United States Patent [19]

Billings

[11] **3,793,200**

[45] **Feb. 19, 1974**

[54] **LUBRICATING OIL ADDITIVES**

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[22] Filed: **July 13, 1970**

[21] Appl. No.: **54,651**

[52] **U.S. Cl.** ..... **252/32.7 E,** 252/47.5, 252/59

[51] **Int. Cl.** **C10m 1/48,** C10m 1/38

[58] **Field of Search** ..... 252/32.7 E, 47.5, 75, 59; 44/68

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[57] **ABSTRACT**

The addition of minor amounts of an asphaltene and a zinc 0,0-di-alkylphosphorodithioate minimizes viscosity increases of mineral lubricating oils containing hydrogenated butadiene-styrene copolymer VI improvers when subjected to extreme operating conditions that ordinarily cause substantial viscosity increases. The compositions are not subject to substantial viscosity increases when heated to elevated temperatures for prolonged periods.

4 Claims, No Drawings

LUBRICATING OIL ADDITIVES

BACKGROUND OF THE INVENTION

This invention relates to improved lubricating oils and processes of preparing the same. In accordance with another aspect, this invention relates to the addition of asphaltenes and a zinc 0,0-dialkylphosphorodithioate to lubricating oils containing polymeric VI improvers to improve the viscosity characteristics of the lubricating oil formulation when subjected to high temperatures for prolonged periods of time. In accordance with a further aspect, this invention relates to lubricating oil formulations containing hydrogenated butadiene-styrene copolymers as VI improvers to which has been added the combination of an asphaltene and a zinc 0,0-dialkylphosphorodithioate to minimize the viscosity increase of the oil formulation when subjected to extreme operating conditions that ordinarily cause substantial viscosity increases.

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 or 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 relationship and shear stability, of lubricating oils. It has been proposed to add various materials to the lubricating oils for this purpose. Although some of the prior art additives have met with some success, most do not minimize the viscosity increase of lubricating oils when heated to elevated temperatures such as 300°F for extremely long periods of time.

In accordance with the invention, I have discovered that the addition of minor amounts of an asphaltene and a zinc 0,0-dialkylphosphorodithioate minimizes the viscosity increase of lubricating oils when heated to and maintained at an elevated temperature for prolonged periods of time.

Accordingly, an object of this invention is to improve lubricating oils and especially the viscosity-temperature relationship of mineral lubricating oils.

Another object of this invention is to improve lubricating oils by adding specific additives thereto to stabilize the viscosity characteristics of the oil when subjected to high temperature operating conditions.

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

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

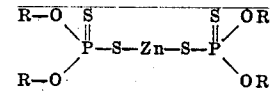
SUMMARY OF THE INVENTION

In accordance with the invention, lubricating oils exhibiting minor viscosity increases when heated to a high temperature and maintained at an elevated temperature for prolonged periods are produced by addition of minor amounts of a combination of an asphaltene and a zinc 0,0-dialkylphosphorodithioate to the oil.

In accordance with one embodiment of the invention, a lubricating oil containing a hydrogenated butadiene-styrene copolymer as a VI improver is improved with respect to its viscosity characteristics when subjected to high temperature operating conditions by the addition of an asphaltene and a zinc 0,0-dialkylphosphorodithioate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The zinc 0,0-dialkylphosphorodithioates that can be employed according to this invention are represented by the formula:



wherein R is an alkyl having from 2 to 30 carbon atoms, the R's can be the same or different, and they can have the same or different number of carbon atoms.

Examples of specific compounds which can be used include: zinc 0,0-diethylphosphorodithioate, zinc 0,0-diisopropylphosphorodithioate, zinc 0,0-di-n-propylphosphorodithioate, zinc 0,0-dibutylphosphorodithioate, zinc 0,0-di-4-methyl-2-pentylphosphorodithioate, zinc 0,0-di-3,3-dimethyl-2-butylphosphorodithioate, zinc 0,0-didecylphosphorodithioate, zinc 0,0-dieicosylphosphorodithioate, zinc 0,0-triacontylphosphorodithioate, zinc 0,0-diamylphosphorodithioate, and mixtures thereof.

The zinc 0,0-dialkylphosphorodithioate compounds that can be employed according to the invention are well known in the art and can be prepared according to any known procedure. For example, mixtures of alkyls in these compounds can be prepared as described in U.S. Pat. No. 3,442,804.

The amount of zinc 0,0-dialkylphosphorodithioate employed can range from 0.5 to 1.2 weight per cent, preferably from 0.90 to 1.05 weight per cent.

The asphaltenes that can be employed according to the invention are derived from conventional sources by conventional techniques. Known asphaltic products containing asphaltenes that can be used as additives according to the invention include heavy asphaltic crude oils, straight run residues of asphaltic crude oils, solvent tars produced by treatment of residues, cracked residues, and various petroleum asphalts. The asphaltenes can be separated, for instance, from crude oils or other asphaltic sources by extraction with pentane or similar hydrocarbon solvents or other known solvents to separate same from the crude.

The asphaltenes can be characterized as particulate materials and have the following characteristics as set forth in the *PETROLEUM REFINER*, Vol. 31, No. 2, page 138, February 1952:

Asphaltenes seem to be constant in composition, despite source, as determined by carbon-hydrogen analysis. They vary, however, in molecular weight. Determination of asphaltenes is standardized, and the fraction is variously termed as pentane, hexane, or naphtha insoluble, depending upon the precipitant used. In character, asphaltenes are predominantly aromatic. Ultimate analysis of Thurston and Knowles (IEC 28, No. 1, pp. 88–91, 1936) of asphaltenes from six different bitumens show that they are composed of from 80 to 90 per cent carbon, 6 to 10 per cent hydrogen, 0.6 to 8 per

cent sulfur, and a small proportion of oxygen and ash, with possibly nitrogen and traces of chlorine present.

The amount of asphaltenes employed according to the invention range from 0.001 to 0.2 weight per cent, preferably 0.01 to 0.1 weight per cent.

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, polymerization, 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. The additives of the invention have special advantages when employed with paraffinic types of oil such as are obtained by solvent extraction of a suitable refinery stream. Many suitable lubricating compositions are available as commerical products such as those used as motor oils, fuel oils, automatic transmission oils, and the like. The invention is applicable to any of the lubricating oils having a problem with respect to the viscosity when subjected to the high temperature conditions for long periods of time.

As indicated above, the lubricating oil to be improved with respect to viscosity characteristics according to the invention preferably contains a small amount of a hydrogenated butadiene-styrene copolymer. The amount of copolymer present is generally in the range 0.5 to 5 weight per cent, preferably 1 to 3 weight per cent, of the lubricating oil.

The copolymers or VI improver additives that can be employed according to the invention have a molecular weight in the approximate range of 25,000 to 125,000, preferably 30,000 to about 75,000. The copolymer can be one containing from about 30 to about 45 parts by weight butadiene per 100 parts by weight of total monomers. The values for butadiene content of the polymers are actually those of the butadiene and the monomers charged. However, these values are very close to those for the butadiene content of the polymers because essentially complete conversion is obtained during the polymer synthesis. The copolymers have a vinyl content before hydrogenation of less than 35 weight per cent. During hydrogenation olefinic group hydrogenation is 95 weight per cent or more and phenyl group hydrogenation is 5 weight per cent or less.

The copolymers can be prepared by any conventional techniques known in the art such as those described in U.S. Pat. No. 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. No. 2,864,809, R. V. Jones et al., issued Dec. 16, 1958, or that of U. S. Pat. No. 3,113,986, D. S. Breslow et al., issued Dec. 10, 1963, or that of U. S. Pat. No. 3,025,278, S. J. Lapporte, issued Sept. 7, 1965. The copolymer can be hydrogenated over a reduced nickel-kieselguhr catalyst or over a nickel octoate-triethylaluminum catalyst system. The hydrogenated butadiene-styrene copolymers 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 addition of the copolymers defined above to lubricating oils to improve viscosity index is disclosed and claimed in copending application Ser. No. 686,825, filed Nov. 30, 1967, now U. S. Pat. No. 3,554,911.

In addition to the copolymer, asphaltene and zinc 0,0-dialkylphosphorodithioate additives of this invention, the lubricating compositions can comprise one or more of the other additives known to those skilled in the art such as antioxidants, pour point depressants, dyes, detergents, etc. Examples of these additives are metal petroleum sulfonates, and alkyl succinimides. To be of commerical interest as a motor oil, lubricating oil compositions ordinarily have a viscosity index of at least about 134, preferably at least about 140.

SPECIFIC EXAMPLE

Tests were carried out to compare the viscosity increases for lubricating oil samples with and without the additive combination of the invention by heating the samples in a forced air oven at 300°F for 60 hours.

A 20 stock oil was clay-treated with Attapulgas Clay by heating 20 parts of oil with one part of clay (by weight) to 320°F. The oil was separated by filtration through Celite. Following clay-treating, 2.5 weight per cent of a hydrogenated butadiene-styrene copolymer was added to the oil.

A comparison was made between the viscosities obtained with the Mid-Continent SAE 20 stock thus prepared containing no additional additive, containing an asphaltene and zinc 0,0-dialkylphosphorodithioate alone, and one sample containing both the asphaltene and zinc 0,0-dialkylphosphorodithioate. The viscosity at the beginning and at the end of the tests were:

Additive in SAE 20 Oil Stock Containing 2.5 wt. % Polymer	SUS at 100°F		PERCENT Increase in Viscosity After 60 Hr. at 300°F
	Initial	Final*	
None	437	594	35
0.1 wt. % Asphaltenes	437	603	38
0.925 wt. % zinc 0,0-di(mixture of isobutyl and amyl) Phosphorodithioate**	441	715	62
0.1 wt. % asphaltenes and 0.925 wt. % Zinc 0,0-di (mixture of isobutyl and amyl) Phosphorodithioate**	441	533	21

* The average of six separate runs.

** Added 0.72 vol. percent of a concentrate comprising 93.6 weight percent mixed isobutyl and amyl phosphorodithioates and 6.4 weight percent inert diluent. The density of this concentrate was 1.15 g./cc and the density of the oil was 0.84 g./cc.

As can be seen from the above data, the viscosity increase at high temperature for the lubricating oil formulation can be substantially reduced by the addition of both an asphaltene and a zinc 0,0-dialkylphosphorodithioate in small amounts. As further demonstrated by the above data, neither additive by itself was able to minimize the viscosity increase when the lubricating oil was subjected to the high temperature severe operation.

The asphaltene used was Wafra asphaltene passing 20 mesh and retained by 40 mesh screen. The asphaltene was precipitated by n-pentane from a Middle East crude that had been topped at 1,025°F. The asphaltene represented 14.5 per cent of the charge and gave the following analysis:

Carbon	82.7 wt. %
Hydrogen	8.1 wt. %
Oxygen	0.67 wt. %
Nitrogen	0.71 wt. %
Sulfur	7.7 wt. %

Molecular weight was about 3,000. Metal content was:

V_2O_5	668 parts per million
NiO	156 parts per million
Fe_2O_3	945 parts per million

I claim:

1. A lubricating oil formulation having stable viscosity properties when subjected to extreme operating conditions which comprises:

a. a major proportion of a mineral lubricating oil;

b. 0.5–5.0 weight per cent of a hydrogenated butadiene-styrene copolymer having a butadiene content of 30–45 weight per cent, the remainder being styrene, and a molecular weight of 25,000–125,000,

c. 0.001–0.2 weight per cent of an asphaltene, said asphaltene being characterized as a particulate material which is predominantly aromatic in character and having been separated from an asphaltic product containing same, and

d. 0.5–1.2 weight per cent of a zinc 0,0-dialkylphosphorodithioate wherein the alkyl groups have two to 30 carbon atoms.

2. A composition according to claim **1** wherein the mineral lubricating oil is a clay pre-treated lubricating oil and said asphaltene is composed of from 80 to 90 per cent carbon, 6 to 10 per cent hydrogen, 0.6 to 8 per cent sulfur, and a small proportion of other materials including oxygen, ash, nitrogen, and chlorine.

3. A composition according to claim **1** wherein the alkyl in the zinc 0,0-dialkylphosphorodithioate is a mixture of isobutyl and amyl.

4. A composition according to claim **2** wherein the mineral lubricating oil has a viscosity at 210°F in the range of 30–250 SUS and said hydrogenated butadiene-styrene copolymer has a vinyl content before hydrogenation of less than 35 weight per cent, an olefinic group hydrogenation of 95 weight per cent or more, and a phenyl group hydrogenation of 5 weight per cent or less.

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