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3,630,905

OIL-EXTENDED VI IMPROVERS

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5 Claims

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ABSTRACT OF THE DISCLOSURE

An oil-extended VI improver which by outward appearance is dry comprising (a) 40–60 weight percent hydrogenated butadiene-styrene polymer and (b) 60–40 weight percent of a paraffinic oil. The oil-extended VI improver can be readily dispersed in a lubricating oil following storage and/or shipping to a place of utilization.

BACKGROUND OF THE INVENTION

This invention relates to improved lubricating oils, particularly mineral lubricating oils, and processes of preparing the same. In accordance with another aspect, this invention relates to the addition of a lubricating oil in defined amounts to a hydrogenated random butadiene-styrene copolymer to produce a storable-dry-appearing product which can be subsequently dispersed in a lubricating oil to produce formulations that are shear-stable and have a high viscosity index (VI). In accordance with a further aspect, this invention relates to hydrogenated random butadiene-styrene copolymers having defined amounts of butadiene and styrene which are blended with paraffinic oils in controlled amounts to produce an oil-containing VI improver which by outward appearance is dry which, subsequent to shipping and/or storage, can be readily dispersed in a lubricating oil.

As is well known, the viscosity of lubricating oils varies with the temperature. Many oils must be employed over a wide temperature range, e.g., 0° F. to 300° F., and it is important that the oil not be too viscous at low temperatures nor too thin at high temperatures. Variation of the viscosity-temperature relationship of an oil is indicated by the well-known viscosity index value. The higher the viscosity index, the less the change in viscosity with change in temperature. Viscosity at 210° F. and at 100° F. is used to determine the viscosity index.

Many attempts have been made to improve the properties, particularly the viscosity-temperature relationships and shear stability of lubricating oils. It has been proposed to add various materials to the lubricating oils for this purpose, among which are high molecular weight hydrocarbon materials, e.g., polymerized isobutylene, hydrogenated rubber, unvulcanized rubber, and the like. These additives have met with some success, but have solubility problems which result in too low a 210° F. viscosity and too low a viscosity index. Additionally, difficulties have been experienced in the time required to disperse some of these VI improvers into a lubricating oil for subsequent use. It would be highly desirable to provide a VI improver which can be readily stored for long periods of time and subsequently shipped to a place of utilization for incorporating at the place of utilization into a lubricating oil composition with a minimum of effort and time for effecting the dispersion.

In accordance with the invention, it has been discovered that oil-extended hydrogenated butadiene-styrene VI improvers can be readily and effectively incorporated by dispersing in lube oils subsequent to extended periods of storage and/or times involved in shipping from one place to another.

Accordingly, an object of this invention is to provide a readily dispersible oil-extended VI improver.

A further object of this invention is to provide new and improved lubricating oils and methods for preparing the same.

Another object of this invention is to improve mineral and lubricating oils by adding specific hydrogenated random rubbery copolymers thereto.

A further object of this invention is to provide a method for preparing an oil-extended VI improver which can be readily stored for long periods of time and subsequently dispersed into a lubricating oil.

Other aspects and objects, as well as the several advantages of the invention, will be apparent to those skilled in the art upon further study of the specification and appended claims.

SUMMARY OF THE INVENTION

In accordance with the invention, an oil-extended VI improver is provided comprising 40–60 weight percent of a hydrogenated random butadiene-styrene copolymer and 60–40 weight percent of a paraffinic oil.

Further, in accordance with the invention, the hydrogenated random butadiene-styrene copolymer blended with the paraffinic oil has a butadiene content of 30–44 weight percent.

A presently preferred composition comprises 50 weight percent hydrogenated butadiene-styrene rubber polymer and 50 weight percent of a paraffinic oil.

In accordance with a further embodiment of the invention, the method of providing a readily dispersible VI improver is provided comprising forming an oil-extended composition by blending together 40–60 weight percent of a hydrogenated butadiene-styrene VI improver and 60–40 weight percent of a paraffinic oil and either prior to or subsequent to storage and/or shipping dispersing the oil-extended VI improver composition with a lubricating oil in an amount sufficient to form a lubricating oil composition containing up to 20 weight percent polymer.

At present, the oil-extended additives, which have an appearance, externally at least, of being dry and a solid, are usually employed in an amount in the approximate range of 0.5 to 20 weight percent polymer and a lubricating oil, preferably 1 to 15 weight percent polymer in the final lubricating oil composition. One skilled in the art in possession of this disclosure, having studied the same, can routinely determine the optimum proportion of copolymer for his purpose.

The copolymers or additives of the present invention have a molecular weight in the approximate range of 25,000 to 125,000, a now preferred range being from about 30,000 to about 75,000. The copolymer can be one containing from about 30 to about 44 parts by weight butadiene per 100 parts by weight of total monomers. The values for butadiene content of the polymers are actually those for the butadiene in the monomers charge. However, these values are very close to those for the butadiene content of the polymers because essentially complete conversion was obtained in all polymer synthesis runs. The copolymers have a vinyl content before hydrogenation of less than 35 weight percent. During hydrogenation, olefinic group hydrogenation is 95 weight percent or more and phenyl group hydrogenation is 5 weight percent or less.

The molecular weights given throughout this application was calculated from the amount of initiator used in preparing the polymers, with an allowance for the known scavenger level. These values, known as kinetic molecular weight values, are within experimental error, the same as number average molecular weights [see Journal of Polymer Science, Part A, vol. 3, page 191 (1965)].

The copolymers of the present invention presently preferred can be prepared by any of the conventional techniques known in the art, such as those described in U.S. Pat. 2,975,160, R. P. Zelinski, issued Mar. 14, 1961. For

example, a mixture of butadiene and styrene monomers can be polymerized using butyllithium as a catalyst and tetrahydrofuran as a randomizing agent. The hydrogenation can be carried out in any manner known in the art, such as by the process of U.S. Pat. 2,864,809, R. V. Jones et al., issued Dec. 16, 1958, or that of U.S. Pat. 3,113,986, D. S. Breslow et al., issued Dec. 10, 1963, or that of U.S. Pat. 3,205,278, S. J. Lapporte, issued Sept. 7, 1965. For example, the copolymer can be hydrogenated over a reduced nickel-kieselguhr catalyst or over a nickel octoate-triethylaluminum catalyst system. The hydrogenated butadiene-styrene copolymers of the present invention are polymers which have been sufficiently hydrogenated to remove substantially all of the olefinic unsaturation, leaving only the aromatic (i.e., phenyl group) unsaturation.

The extent of hydrogenation of the olefinic bonds and of the phenyl groups in the butadiene-styrene random copolymers was determined by infrared analysis before and after hydrogenation.

The paraffinic oils added as extender oils for the hydrogenated butadiene-styrene polymer are paraffinic oils of the nature of and compatible with lube oils. These paraffinic oils normally have a molecular weight in the range of 325 to 400 and a stable viscosity at 100° F. in the range of 90 to 125 SUS. A typical example of such paraffinic oils is Pennsylvania petroleum.

In actual operation, the oil-extended hydrogenated butadiene-styrene VI improver of the invention can be prepared by blending together a rubbery polymer and a paraffinic oil in the amount set forth above under the following conditions:

Method A: The rubbery polymer is heated to about 300° F. and the paraffinic oil is added with stirring, to give a uniform mixture. Upon cooling to room temperature, a slightly tacky solid is obtained in which the oil is uniformly dispersed.

Method B: The rubbery polymer dissolved in a solvent such as cyclohexane (about 14 percent solids) is mixed with the paraffinic oil, and then the solvent is removed by steam stripping, and the oil-extended polymer is oven-dried.

The oil-extended additives thus prepared yields a product which by outward appearance is dry. This oil-extended additive can be conveniently stored for extended periods of time or shipped immediately or after storage to a place of utilization. Subsequently, when it is desired to mix the oil-extended hydrogenated butadiene-styrene VI improver with a lubricating oil this can be accomplished by conventional techniques.

In the preparation of the lubricating compositions, various mineral oils are employed. Generally, these are petroleum origin and are complex mixtures of many hydrocarbon compounds. Preferably, the mineral oils are refined products such as are obtained by well-known refining processes, such as by hydrogenation, by polymerization, by dewaxing, etc. Frequently, the oils have a Saybolt viscosity at 100° F. in the range of about 60 to 5,000, and a Saybolt viscosity at 210° F. of about 30 to 250. The oils can be of paraffinic, naphthenic, or aromatic types, as well as mixtures of one or more types. However, the additives of the invention have special advantages when employed with paraffinic types of oils such as are obtained by solvent extraction of a suitable refinery stream. Many suitable lubricating compositions are available as commercial products, such as those used as motor oils, gear oils, automatic transmission oils, and the like.

The final lubricating compositions of the invention can comprise one or more of other additives known to those skilled in the art, such as anti-oxidant, pour point depressants, dyes, detergents, etc.

EXAMPLE I

An oil-extended hydrogenated butadiene-styrene VI improver was prepared by blending together 40 percent polymer and 60 percent of a paraffinic oil.

The hydrogenated polymer used in this example was a solution-polymerized random butadiene-styrene copolymer having a molecular weight of about 50,000, and was prepared using the following recipe and conditions:

	Parts by weight
Butadiene -----	35
Styrene -----	65
Cyclohexane -----	800
Tetrahydrofuran -----	1.5
sec-Butyllithium -----	0.154
Initiation temperature, °F. -----	122
Initiation pressure, p.s.i.g. -----	20

Charge order was cyclohexane, reactor purged with nitrogen, butadiene, styrene, tetrahydrofuran, and sec-butyllithium. Essentially quantitative conversion was obtained in 3 hours. At that time the unreacted product was transferred to a hydrogenation reactor, 0.13 g. of nickel (as nickel octoate) and 1.05 g. of triethylaluminum in cyclohexane were added, the reactor was pressured to 50 p.s.i.g. with hydrogen, the temperature was increased slowly to 350° F., the hydrogen pressure was increased to 400 p.s.i.g., and the temperature rose quickly to 395° F. and fell to 350° F. in about 30 minutes. Reaction was continued for 1.5 hours at 350° F. and 400 p.s.i.g., the reactor was cooled to 170° F., and the essentially completely hydrogenated polymer was recovered. With respect to the polymers in this and succeeding examples, "essentially completely hydrogenated" means that 95 weight percent or more of the olefinic groups are hydrogenated and 5 weight percent or less of the phenyl groups (when present) are hydrogenated. The polymers of the invention in this and succeeding examples all contained less than 35 weight percent vinyl unsaturation before hydrogenation.

The paraffinic oil had the following properties:

API gravity -----	32.9
Flash point, °F. -----	390
Viscosity, SUS at 100° F. -----	98.2
Viscosity, SUS at 210° F. -----	39.3
Viscosity index -----	101
Pour point, °F. -----	+5
Carbon residue -----	nil
Color, ASTM -----	1

The materials used in the example above were made by mixing the paraffinic oil with the cyclohexane solution of polymer (about 14 percent solids) followed by steam stripping to remove cyclohexane solvent and then oven drying the oil-extended additive. The oil-containing VI improver, following drying, is a solid that can be readily stored and/or shipped to a place of utilization.

The oil-extended hydrogenated butadiene-styrene VI improver formed above (40 percent polymer-60 percent paraffinic oil) was subsequently added to sufficient lubricating oil at 300° F. to produce an additive package containing 15 weight percent polymer. The polymer went into solution into the lubricating oil in about 10 minutes with stirring.

Solution of polymer crumb at 300° F. takes about 20 minutes and solution of compacted polymer takes considerably longer, demonstrating a marked improvement of dissolution of polymer using the oil-extended polymer according to the invention.

EXAMPLE II

A control run was carried out whereby an oil-extended hydrogenated butadiene-styrene VI improver prepared containing 75 percent polymer and 25 percent paraffinic oil.

The oil-extended VI improver (75 percent polymer-25 percent oil) was added to a lubricating oil at 300° F. in an amount sufficient to make an additive package containing 15 weight percent polymer. In this example, 40 g. of a glob (cut into pieces) of the 75 percent polymer-25 percent oil was added at 300° F. to the lubricating stock,

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Solution of the oil-extended VI improver was not complete in 40 minutes of stirring.

It can be seen from this example that there was insufficient paraffinic oil in the oil-extended VI improver and that the results were even poorer than a control with no oil.

EXAMPLE III

In another run, a 50-50 polymer-oil-extended hydrogenated butadiene-styrene VI improver was prepared. The butadiene-styrene rubber and paraffinic oil were the same materials as employed in the previous examples.

The oil-extended hydrogenated butadiene-styrene VI improver was dissolved in 4 minutes in enough lubricating oil to make a final 50 percent solution of polymer (weight percent). The temperature of the effecting solution of the oil-extended polymer was 300° F.

The 50-50 composition is a somewhat tacky solid exhibiting no cold flow which constitutes a very desirable product to sell and use as an additive for lubricating oils.

I claim:

1. A solid, substantially dry appearing, oil dispersible viscosity index improver composition consisting essentially of (a) 40-60 weight percent of a hydrogenated random butadiene-styrene rubbery copolymer having a butadiene content of 30-44 weight percent and the remainder being styrene, and (b) 60-40 weight percent of a paraffinic oil.

2. A composition according to claim 1 wherein the

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hydrogenated random butadiene-styrene copolymer has a molecular weight in the range of 25,000-125,000.

3. A composition according to claim 1 wherein said copolymer is substantially free of all olefinic unsaturation.

4. A composition according to claim 1 wherein (a) comprises 50 percent of said composition and (b) comprises 50 percent of said composition.

5. A composition according to claim 1 wherein the oil-extended viscosity index improver composition of (a) and (b) are combined with a lubricating oil in an amount sufficient to form a final lubricating oil composition having a viscosity index of at least 140 and the amount of (a) present in said composition being in the range of 0.5 to 20 weight percent.

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