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LUBRICANT COMPOSITION

Rudolf J. A. Eckert and Jan Heemskerk, Amsterdam, Netherlands, assignors to Shell Oil Company, New York, N.Y.

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6 Claims

ABSTRACT OF THE DISCLOSURE

Lubricant compositions comprising hydrogenated random copolymers of a conjugated diene and a vinylaromatic compound and a suitable lubricating oil have improved viscosity properties.

BACKGROUND

The viscosity of lubricating oils varies with temperature. Since many oils are to be used at widely divergent temperatures, ranging from, for instance, about -20°C. to about $+150^{\circ}\text{F.}$ (for instance, in automotive engines), it is of paramount importance that the lubricating oil should be able to fulfill its lubricating function over a large temperature range; it should, for example, neither be too viscous at low temperatures nor too thin-flowing at high temperatures.

According to the American Society of Automotive Engineers' SAE classification, lubricating oils for internal combustion engines are classified into two groups on the basis of their viscosity at -18°C. and 99°C. , respectively. These groups are the winter grades and the normal grades. The normal grades must have a viscosity at 99°C. within a specified range. Generally, oils complying to a certain winter grade do not comply with the viscosity requirement for any normal grade as well, and, conversely, oils complying to a certain normal grade do not comply with the viscosity requirement for a winter grade. Lubricating oils which do in fact comply with the specification of both a winter grade and a normal grade are designated multigrade lubricating oils.

In general, lubricating oils obtained by conventional processes from mineral oils do not meet multigrade specifications, and hence do not meet the very high demands with respect to viscosity made thereon in modern automotive engines. For this reason many compounds have been proposed which, when added to a lubricating oil, improve the viscosity properties thereof. These compounds, which in most cases are polymeric compounds, are called viscosity index- (VI) improvers.

In order to be a good VI-improver, a compound must not only have a beneficial influence on the viscosity properties of a fresh lubricating oil, but it must remain stable in order to perform its function under engine operating conditions. Therefore, a good VI-improver must be shear-stable as well as resistant to high temperatures, oxygen and acids. Furthermore, a VI-improver should have a beneficial influence on the pour point of the lubricating oil into which it is incorporated; at the least, it should not have a disturbing influence on the function of pour-point depressants.

THE INVENTION

A type of compound has now been found which is very suitable as a VI-improver, because it meets all the requirements discussed above. This type of compound consists of hydrogenated random copolymers of a conjugated diene and a vinylaromatic compound, which conjugated diene and/or vinylaromatic compound contain at least one alkyl substituent.

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The invention therefore relates to a lubricant composition comprising therefor a minor proportion (0.1–15% viscosity improver therefor a minor proportion (0.1–15% wt.) of a hydrogenated random copolymer—with a number average molecular weight between about 5000–500,000 of a C_{4-6} conjugated diene and a styrene in which the conjugated diene and/or the styrene contain at least one lower (C_{1-6}) alkyl substituent with at least 50% of the olefinically unsaturated bonds originally present saturated.

The random copolymers may comprise units derived from more than one conjugated diene and/or more than one vinylaromatic compound and/or units derived from other types of monomers. That is, they may contain, for example, butadiene or isoprene and/or mixtures thereof and styrene or an alkylated styrene such as butylated styrene and/or mixtures thereof.

Advantageous conjugated dienes are piperylene, 2,3-dimethylbutadiene, isoprene and butadiene, the last two being preferred. As noted above mixtures of conjugated dienes, e.g., butadiene and isoprene, are also advantageous. Butadiene, however, must only be used as the only conjugated diene with a vinylaromatic compound when the vinylaromatic compound contains at least one alkyl substituent.

The vinylaromatic compound according to the invention is styrene or an alkylated styrene. The alkyl group in the alkylated styrene may be attached to the alpha-carbon atom of the styrene (as, for instance, in alpha-methylstyrene) or to the aromatic ring (as, for instance, in o-, m- or p-methylstyrene, tert-butylstyrene). Styrene and tert-butylstyrene are preferred. Mixtures of vinylaromatic compounds, e.g., of styrene and tert-butylstyrene are also used. Styrene must only be used as the only vinylaromatic compound for copolymerization with a conjugated diene when the conjugated diene contains at least one alkyl substituent.

The molar ratio between the conjugated diene and the vinylaromatic compound may vary between wide limits, but it is essential that the copolymer, after hydrogenation, should be soluble in the lubricant in which it is to be incorporated. This limits the amount of the vinylaromatic compound which can be incorporated into the copolymer; since the solubility depends on the structure of the vinylaromatic compound incorporated in the copolymer, the amount which can be tolerated in the copolymer may vary between 70% m. when the vinylaromatic compound entirely consists of styrene to 99% m. in cases wherein the vinylaromatic compound contains alkyl chains with sufficient oil-solubilizing properties (e.g., p-tert-butylstyrene). Copolymers with ratios of the number of units originating from the vinylaromatic monomer to the number of units originating from the conjugated diene between 1 to 99 and 90 to 10, in particular between 5 to 95 and 85 to 15, and more in particular between 30 to 70 and 75 to 25, are very suitable.

If desired, relatively small amounts of other monomers may be incorporated into the copolymers during copolymerization. For example, vinylpyridines, alkyl esters of acrylic and methacrylic acid (e.g., methyl methacrylate, dodecyl methacrylate, octadecyl methacrylate), vinyl chloride, vinylidene chloride, vinyl esters of carboxylic acids (e.g., vinyl acetate, vinyl stearate).

The random hydrogenated copolymers of the invention are conveniently prepared by copolymerization of a conjugated diene and a vinylaromatic hydrocarbon in emulsion. Preferably, the copolymerization is carried out in solution with the aid of an alkali metal or an alkali-metal hydrocarbon (e.g., sodium naphthalene) as a catalyst, preferably with the aid of lithium metal or a lithium hydrocarbon as a catalyst. For example, allyl

lithium, methallyl lithium, aromatic compounds such as phenyllithium, the tolyllithium, the xylolithiums and the naphthyllithiums, and in particular alkylolithiums such as methylolithium, ethyllithium, propyllithium, butyllithium, amyllithium, hexyllithium, 2-ethylhexyllithium and n-hexadecyllithium are very suitable. Sec-butyllithium is a preferred catalyst and di(-alkali metal) hydrocarbons such as dilithium hydrocarbons are also useful.

Suitable solvents which are inert under the conditions prevailing during the copolymerization are aliphatic hydrocarbons, such as pentane, hexane, heptane, octane, 2-ethylhexane, nonane, decane, cyclic hydrocarbons, such as cyclohexane, methylcyclohexane, or aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, the xylenes, diethylbenzenes, propylbenzenes. Mixtures of these hydrocarbons can also be used.

Since the activities of the two types of monomers to be incorporated in the copolymer differ greatly, a random copolymer is not obtained unless special measures are taken. In one method of obtaining random copolymers according to the invention, the most reactive monomer is added gradually during copolymerization, in such a manner that the molar ratio of the monomers present in the polymerizing mixture is kept constant. It is also possible to so add a mixture of the monomers to the polymerizing mixture.

The preferred procedure, however, is to copolymerize in the presence of a randomizer. Randomizers are polar compounds which do not inactivate the catalyst and which bring about a tendency to random copolymerization. Suitable randomizers are tertiary amines, such as trimethylamine, dimethylethylamine, tri-n-butylamine, dimethylaniline, pyridine, quinoline, N-ethylpiperidine, N-methylmorpholine, thioethers, such as diethyl sulfide, di-n-propyl sulfide, methyl ethyl sulfide and in particular ethers, such as dimethyl ether, methyl ethyl ether, di-n-butyl ether, di-octyl ether, di-benzyl ether, anisole, 1,2-dimethoxyethane, and in particular tetrahydrofuran or diethyl ether.

The amount of randomizer to be used varies between wide limits; for instance, from 0.05 to 50% wt., preferably from 0.05 to 10% wt. of the total solvent. The remainder of the solvent mixture consists of one or more aliphatic and/or aromatic hydrocarbons as described above.

The polymerization can be carried out under any pressure, but since it is desirable to maintain the monomers and the solvent substantially in the liquid phase, generally the pressure applied is that least amount sufficient to keep the monomers and the solvent in the liquid state. The pressure thus will depend on the temperature of the copolymerization and on the types of monomers and solvent components used. If desired, higher pressures can be used.

The number average molecular weight of the random copolymers according to the invention is between 5000 and 500,000, preferably between 40,000 and 150,000. The molecular weight is regulated by the ratio between the number of moles of catalyst and the number of moles of monomers present during polymerization. The number of units originating from the monomers in a polymer molecule is substantially equal to the ratio between the number of moles of monomer and the number of moles of catalyst (in case each catalyst molecule, e.g., butyllithium, contains one alkali-metal atom) present during polymerization, provided that no contaminants which give rise to side reactions with the catalyst, such as oxygen, water, carbon dioxide, are present.

When the polymerization has been completed and preferably virtually all of the monomer molecules which were present in the polymerizing mixture have been incorporated into the polymer, the polymer is hydrogenated. Usually the catalyst is inactivated before hydrogenation and, if desired, the polymer recovered.

The catalyst can be inactivated by addition of any of several compounds which react with the catalyst to in-

tivate it, for instance, compounds with an active hydrogen atom, such as alcohols (e.g., methanol, ethanol and isopropanol) and carboxylic acids (e.g., acetic acid).

After the inactivation of the catalyst the copolymer can be recovered in any desired way, for example, by precipitation accomplished by addition of relatively large amounts of non-solvents for the copolymer such as an alcohol, e.g., methanol, ethanol or isopropanol.

However, the copolymer is generally not recovered, but kept dissolved and hydrogenated in the solvent in which it was prepared.

The hydrogenation may be complete, i.e., all olefinic double bonds and all aromatic rings are saturated, or it may be only partial. In the latter case part or both or part of one of the two types of unsaturation (viz, olefinically unsaturated bonds and aromatic rings) may be saturated.

It is preferred that at least 50% of the olefinically unsaturated bonds originally present in the random copolymer are saturated in the hydrogenated random copolymer to be used in lubricant compositions according to the invention. Hydrogenated random copolymers wherein more than 95% of the olefinically unsaturated bonds originally present in the random copolymers are saturated are also very suitable. It is also preferred that less than 10%, in particular less than 5%, of the aromatic unsaturation originally present in the random copolymer is saturated in the hydrogenated random copolymer. Hydrogenated random copolymers in which virtually none of the aromatic rings have been saturated during hydrogenation are very suitable.

The hydrogenation can be carried out in any desired way with any desired hydrogenation catalyst; for instance, copper or molybdenum compounds. Catalysts containing noble metals or noble-metal compounds can very suitably be used as hydrogenation catalysts. Preferably, catalysts containing a non-noble metal or a compound of Group VIII of the Periodic Table, viz, iron, cobalt and in particular nickel, are used, e.g., Raney nickel and nickel on kieselguhr. Especially preferred are hydrogenation catalysts obtained by causing metal hydrocarbyl compounds to react with organic compounds of any one of the Group VIII metals, iron, cobalt or nickel, the latter compounds containing at least one organic radical attached to the metal atom by means of an oxygen atom. Also highly preferred are hydrogenation catalysts obtained by causing an aluminum trialkyl (e.g., aluminum triethyl or aluminum triisobutyl) to react with a nickel salt of an organic acid (e.g., nickel diisopropyl salicylate, nickel naphthenate, nickel 2-ethyl hexanoate, nickel di-tert-butyl benzoate, nickel salts of saturated monocarboxylic acids obtained by reaction of olefins having from 4 to 20 carbon atoms in the molecule with carbon monoxide and water in the presence of acid catalysts), or with nickel enolates or phenolates (e.g., nickel acetonylacetate, the nickel salt of butyrylacetophenone).

The hydrogenation of the copolymer is most suitably carried out in solution in a solvent which is inert during the hydrogenation reaction. Saturated hydrocarbons and mixtures of saturated hydrocarbons and tertiary amines or ethers are very suitable, and as, discussed above, it is advantageous to carry out the hydrogenation in the same solvent in which the copolymerization took place.

Partly or totally hydrogenated random copolymers of the conjugated diene and styrene containing an alkyl substituent attached to the ring and/or styrene with a molecular weight of about 5000-500,000 are novel compounds especially suited to the lubricant compositions of the invention; for example, random copolymers of 1,3-butadiene and p-tert-butylstyrene and of 1,3-butadiene, p-tert-butylstyrene and styrene in which at least 50% of the olefinically unsaturated double bonds originally present have been saturated.

The lubricant into which the hydrogenated random copolymer according to the invention is to be incorporated

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may comprise a synthetic lubricating oil, such as an ester oil, or preferably a mineral lubricating oil, prepared from a crude mineral oil by known processes, such as distillation, extraction, deasphalting, dewaxing, hydrofining, polymerization, hydrocracking and the like. The lubricant may also comprise fatty oils. The hydrogenated random copolymers according to the invention can also be incorporated into greases, distillate and residual fuels and crude oils.

The concentration of the hydrogenated random copolymers in the lubricant may vary between wide limits. Concentrations from 0.1 to 15% wt. are suitable, concentrations between 1 and 10% wt. are preferred.

The hydrogenated random copolymers can be incorporated into the lubricant as such, but they are conveniently incorporated into the lubricant in the form of a concentrate in a solvent. The solvent may be a lubricat-

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2-ethyl hexanoate in cyclohexane and 5 ml. of a 0.2 molar solution of aluminum triethyl in cyclohexane was prepared at 40° C. and stirred for 10 minutes. This mixture was added to the autoclave, which was subsequently pressurized with hydrogen to 40 kg./cm.². The extent of the hydrogenation was determined by ozone titration of samples of the mixture. At the end of the hydrogenation the pressure was released and the catalyst inactivated by addition of a mixture of aqueous hydrochloric acid and methanol. The organic layer was washed with water till neutral and dried and the polymer recovered.

In Table I reaction conditions for the polymerization and hydrogenation of several copolymers according to the invention have been recorded. They were all prepared in a way similar to that described for polymer 3. Table I shows the molecular weight, the extent of hydrogenation and the viscosity of the polymers in a lubricating oil.

TABLE I

Polymer No.	Composition of polymer (molar)					Polymerization conditions							Percent of olefinic bonds hydrogenated	Viscosity, cs. ¹ at 99° C.
	Styrene	Vinyl Toluene	p-tert-Butylstyrene	Iso-prene	Butadiene	Randomizer (percent weight)	Concentration monomers, (percent weight)	Total moles monomers	Mmoles sec. butyl-Li	Time (hrs.)	Temperature, ° C.	Molecular weight (×10 ⁻³)		
1-----	1.00	-----	-----	1.43	-----	² 2.76	11.1	1.207	1.34	5	40	75	95.8	12.06
2-----	1.00	-----	-----	1.00	-----	² 2.76	11.1	1.162	1.33	3.25	40	75	96.0	11.08
3-----	-----	-----	1.00	-----	1.33	³ 0.079	13.9	1.326	1.73	4	50	76	98.1	12.26
4-----	0.50	-----	0.50	-----	1.33	³ 0.078	12.0	1.326	1.73	3	50	67	97.9	13.17
5-----	-----	-----	1.00	-----	1.33	³ 0.076	13.5	1.326	1.24	5	50	106	99.1	13.09
6-----	0.75	-----	0.25	-----	1.33	³ 0.078	11.3	1.326	1.24	12	50	87	98.7	13.00
7-----	1.00	-----	-----	-----	1.33	³ 0.078	11.3	1.326	1.73	5	50	62	98.2	11.80
8-----	-----	-----	1.00	-----	5.00	³ 0.078	11.3	1.396	1.14	5	50	88	92.7	16.08

¹ Measured as 1.5% weight solution of polymer in a mineral lubricating oil with a viscosity of 7.37 cs. at 99° C.

² Diethylether.

³ Tetrahydrofuran.

ing oil if the solubility of the copolymer is sufficient to enable preparation of a concentrate; volatile solvents which can be removed after blending of the copolymer concentrate with the lubricant are also very suitable. Concentrates containing from 15 to 50% wt. of the hydrogenated random copolymer are especially suitable.

The lubricant compositions according to the invention may contain additional additives, such as antioxidants (e.g., phenolic antioxidants); detergents (e.g., calcium petroleum sulfonates; polyamines containing a hydrocarbon chain with at least 50 carbon atoms, such as polyisobutenyl-tetraethylenepentamine and reaction products of a polyamine (e.g., tetraethylenepentamine) and an alkylsuccinic anhydride in which the alkyl group contains at least 50 carbon atoms); E.P. additives, such as zinc dialkyl dithiophosphates; pour-point depressants, such as polyalkyl acrylates with 16-22 carbon atoms in the alkyl chains, polymethacrylates with an average of 12.5-15 carbon atoms in the alkyl chains, and the like.

EXAMPLE I

A hydrogenated random copolymer of p-tert-butylstyrene and butadiene (polymer 3) was prepared as follows:

A two liter glass-lined autoclave with stirrer was charged under nitrogen with 1120 ml. of a mixture of cyclohexane and hexane (3:1 vol.), 98.2 ml. of p-tert-butylstyrene, 61.6 ml. of liquid butadiene and 12.5 ml. of a solution of 60 g. tetrahydrofuran in one liter cyclohexane. The reactor was heated to 50° C. The impurities still present in the mixture were scavenged by addition of small portion of a 0.097 molar solution of sec.-butyllithium in cyclohexane until the temperature started to rise. Then 12.8 ml. of the same solution of sec.-butyllithium was added as a catalyst. The reaction mixture was stirred at 50° C. under nitrogen for 5 hours. The polymerization was terminated by addition of 2.8 ml. of a solution of 60 g. isopropyl alcohol in one liter cyclohexane.

1250 ml. of the solution so obtained was transferred under nitrogen to another two liter autoclave, the nitrogen replaced by hydrogen and the temperature raised to 70° C.

A mixture of 10 ml. of a 0.05 molar solution of nickel

EXAMPLE II

Multigrade formulations were prepared from 6 of the polymers recorded in Table I by dissolving them in a mineral oil together with 0.5% wt. of a polymeric pour point depressant and 7.5% wt. of a commercial lub oil additive package which contained a polyalkyl succinimide and a zinc dialkyldithiophosphate. Table II shows the kinematic viscosity of the formulations at 99° C. and their dynamic viscosity at -18° C. determined according to ASTM D 2602 method.

The shear stability of the formulations was investigated by pressing each oil 30 times through a diesel injector under a pressure of 190 atmospheres at room temperature at a rate of 250 ml. per minute. The diesel injector for this test is by Kurt Orbahn of Hamburg, "Apparat zu Bestimmung der Scherfestigkeit von Mineralölen." Table II shows that the kinematic viscosity measured at 99° C. after this treatment is only slightly lower than that before.

TABLE II

Polymer No.	Percent weight of polymer in solution	V _k at			V _k at 99° C. cs. after shear
		99° C. cs.	-18° C. P	99° C. cs.	
1-----	4.2	17.9	27.6	17.2	
3-----	3.9	18.1	26.0	17.6	
4-----	3.3	17.8	12.0	17.4	
5-----	3.4	17.9	24.0	17.1	
6-----	3.4	17.5	17.5	17.0	
7-----	4.0	17.5	19.0	17.2	

EXAMPLE III

Polymers 1 and 3 were tested in a Gardner IL 2 single-cylinder diesel engine that was run under constant conditions at a moderately high speed and load, with constant fuel supply. The temperature of the upper ring groove was maintained at 290° C.

The polymers were dissolved in a lubricating oil in such an amount that a multigrade 20W-40 oil was obtained. In the oil were also dissolved 6.5 wt. of calcium salt of an alkylsalicylic acid (the alkyl chains containing 14-18 carbon atoms) with a basicity of 200%, 2% wt. of a commercial polyisobutenylsuccinimide of tetraethylene pent-

amine and 0.4% wt. of a commercial zinc dialkyldithiophosphate.

For comparison the same oil containing, instead of polymer 1 or 3, a commercial polyisobutene, was also tested. The piston cleanliness rating of the oils containing polymer 1 or 3 was 1.4 and 1.5 points higher, respectively, than that of the comparative oil containing polyisobutene (cleanliness scale from 0-10).

What is claimed is:

1. A lubricant composition comprising a major proportion of a lubricating oil and as viscosity improver therefor 0.1-15% wt. of a hydrogenated organolithium-initiated solution polymerized random copolymer of a C_{4-6} conjugated diene and styrene in which the diene and/or the styrene contains at least one lower alkyl substituent, said copolymer having a number average molecular weight between about 40,000 and 150,000 and having at least 95% of the olefinically unsaturated bonds originally present saturated.

2. The composition of claim 1 in which less than 5% of the aromatic unsaturation originally present is saturated.

3. The composition according to claim 1 in which the conjugated diene is selected from the group of butadiene,

piperylene, isoprene and 2,3-dimethyl butadiene or mixtures thereof and the styrene is selected from the group of styrene and alkylated styrene or mixtures thereof.

4. The composition according to claim 3 in which the diene is butadiene and the alkylated styrene is para-tertiary-butylstyrene.

5. The composition of claim 4 in which the diene is butadiene, and the styrene is para-tertiary-butylstyrene and styrene.

6. The composition according to claim 1 in which the lubricating oil is a mineral lubricating oil.

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DANIEL E. WYMAN, Primary Examiner

W. H. CANNON, Assistant Examiner

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