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LUBRICANTS HAVING A HIGH VISCOSITY INDEX

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The present invention concerns hydrocarbon oil compositions whose viscosity-temperature relationships have been improved by adding thereto certain stereo-oriented polymers of butadiene and related C_4 or C_5 diolefins.

In many applications of lubricating oils and particularly when they are employed as crankcase oils in piston-type internal combustion engines, it is desirable that the lubricants undergo relatively small changes in viscosity through the operating temperature range of the engine, i.e. from the time that the engine is started cold until it has fully warmed up. The term "viscosity index" or "V.I." can be applied to express the relative viscosity change which an oil undergoes with changes in temperature. More specifically, the V.I. indicates the relation which the viscosity of a particular oil at 100° F. bears to the viscosities of a representative Pennsylvania oil and a representative Coastal oil at 100° F., where all three oils have the same viscosity at 210° F. In this relationship the Pennsylvania oil is considered to have a viscosity index of 100, and the Coastal a viscosity index of 0. Usually viscosity indexes are determined by the well-known Dean and Davis Method which has been described in A.S.T.M. D–567.

Among the viscosity index improvers that have been used in the prior art are included various olefin polymers, e.g. polyisobutylene, as well as various polymers of other unsaturated organic compounds such as aliphatic esters of unsaturated monocarboxylic or polycarboxylic acids, e.g. methacrylic esters, fumaric or maleic acid esters, alkylene esters of fatty acids, e.g. vinyl acetate, and the like.

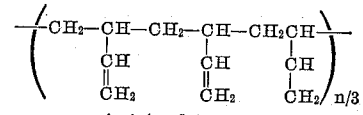
One major advantage that is obtained by using a satisfactory V.I. improver in a crankcase lubricant is that it makes available an oil that meets the specifications of more than one SAE viscosity grade, i.e. a combined SAE 10 and SAE 20 oil or one bridging the SAE 10, SAE 20, and SAE 30 grades. A multigraded oil that spans the grades from 5W through SAE 30 is particularly desirable because it enables the motorist to employ a single grade of crankcase lubricant through all seasons of the year, even in regions that have fairly severe weather.

An acceptable all-weather lubricant must meet three basic requirements: it must have a sufficiently low viscosity at the starting temperature of the engine; it must have a sufficiently high viscosity at the high operating temperature; and it must have a relatively low volatility at the operating temperature in order to minimize oil consumption. To produce a lubricant oil having a high viscosity index of the order of 130 to 150 usually requires a low viscosity base oil along with a considerable amount of V.I. improver. However, the low viscosity base oils are relatively volatile and thus increase oil consumption. A higher viscosity base stock with the same amount of V.I. improver will give an oil composition having lower volatility, but the oil will then be too viscous at a lower temperature, for example, at 0° F. If less viscosity improver is employed in a thicker base stock, the cold starting characteristics will be improved, but because of the lower viscosity index of such a blend, there will be a lower viscosity at the operating temperature, which is also undesirable. Thus there is a need for a V.I. improver having a sufficient potency to maintain the oil at a satisfactory operating temperature viscosity, while at the same time affording an acceptable low temperature

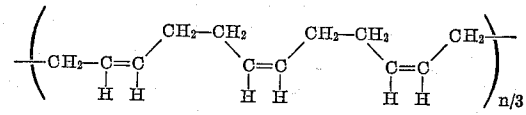
starting viscosity. It has now been found in accordance with the present invention that certain polymers of C_4 or C_5 conjugated diolefins are outstanding in V.I. improver potency, and thus are highly suitable for the preparation of lubricating oil compositions for internal combustion engines. The polymers used in this invention are those that predominate in a 1,4-addition configuration and in which the 1,2-addition configuration does not exceed 10 percent. The polymers used in this invention have number-average molecular weights in the range of from about 75,000 to about 300,000. Particularly preferable for use in this invention are polymers of the type described that have molecular weights in the range of from about 150,000 to about 250,000. The polymers are formed from conjugated diolefins having 4 to 5 carbon atoms and no more than one methyl side chain. While butadiene is preferred, isoprene and 1,3-pentadiene may also be used, as well as copolymers of any of these diolefins.

The different modes of polymerization referred to above in the case of butadiene are as follows:

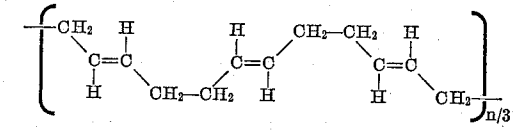
1,2-polybutadiene



cis-1,4-polybutadiene



trans-1,4-polybutadiene



wherein each instance n is the number of butadiene units in the polymer.

Where the configuration is predominantly cis-1,4, say 80 to 100 percent, the polymer has the greatest V.I. potency. Where the extent of cis-1,4 configuration is less, say in a polymer having 30 to 50 percent cis-1,4 configuration and 40 to 60 percent trans-1,4 configuration the V.I. potency is slightly reduced, but the stability to shear breakdown is enhanced. From a commercial standpoint V.I. potency is the more valuable property; accordingly, polymers having 80 to 100 percent cis-1,4 configuration are particularly preferred.

The processes for the polymerization of conjugated diolefins to high molecular weight polymers in which the mode of polymerization is predominantly of a 1,4 configuration are well known in the art. The catalysts for such polymerization may comprise metallic lithium or lithium alkyls such as ethyl lithium, n-butyl lithium, hexyl lithium, or the like, as taught in Australian patent specification 223,817. They may also comprise lithium dihydrocarbon amide as taught in U.S. Patent 2,849,432. Complexes of titanium tetrachloride and aluminum trialkyls, e.g. aluminum triisobutyl, may also be used. The polymerization is conveniently conducted in solution using a nonpolar, nonacidic organic solvent, as for example, C_3 to C_{16} straight chain, branched or cyclic paraffin hydrocarbon. Polymerization temperatures may range from 0 to about 150° C. Prior to polymerization the diolefins must be dried, as for example, by treatment with silica gel, alumina, or the like.

In preparing the compositions of the present invention, the polymers are employed in concentrations in the range of from about 0.1 to about 3 weight percent in hydro-

carbon lubricating oil base stocks having viscosities in the range of about 75 to about 325 SUS at 100° F. More generally they will be used in crankcase lubricants in concentrations ranging from about 0.5 to about 2 weight percent. Conveniently they may be dissolved in 10 to 20 weight percent concentration in a solvent refined neutral mineral lubricating oil of say 100 or 150 SUS viscosity for ease in blending back to the desired concentration in a finished lubricating oil formulation. The preparation of the concentrate simply involves comminuting the polymer and stirring it into the lubricating oil at a suitable temperature, e.g. 140 to 180° F., for a sufficient time to effect complete solution.

Because of the high V.I. potency of the diolefin polymers, they may be used not only as the sole V.I. improver in a composition, but also in conjunction with conventional V.I. improvers. These include: polyisobutylene; copolymers of vinyl acetate, maleic anhydride and aliphatic alcohol fumarates; alkyl methacrylates; copolymers of alkyl methacrylates and alkyl fumarates; and the like. Particularly useful are combinations of the polybutadienes of the present invention in concentrations ranging from about 0.1 to about 1 weight percent with polyisobutylenes having number-average molecular weights in the range of from about 40,000 to about 160,000, using concentrations of the latter of from about 0.5 to about 1.5 weight percent.

Conventional lubricating oil additives including antioxidants, extreme pressure additives, antiwear additives, pour point depressants, detergents and dispersants, etc. may also be present in the lubricating oil compositions of this invention.

The hydrocarbon lubricating oil base stocks may comprise synthetic hydrocarbons as well as the usual mineral lubricating oils derived from paraffinic, naphthenic, asphaltic or mixed base crude oils by suitable refining methods.

The following examples serve to illustrate this invention.

EXAMPLE 1

Three separate commercially available high molecular weight polybutadienes were blended into separate portions of a refined paraffinic lubricating oil having a viscosity of 43 SUS at 210° F. by stirring the blends for a 12 to 24 hour period at 150° F. A fourth blend, also prepared in the same manner, consisted of 2 weight percent of polyisobutylene in the same base oil. The molecular weights of each of the polymers, the measured viscosities, the calculated viscosity indexes, and the extent of viscosity loss in the sonic breakdown test for each blend are given in Table I. The sonic breakdown test is a measure of shear stability and is conducted according to the procedure described in ASTM Standards, volume I (1961), page 1160, "Test for Shear Stability of Polymer-Containing Oils."

The superiority of the polybutadiene V.I. improvers over the conventional polyisobutylene V.I. improvers is readily evident from the data in Table I. It will be noted that Diene 35, which had only about 40 percent of the polymers of the cis-1,4 configuration, was not as effective in increasing the V.I., as were the polybutadienes having 95 to 98 percent of the cis-1,4 configuration, but at the same time was better in shear stability. All of the sonic breakdown losses given in Table I are within acceptable limits for crankcase lubricant viscosity index improvers.

EXAMPLE 2

Blends of the three polybutadienes employed in Example 1 were also prepared in a base oil consisting of 92.8 weight percent of a refined neutral mineral oil of 100 SUS viscosity at 100° F., having a viscosity index of 118, 4.5 weight percent of a polyamine derivative ashless dispersant, 1.5 weight percent of an overbased calcium petroleum sulfonate dispersant, 1.0 weight percent of a zinc dialkyl dithiophosphate wear inhibitor derived from isobutanol and mixed amyl alcohols and 0.2 weight percent of a pour point depressant. The polyamine derivative ashless dispersant was prepared by heating 36 pounds of polyisobutylene with 4.5 pounds of maleic anhydride for 24 hours at 450° F. to form polyisobutenyl succinic anhydride, adding to the product sufficient light mineral lubricating oil (150 SUS viscosity at 100° F.) to form a 75 weight percent concentrate in oil, adding thereafter 3.5 pounds of tetraethylene pentamine and 1.1 pounds of acetic acid, heating the mixture at 300° F. with nitrogen blowing until water evolution ceased (about 10 hours reaction time) and filtering the product. The viscosities of each of these blends were measured at 100° F. and at 210° F., and the viscosity indexes were calculated. The viscosity of each of the blends at 0° F. was also measured, using the Ferranti-Shirley viscosimeter and converting the values to Saybolt seconds. The data thereby obtained are given in Table II.

TABLE II.—BLENDS IN 100 REFERENCE OIL

Additive	SUS Viscosity at 210° F.	V.I.	Measured Viscosity at 0° F. SUS
0.85 wt. percent Cis-4	76.85	158	7,000
1.2 wt. percent Ameripol	70.32	155	7,600
1.1 wt. percent Diene 35	68.22	149	8,000
2.1 wt. percent Polyisobutylene	68.00	138	10,000

The data in Table II show that the superior potency of the polybutadienes of this invention as V.I. improvers is unimpaired in a fully formulated crankcase lubricant.

EXAMPLE 3

Formulations similar to those of Example 2 were prepared using as the base oil a refined neutral mineral oil of 150 SUS viscosity at 100° F. and 109 viscosity index, together with the same detergent, dispersant, antiwear and pour point depressant additives and in the same concentrations as in Example 2. The measured viscosities at 210° F., the calculated viscosity indexes, and the comparative measured viscosities at ° F. are given in Table III.

TABLE I.—BLENDS IN 43 SUS VISCOSITY OIL

Additive	Number-Average Molecular Weight	Viscosity at 210° F. SUS	V.I.	Percent Viscosity Loss
1 wt. percent Cis 4 [1]	200,000	71.47	151	39
1 wt. percent Ameripol [2]	160,000	61.16	150	30
1 wt. percent Diene 35 [3]	180,000	63.45	146	22
2 wt. percent Polyisobutylene	130,000	62.37	135	25

[1] 94.4% 1,4-cis type; 2.1% 1,4-trans type; 3.5% 1,2-type configuration.
[2] 97.6% 1,4-cis type; 1.2% 1,4-trans type; 1.2% 1,2-type configuration.
[3] 39.3% cis type; 51.5% 1,4-trans type; 9.6% 1,2-type configuration.

TABLE III.—BLENDS IN 150 REFERENCE OIL

Additive	SUS Viscosity at 210° F.	V.I.	Measured °F. Viscosity as Percent of Base Oil
0.65 wt. percent Cis-4	65.27	144	104
0.97 wt percent Ameripol	66.07	144	105
0.93 wt. percent Diene 35	69.95	141	112

Particularly noteworthy is that while the polybutadienes effectively raised the viscosity index of the base blend, they increased the actual viscosity of the base blend at 0° F. by only a small percentage.

EXAMPLE 4

A fully formulated crankcase lubricant was prepared consisting of 1.2 weight percent of Ameripol polybutadiene, 1.3 weight percent of the antiwear additives used in Example 2, about 3.8 weight percent and about 1 weight percent of the ashless dispersant and calcium sulfonate additives, respectively, used in Example 2, about 0.5 weight percent of the same pour point depressant as used in that example, and about 92.2 weight percent of a mineral lubricating oil base stock. The latter was a blend of refined mineral lubricating oils, of which about 81 percent was a 100 viscosity oil, about 10 percent a 150 viscosity oil, and about 9 percent a 450 viscosity oil, the viscosity numbers in each instance being SUS viscosities at 100° F. In a Cooperative Research Council L–38 test, the blended lubricant gave a bearing weight loss of 43 mg. (passing is 50 mg. weight loss) and a varnish merit rating of 10. The CRC–L–38 test is described in Federal Test Methods, Standard No. 3,407.

The formulated crankcase oil was also subjected to a Cyclic Temperature Sludge Test which, from prior experience, has been shown to give sludge deposits similar to those obtained in stop-and-go driving such as would be experienced in taxicab operation. Briefly described, in this test a Ford 6-cylinder engine is run on a dynamometer stand through alternate cycles, the first cycle lasting 5 hours, at 1,500 r.p.m., and the second cycle lasting 2 hours, at the same operating speed, with the oil sump and water jacket temperatures being slightly higher in the second cycle than in the first. The two cycles are alternated in sequence until the desired total test time has elapsed. Make-up oil is added as required so as to maintain the oil level in the crankcase at all times between about 3½ and 4 quarts. At the end of selected periods of test time, the engine is inspected by disassembling it sufficiently to permit visual examination of several of the parts, including the rocker arm assembly, the rocker arm cover, the cylinder head, the push rod, chamber and its cover, the crankshaft and the oil pan. These parts are visually and quantitatively rated for sludge deposits, using a CRC Sludge Merit rating system in which a numerical rating of 10 represents a perfectly clean part, and the numerical scale decreases to a minimum value representing a part covered with the maximum amount of sludge possible. The several merit ratings are averaged to give an overall engine merit rating. In this test the formulated oil gave a merit rating of 9.5 after 105 hours, a merit rating of 9.13 after 126 hours, and a merit rating of 6.1 after 147 hours, these results being at least as good as those obtained with a comparable blend employing the conventional polyisobutylene V.I. improver, and indicating that the double bonds in the polybutadiene do not contribute to any degradation of the additive in actual service use.

EXAMPLE 5

A blend is prepared by adding 1 weight percent of polyisoprene having a number-average molecular weight of about 240,000 and about 93 percent cis 1,4-configuration to a refined lubricating oil base stock of 100 SUS viscosity measured at 100° F., imparting thereto a V.I. of about 151.

EXAMPLE 6

Blends were prepared using the same base stock as in Example 1 and adding thereto various proportions of the Ameripol polybutadiene and the polyisobutylene employed in Example 1. The viscosity indexes of the blends are given in Table IV.

TABLE IV

Weight Percent Polyisobutylene	Weight Percent Polybutadiene	Viscosity Index of blend
2	0	135
1.4	0.3	140
1	0.5	142.5
0.6	0.7	144

It will be understood that the examples given in the preceding disclosure are intended to be merely illustrative of the invention and as not limiting it in any manner.

What is claimed is:

1. A lubricating oil composition of enhanced viscosity-temperature characteristics which comprises a major proportion of a hydrocarbon lubricating oil and from about 0.1 to about 3 weight percent of a polymer of a conjugated diolefin of from 4 to 5 carbon atoms, said polymer having a number-average molecular weight in the range of from 75,000 to 300,000 and having at least 90 percent 1,4 configuration.

2. A lubricating oil composition as defined by claim 1 wherein said polymer has a number-average molecular weight in the range of from about 150,000 to about 250,000.

3. A lubricating oil composition as defined by claim 1 wherein said polymer is a polymer of butadiene.

4. A lubricating oil composition as defined by claim 1 wherein the mode of polymerization in said polymer is predominantly in the cis-1,4 configuration.

5. A lubricating oil composition as defined by claim 1 which also contains in the range of 0.5 to 1.5 weight percent of polyisobutylene having a number-average molecular weight in the range of from about 40,000 to about 160,000.

6. A lubricating oil composition as defined by claim 1 wherein said polymer is a polymer of isoprene.

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