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3,554,911

VISCOSITY INDEX IMPROVERS

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6 Claims

ABSTRACT OF THE DISCLOSURE

Shear-stable, high viscosity index lubricating oil formulations are formed by the addition of a small amount of a hydrogenated random butadiene-styrene copolymer having a butadiene content of 30 to 44 weight percent.

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 small amount of a hydrogenated random butadiene-styrene copolymer to lubricating oils to produce formulations that are shear stable and have a high viscosity index (V.I.). 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 suitable mineral oils to increase the viscosity and improve the viscosity index.

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.

In accordance with the invention, we have discovered that excellent modifiers for increasing the viscosity and improving the shear stability and viscosity index of lubricating oils are hydrogenated random butadiene-styrene copolymers having specific butadiene and styrene contents.

Accordingly, an object of the present invention is to improve lubricating oils, and particularly the viscosity-temperature relationships of mineral lubricating oils.

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 new and improved mineral lubricating oils and methods for preparing the same.

Other aspects, 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, shear-stable, high V.I. lubricating oil formulations result from the inclusion

of a small amount of a hydrogenated random butadiene-styrene copolymer having a butadiene content of 30–44 weight percent.

At present, the additives of the invention are usually employed in an amount in the approximate range of 0.5 to 5 volume percent of the lubricating oil. 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 were 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 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.

In the preparation of the lubricating compositions, various mineral oils are employed. Generally, these are of 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.

In addition to the additives of this invention, the lubri-

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cating compositions can comprise one or more of other additives known to those skilled in the art, such as anti-oxidants, pour point depressants, dyes, detergents, etc. Examples of these additives are metal petroleum sulfonates, zinc dialkyldithiophosphates, and alkyl succinimides. To be of commercial interest as a motor oil, the lubricating composition should have a viscosity index of at least about 140.

Example I

A hydrogenated random 35/65 butadiene/styrene copolymer, whose preparation is described below, was compared with a methacrylate/N-vinylpyrrolidone copolymer (Acryloid 909) in the following premium motor oil formulations:

	Weight percent	
	Commercial formulation	Experimental formulation
Mid-Continent SAE 10 stock.....	73.5	77.8
Mid-Continent SAE 50 stock.....	10.5	9.0
Phil-Ad 100 ^a	8.0	8.0
Lubrizol 925 ^b	1.6	1.6
Lubrizol 1360 ^c	0.9	0.9
Acryloid 909.....	5.5	-----
Experimental polymer.....	-----	2.8
Viscosity, SUS:		
210° F.:		
Before shear.....	65.7	65.1
After shear ^d	59.0	64.7
100° F.....	313.9	308.3
Viscosity index.....	144.5	144.7

- ^a A commercially available overbased calcium petroleum sulfonate.
^b A commercially available alkylsuccinimide.
^c A commercially available zinc dialkyldithiophosphate.
^d A sonic shear test equivalent to a 500 to 1,000 mile road test was used in all examples.

It is apparent that the experimental formulation containing an additive of the invention has about the same viscosity index and has considerably greater stability to the sonic shear test than a similar formulation containing a different commercially available copolymer.

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.

Example II

An essentially completely hydrogenated random 35/65 butadiene/styrene copolymer, whose preparation is de-

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scribed below, was compared with a commercial polymeric additive (Acryloid 909) in the following premium motor oil formulations:

	Weight percent	
	Commercial formulation	Experimental formulation
Mid-Continent SAE 10 stock.....	75.5	77.1
Mid-Continent SAE 50 stock.....	8.5	9.0
Phil-Ad 100.....	8.0	8.0
Lubrizol 925.....	1.6	1.6
Lubrizol 1360.....	0.9	0.9
Acryloid 909.....	5.5	-----
Experimental polymer.....	-----	3.1
Santopour C ^a	-----	0.3
Viscosity, SUS:		
210° F.:		
Before shear.....	65.82	65.19
After shear.....	59.0	64.8
100° F.....	302.2	318.0
Viscosity index.....	147	143

^a A wax-alkylated phenol.

It is apparent that, as in Example I, the experimental formulation has about the same viscosity index as the commercial formulation and has considerably greater stability to the sonic shear test. These formulations were compared in a 120 hour Caterpillar 1-H engine test (Federal Test Method Standard #791A, Method 346), and the experimental formulation was found to give a cleaner engine, as indicated by inspection of the pistons at the end of the test. There was also less viscosity index drop-off during the test with the experimental formulation as indicated by viscosity measurements made at the conclusion of the test:

	Commercial formulation	Experimental formulation
Viscosity, SUS:		
210° F.....	62.37	67.3
100° F.....	312.0	338.0
Viscosity index.....	138	142

The hydrogenated polymer used in this example was prepared using the same recipe used in preparing the polymer of Example I, and had the same molecular weight. Charge order was the same, except that the styrene was charged before the butadiene. Operating conditions were the same. Unreacted product was hydrogenated in the same manner as in Example I, using the same amounts of catalyst. The only difference was that the reactor was held at about 395° F. for 2 hours instead of about 350° F. for 1.5 hours. Essentially completely hydrogenated product was recovered. About 0.5 gram of water was added to the recovered polymer solution and the mixture was stirred vigorously to coagulate the catalyst. Then 25 g. of Celite filter aid and one liter of cyclohexane were added, the mixture was stirred and vacuum filtered. About 1,000 g. of Mid-Continent SAE 10 stock was added, and the cyclohexane was distilled off at 300° F. and 10 mm. Hg pressure.

Example III

A comparison was made between the viscosities and viscosity indexes (V.I.) obtained in a Mid-Continent SAE 10 stock with an essentially completely hydrogenated polybutadiene and an essentially completely hydrogenated random 35/65 butadiene/styrene copolymer:

	Viscosity at 210° F. SUS	V.I.
SAE 10 stock.....	39.6	107
Same plus 4 wt. percent hydrogenated polybutadiene.....	42.3	128
Same plus 6 wt. percent hydrogenated polybutadiene.....	44.1	134
Same plus 4 wt. percent hydrogenated copolymer.....	54.5	~141

At the same concentration level the hydrogenated random copolymer provided about 6 times as much thickening effect as the hydrogenated polybutadiene. An extrapolation of the data for the two levels of hydrogenated polybuta-

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diene indicates that about 15 weight percent hydrogenated polybutadiene would be required to obtain the 54.5 SUS viscosity obtained with 4 weight percent hydrogenated copolymer. This is obviously impractical, even if the hydrogenated polybutadiene were soluble in oil at that high concentration level. It is also apparent that at the 4 weight percent level a considerably greater increase in viscosity index is obtained with the hydrogenated copolymer than with the hydrogenated polybutadiene.

The polybutadiene used in this example was prepared in the same manner as described in Example I of U.S. Pat. 2,631,175, using 1.25 lb. of finely-divided sodium for each 100 lb. of butadiene. It had a molecular weight of about 2,000. It was hydrogenated in the following manner: 35 g. of polymer dissolved in 400 ml. of cyclohexane was placed in a nitrogen-flushed reactor, followed by 0.059 g. of Ni (as nickel octoate) and 0.475 g. of triethylaluminum in 8.5 ml. of cyclohexane. The reactor was pressured to 50 p.s.i.g. with hydrogen, stirred, and heated to 350° F., after which hydrogen pressure was increased 400 p.s.i.g. The temperature rose to about 385° F. and returned to 350° F. in 35 minutes. Stirring was continued at 350° F. and 400 p.s.i.g. for 2.5 hours. The reactor was cooled to 170° F. and the product was withdrawn. Sufficient product was mixed with 95 g. of the SAE 10 stock to give a final material containing 6 weight percent hydrogenated polybutadiene after vacuum distillation at 300° F. and 10 mm. Hg pressure to remove the reaction solvent. A portion of the material containing 6 percent polymer was diluted with further 10 stock to give the material containing 4 weight percent hydrogenated polymer.

The 35/65 butadiene/styrene copolymer was prepared and hydrogenated in the same manner as that used in Example I, and had the same molecular weight.

Example IV

Unsuccessful attempts were made to prepare a 4 weight percent solution of a hydrogenated polybutadiene, whose preparation is described below, in a Mid-Continent SAE 10 stock. Following these tests a test was made in which 0.5 weight percent of the hydrogenated polymer was dissolved in the 10 stock by heating and stirring for one hour at 295° F. Even at this level, precipitation occurred on cooling. Viscosity data for the cooled, centrifuged material and for the 10 stock are:

	Viscosity, SUS		Viscosity index
	210° F.	100° F.	
Centrifuged material.....	39.29	97.77	103
SAE 10 stock.....	39.32	97.26	105

It is apparent that the hydrogenated polybutadiene is not sufficiently soluble to improve the viscosity index of the oil.

The hydrogenated polybutadiene used in this example was prepared by hydrogenation of a polybutadiene having a molecular weight of about 50,000, which was prepared using the following recipe:

Cyclohexane, ml.	420
Butadiene, g.	40
Sec-butyllithium, mmols	1.04

Charge order was cyclohexane, 5-minute nitrogen purge, butadiene, sec-butyllithium. Reaction time was 5.5 hours at 122° F. This polymer solution was then mixed with the hydrogenation catalyst consisting of 0.057 g. of nickel stearate and 0.071 g. of triisobutylaluminum dissolved in 20 ml. of cyclohexane, reacted for 30 minutes under 300 p.s.i.g. hydrogen pressure at 175° C., cooled overnight, another portion (same size) of catalyst added, and reaction was continued for 40 minutes under 300 p.s.i.g. hydrogen pressure at 250° F. The essentially completely hydrogenated product was coagulated with methyl alcohol, filtered, and dried in a vacuum oven.

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Example V

An essentially completely hydrogenated random 41/59 butadiene/styrene copolymer, whose preparation is described below, was compared with a commercial polymeric additive (Acryloid 909) in the following premium motor oil formulations:

	Weight percent	
	Commercial formulation	Experimental formulation
Mid-Continent SAE 10 stock.....	75.5	83.2
Mid-Continent SAE 50 stock.....	8.5	4.0
Phil-Ad 100.....	8.0	8.0
Lubrizol 925.....	1.6	1.6
Lubrizol 1360.....	0.9	0.9
Santopour C.....	5.5	0.5
Acryloid 909.....		1.8
Experimental polymer.....		
Viscosity, SUS:		
210° F.:		
Before shear.....	65.82	65.19
After shear.....	58.3	63.85
100° F.:	302.2	319.9
Viscosity index:		
Before shear.....	147	144
After shear.....	141	143
Pour point, ° F.....	-30	-30

It is apparent that use of the experimental polymer instead of the commercial polymer resulted in the production of a high V.I. premium motor oil having the same pour point and considerably greater shear stability than the commercial formulation.

The random butadiene/styrene copolymer used in the tests of this example were prepared using the following recipe:

Cyclohexane, parts by weight	800
Butadiene, parts by weight	41
Styrene, parts by weight	59
Tetrahydrofuran, parts by weight	0.75
n-Butyllithium, millimoles	1.73

The charge order was as indicated, with a 3-minute nitrogen purge following solvent addition to the reactor, and 10 minutes stirring following tetrahydrofuran addition while the temperature was raised to 122° F. The reaction period was 2 hours. The untermminated polymer solution was hydrogenated 2 hours at 225 p.s.i.g. and 275° F. using 7.8 millimoles of nickel octoate per 100 parts of rubber by weight and a triethylaluminum to nickel mol ratio of 3 to 1. Essentially completely hydrogenated polymer was recovered by the technique described in Example III. The polymer had a vinyl content before hydrogenation of 22.5 weight percent, and had a molecular weight of about 75,000.

Example VI

A blend of 2.6 weight percent hydrogenated 50/50 butadiene/styrene block copolymer, whose preparation is described below, in a Mid-Continent SAE 10 stock had the following properties:

Viscosity, SUS:	
210° F.	47.53
100° F.	180.1
Viscosity index	128

This polymer also had limited solubility in the SAE 10 stock, forming a gel at a concentration of 11.6 volume percent. It is apparent that the hydrogenated block copolymer is not effective in improving the viscosity index of the SAE 10 stock whereas the hydrogenated random copolymer is effective (see Example III).

The block butadiene/styrene copolymer used in the tests of this example was prepared using the following recipe:

Cyclohexane, parts by weight	800
Styrene, parts by weight	50
Tetrahydrofuran, parts by weight	1.5
Butadiene, parts by weight	50
Sec-butyllithium millimoles	4.4

The charge order was as indicated, and the styrene was allowed to polymerize for 1.5 hours at 122° F. before addition of the tetrahydrofuran and butadiene, after which reaction was continued for 3 hours at 122° F. The un-
 5 terminated polymer solution was hydrogenated 0.5 hour at 400 p.s.i.g. and 350° F. using 6.5 millimoles of nickel octoate per 100 parts of rubber by weight and a triethyl-
 10 aluminum to nickel mol ratio of 4.1 to 1. Essentially completely hydrogenated polymer was recovered by the technique described in Example III. The polymer had a
 15 molecular weight of 25,000.

Example VII

Additional runs were conducted varying the butadiene/styrene ratio in the hydrogenated random copolymer which was blended with lubricating oil and the resulting
 15 products evaluated. The data presented in the table below were obtained in an effort to provide products having a balance of properties and a minimum V.I. of 140 along with complete polymer solubility. The lubricating oil
 20 formulation used in these tests was:

	Weight percent
Mid-Continent SAE 10 stock -----	78.7
Mid-Continent SAE 50 stock -----	8.0
Phil-Ad 100 -----	8.0
Lubrizol 925 -----	1.6
Lubrizol 1360 -----	0.9
Santopour C -----	0.5
Experimental polymer -----	2.3

These random butadiene/styrene copolymers were made in the same manner as the polymer of Example I, using the amount of tetrahydrofuran (THF) randomizing agent shown in the table and varying the level of sec-butyllithium initiator to obtain the indicated molecular weight, and
 30 were hydrogenated in the same manner to give essentially completely hydrogenated polymers.

TABLE I.—BLENDING DATA OF HYDROGENATED BUTADIENE-STYRENE COPOLYMERS

Sample:	Bd/St	Molecular weight	THF, p.h.m. ¹	Viscosity 210° F., SUS	V.I.
1-----	25/75	25,000	-----	(?)	-----
2-----	25/75	50,000	-----	(?)	-----
3-----	25/75	100,000	-----	(?)	-----
4-----	30/70	25,000	1.5	57.5	143
5-----	30/70	25,000	3.0	55.4	137
6-----	35/65	25,000	1.5	57.2	138
7-----	35/65	50,000	1.5	61.5	141
8-----	35/65	50,000	3.0	62.2	143
9-----	35/65	50,000	5.0	66.2	146
10-----	35/65	75,000	3.0	69.1	145
11-----	40/60	50,000	0.75	66.9	141
12-----	40/60	50,000	5.0	63.3	138
13-----	40/60	75,000	0.75	71.2	144
14-----	40/60	75,000	1.0	73.5	144
15-----	40/60	75,000	3.0	79.4	146
16-----	40/60	100,000	3.0	88.0	147
17-----	40/60	100,000	3.0	93.4	148
18-----	42.7/57.3	75,000	0.75	82.96	141
19-----	45/55	75,000	0.75	80.2	136
20-----	45/55	75,000	3.0	74.4	134

¹ Parts by weight per 100 parts of monomers;

² Not soluble.

Noting the table above, it is apparent that copolymers with less than about 56 percent styrene will not provide 140 viscosity index (V.I.) blends. Similarly, copolymers with more than about 70 percent styrene are not soluble in the base oil. Based on V.I. data and solubility considerations, it is apparent from the above tabulation that a rather narrow range of butadiene and styrene contents—
 5 i.e., 30 to 44 weight percent butadiene and 56 to 70 weight percent styrene—yield satisfactory hydrogenated polymers producing a lubricating oil formulation having a minimum V.I. of 140.

We claim:

1. Shear-stable, high V.I. mineral lubricating oil compositions having a minimum V.I. of about 140 comprising a mineral lubricating oil containing a viscosity improving amount of a soluble hydrogenated random butadiene-styrene copolymer dissolved therein, said copolymer having a butadiene content of 30–44 weight percent and the remainder being styrene and a molecular weight ranging from 25,000 to 125,000.

2. A composition according to claim 1 wherein the hydrogenated random butadiene-styrene copolymer has a molecular weight in the range 25,000–125,000, a vinyl content before hydrogenation of less than 35 weight percent, an olefinic group hydrogenation of 95 weight percent or more, and a phenyl group hydrogenation of 5 weight percent or less.

3. A composition according to claim 1 wherein said copolymer has a molecular weight in the range 30,000–75,000.

4. A composition according to claim 1 wherein the mineral lubricating oil has a viscosity at 210° F. in the range of 30 to 250 SUS.

5. A composition according to claim 1 wherein said copolymer is present in an amount in the approximate range of 0.5 to 5 volume percent of lubricating oil.

6. A composition according to claim 1 wherein said copolymer is prepared by copolymerization with a butyllithium catalyst and the hydrogenation is effective to remove substantially all of olefinic unsaturation.

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