher der Viskositätsindexverbesserer (II) eine Verbindung ausgewählt aus der Gruppe bestehend aus hydrierten und teilweise hydrierten Homopolymeren und Interpolymeren von konjugierten Dienen und/oder monovinylaromatischen Verbindungen umfaßt.
12. Konzentrat zum Vermischen mit einem Schmierölbasismaterial zur Herstellung einer Zusammensetzung nach einem der Ansprüche 1 bis 11, wobei in dem Konzentrat (I) in einer Menge von 0,5 bis 6 Gew.% des-
selben anwesend ist; und (II) in einer Menge von 0,5 bis 20 Gew.% desselben anwesend ist.

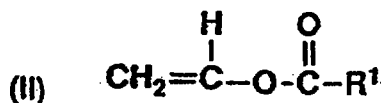
Revendications

1. Composition d'huile lubrifiante, comprenant une huile lubrifiante, un agent améliorant l'écoulement d'une huile lubrifiante et un agent polymérique hydrocarboné améliorant l'indice de viscosité, et ayant
(I) comme agent améliorant l'écoulement d'une huile lubrifiante, une proportion de 0,19 à 1,5 % en poids d'additif consistant essentiellement en au moins un polymère ou interpolymère d'un ester carboxylique non saturé représenté par la formule



dans laquelle R' est choisi dans le groupe comprenant l'hydrogène et un radical COOR et R est un groupe alkyle en C₁₄, le polymère ou l'interpolymère ayant une moyenne numérique du poids moléculaire ne dépassant pas 40 000 ; et
(II) une proportion de 0,01 à 10 % en poids de l'agent polymérique hydrocarboné améliorant l'indice de viscosité.

2. Composition d'huile lubrifiante suivant la revendication 1, dans laquelle le composant (I) est un homopolymère d'un ester carboxylique de formule (I) dans laquelle R' est un groupe COOR.
3. Composition d'huile lubrifiante suivant la revendication 1, dans laquelle le composant (I) est un interpolymère d'un ester carboxylique de formule (I) et d'au moins un comonomère choisi dans le groupe comprenant des esters de vinyle, des alpha-oléfines et des styrènes.
4. Composition d'huile lubrifiante suivant la revendication 3, dans laquelle le composant (I) est un interpolymère d'un ester carboxylique de formule (I) et d'un ester de vinyle représenté par la formule



dans laquelle R¹ comprend un groupe alkyle contenant 1 à 18 atomes de carbone.



5. Composition d'huile lubrifiante suivant la revendication 4, dans laquelle l'ester de vinyle comprend l'acétate de vinyle.
- 5 6. Composition d'huile lubrifiante suivant l'une quelconque des revendications 1 à 5, dans laquelle l'agent polymérique hydrocarboné (II) améliorant l'indice de viscosité a une moyenne numérique du poids moléculaire de 20 000 à 1 000 000.
- 10 7. Composition d'huile lubrifiante suivant l'une quelconque des revendications 1 à 6, dans laquelle l'agent polymérique hydrocarboné (II) améliorant l'indice de viscosité comprend un composé choisi dans le groupe constitué de polymères et d'interpolymères d'oléfines en C₂ à C₃₀.
8. Composition d'huile lubrifiante suivant la revendication 7, dans laquelle le composant (II) comprend un interpolymère d'éthylène et de propylène.
- 15 9. Composition d'huile lubrifiante suivant la revendication 8, dans laquelle l'interpolymère éthylène-propylène renferme en outre un diène.
- 20 10. Composition d'huile lubrifiante suivant la revendication 9, dans laquelle le diène est le 5-éthylidène-2-norbornène.
- 25 11. Composition d'huile lubrifiante suivant la revendication 6, dans laquelle l'agent (II) améliorant l'indice de viscosité comprend un composé choisi dans le groupe constitué d'homopolymères et d'interpolymères hydrogénés et partiellement hydrogénés de diènes conjugués et/ou de composés aromatiques monovinyl-
liques.
- 30 12. Concentré à formuler avec une huile de base pour huile lubrifiante en vue de préparer une composition suivant l'une quelconque des revendications 1 à 11, dans lequel le concentré (I) est présent en une quantité qui en constitue 0,5 à 6 % en poids ; et le composant (II) est présent en une quantité qui en constitue 0,5 à 20 % en poids.
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