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LUBRICATING OIL ADDITIVE AND METHOD OF PREPARING THE SAME

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This invention relates to a lubricating oil additive and a method of preparing lubricating oil additives. In a further aspect, this invention relates to petroleum lubricating oil compositions. In a further aspect this invention relates to an additive which has detergent and corrosion inhibitive properties prepared by treating a hydrocarbon fraction with sulfur.

As the speed and output of internal combustion engines have increased to higher and higher values, the ability of hydrocarbon oils to maintain an engine free from lacquer, sludge and carbon deposits has decreased. Under present day conditions, lubricating oils for use in automotive and diesel engines require use of additive agents which have detergent and corrosion inhibiting properties. Also, stop and go driving in cold weather has a tendency to produce sludge in a lubricating system and additives are used to combat this problem.

The requirements necessary for a satisfactory detergent additive are: (1) compatibility with lubricating oil and other additives which may be present; (2) maintenance of satisfactory cleanliness of engine parts, principally in the ring belt zone of the piston; and (3) chemical inertness with respect to supplemental additives and metal engine parts. Additional desirable characteristics include: (1) ease of handling, either as such or as an oil concentrate; (2) minimum effect on oil properties, such as viscosity, color and odor; (3) low overall cost; and (4) independence with respect to critically limited or expensive raw materials.

The use of additives in lubricating compositions as corrosion inhibitors, oxidation inhibitors, viscosity index improvers, dispersing agents, pour-point depressants, extreme pressure agents, lubricity improvers and ash forming detergents, is well known. The need for additives to improve various specific properties of lubricating oils is acute and necessary because of the severe conditions to which lubricating oils are exposed. In internal combustion engines it is desirable that the lubricating compositions be resistant to sludge and varnish formation and, in the event of such formations, to prevent the deposition of these materials on the metallic parts of the engines.

Each of the objects of this invention will be obtained by at least one of the aspects of this invention.

An object of this invention is to provide a new lubricating oil additive.

A further object of this invention is to provide a method of producing the improved additives of this invention.

A further object of this invention is to provide an improved lubricating oil utilizing an additive derived from petroleum.

Other and further objects of this invention will be apparent to one skilled in the art upon studying the accompanying disclosure.

I have discovered that an additive having detergent and corrosion inhibiting properties can be easily prepared from inexpensive starting materials and which can be incorporated in lubricating oils to form compositions of improved lubricating oil characteristics. The process of this invention comprises heating a hydrocarbon fraction with sulfur. In order that the reaction may be effected most efficiently, the sulfur is preferably finely divided. For the treatment, the temperature should preferably be at least 300° F. so that the reaction may be carried out in a practical length of time. The temperature generally used is in excess of 400° F. There appears to be no advantage in the use of temperatures higher than 600° F. although I have used a temperature as high as 700° F. Superatmospheric pressures are generally used although the range of 10 to 200 p. s. i. a. can be set forth as suitable.

The additives of this invention can be prepared from hydrocarbon material containing at least 40 carbon atoms per molecule. The materials should have a refractive index of between 1.440 and 1.525. In addition to petroleum fractions, hydrocarbon materials which can be used include substantially saturated diene polymers, such as polybutadiene and polypentadiene and polymers of olefins having from 2 to 12 carbon atoms per molecule such as polypropylene, polyethylene, polyisobutylene, etc., preferably having a ratio of carbon atoms to olefin bonds of at least 40 to 1 and not less than 30 to 1, copolymers such as styrene-olefin copolymers, alkylated polystyrene, etc. Another way of stating this unsaturation is to say that the hydrocarbons have a maximum iodine number of approximately 60 and it is preferably below approximately 45.

Petroleum fractions which contain substantially no asphalt either in a natural state or when deasphalted, and which have been solvent extracted to reduce the content of aromatic-type hydrocarbons therein and which have been dewaxed, are also suitable. These include lubricating oils produced from Pennsylvania, Mid-Continent, California, East Texas, Gulf Coast, Venezuela, Borneo, and Arabian crudes. The source of the crude from which the petroleum fraction is derived does not significantly influence the preparation or properties of the detergent material of my invention, provided the petroleum fraction has been prepared by subjecting the crude to certain necessary treatment to extrude certain undesirable materials therefrom.

In the preparation of the preferred petroleum fraction from which the detergent material of this invention is produced, a crude oil is topped, i. e., distilled to remove therefrom the more volatile, lower molecular weight hydrocarbons, such as gasoline and light gas oil, and then vacuum reduced to remove heavy gas oil and light lubricating oil of the SAE 10 and 20 viscosity grade. The vacuum reduced crude is then propane fractionated to remove an overhead fraction of about 100 SUS at 210° F. viscosity and the residual material is subjected to a second propane fractionation to remove another overhead fraction of about 200 SUS at 210° F. viscosity. The residue from the second fractionation may be subjected to a third propane fractionation to remove still another overhead fraction of about 575 SUS at 210° F. viscosity. Propane fractionation may be modified by the presence of butane, ethane or methane to the extent desired.

Following the propane fractionation step, the overhead oil fraction is solvent extracted with a selective solvent which will separate the paraffinic hydrocarbons from the aromatic-type hydrocarbons. Suitable selective solvents

for aromatic hydrocarbons include among others, the various phenols, sulfur dioxide, furfural and β,β-dichlorodiethyl ether. This solvent extraction step for the removal of the more highly aromatic compounds can be carried out in accordance with well-known concurrent or countercurrent solvent extraction techniques, as well as by the Duo-Sol technique.

The resulting solvent extracted material, before or after the removal of the more aromatic hydrocarbons, is preferably dewaxed. Dewaxing may be carried out by any conventional method, e. g., by solvent dewaxing using propane or solvent mixtures, such as methyl ethyl ketone or methyl isobutyl ketone with benzene at a suitable temperature.

Each fraction of the phenol extracted, dewaxed, propane-fractionated oil can be used in preparing the detergent material of this invention with good results but the oil fraction from the second propane fractionation is preferred. It will be recognized by those skilled in the art that propane fractionated oils differing from those described may be used or a single broad viscosity cut can be used. The residual material from the final propane fractionation contains the rejected asphalt and more aromatic oils.

Although the preferred method for preparation of feed stock is as above described, other methods may be used to secure a similar type hydrocarbon fraction. Thus, a vacuum reduced crude which has essentially no asphalt, such as a Pennsylvania oil, may be used directly or after a light acid treatment. Another method, while not feasible commercially at the present time, is ultra-high vacuum (molecular) distillation to obtain the desired fraction.

As pointed out above, a polydiene, such as liquid polybutadiene which is prepared by sodium-catalyzed polymerization of butadiene and which material is subsequently hydrogenated so as to reduce the olefinic unsaturation thereof to the desired amount, is another suitable feed stock for use in the production of the detergent material of this invention. When butadiene is polymerized, only one double bond remains therein for each butadiene group of the polymer. The feed material of this invention should be hydrogenated sufficiently so that the ratio of carbon atoms to double bonds is at least 30 to 1. Preparation of liquid polybutadiene may be carried out by means of the process set forth in U. S. Patent No. 2,631,175, issued March 10, 1953, by W. W. Crouch.

Another suitable feed stock is a liquid or semi-solid polybutadiene which is prepared by conventional emulsion polymerization and coagulation to form synthetic rubber, subsequently hydrogenating said material so as to reduce the olefinic unsaturation thereof to the desired amount and finally thermally depolymerizing it to increase the oil solubility.

Another suitable feed material is a high molecular weight polymer prepared by zirconium tetrachloride polymerization of propylene. Still another material which has proved to be useful as a feed material in the preparation of the detergent material of this invention is a "tacky polymer" prepared by the polymerization of propylene over chromia-silica-alumina catalyst, as more fully disclosed in U. S. application Serial No. 333,576, filed January 23, 1953, now abandoned, by John P. Hogan and Robert L. Banks. Another suitable feed material is a copolymer of styrene with olefins in which the olefin portion constitutes at least 50 percent of the total molecular weight of the molecule. With any of these feed materials, it is desired to reduce the amount of olefinic unsaturation to such an extent that the ratio of carbon atoms to olefinic bonds is preferably at least 40:1 and not less than 30:1.

The hydrocarbon stocks which are useful in the practice of this invention include those materials which are identifiable as having the following properties set forth in Table I.

TABLE I

Property	Broad Range	Preferred Range
Refractive Index n_D^{20}	1.440–1.525	1.480–1.515
Average Molecular Weight	Above 600	650–10,000
Minimum Molecular Weight of a Component	450	
Viscosity, SUS at 210° F	Above 100	Above 150
Viscosity Index (when determinable [1])	50–130	75–125
Carbon Atom Content per Molecule (Ave.)	Above 40	50–720

[1] Viscosity index not determinable for non-Newtonian materials.

Table II sets forth the properties of lubricating oils which are preferred for use in my invention.

TABLE II

Property	Broad Range	Preferred Range
Refractive Index n_D^{20}	1.485–1.525	1.495–1.515
Average Molecular Weight	600–1,300	700–900
Minimum Molecular Weight of a Component	500	
Viscosity, SUS at 210° F	100–1,400	150–600
Viscosity Index	50–115	80–110
Carbon Atom Content per Molecule	40–80	50–70

The amount of sulfur is generally used in an amount of 5 to 20 weight percent based upon the weight of the hydrocarbon fraction. The sulfur is usually added in small increments and the hydrocarbon is preferably agitated during this addition. The addition of sulfur and heating is continued until a noticeable increase in viscosity, measured in Saybolt Universal seconds at 210° F., is obtained. This viscosity increase should be at least 1.5 fold at this temperature and can go as high as 50 fold. This viscosity increase is generally in the range of 1.5 to 10 fold and the range of 1.5 to 2 fold has been found especially valuable with some stock.

The time for this viscosity increase depends upon the temperature but, it may be said, that a time of 2 to 20 hours is usually suitable, the shorter times being associated with higher treating temperatures and vice versa.

For example, using an SAE 250 oil, such an oil coming within the preferred range set forth in Table II above, sufficient sulfur can be added so that after the reaction is complete, the sulfurized oil has a viscosity of 300 to 600° SUS at 210° F. Using a temperature of 700° F. and atmospheric pressure, a process time of at least 2 hours is usually required.

Following completion of the reaction with sulfur, there is an appreciable amount of hydrogen sulfide contained therein. Since it is not desirable to introduce hydrogen sulfide into an internal combustion engine, the treated material is treated so as to remove this hydrogen sulfide. This treatment should be continued until the treated hydrocarbon fraction shows no discoloration when in contact with copper. A method for hydrogen sulfide removal which I have found satisfactory comprises passing a gas such as carbon dioxide or natural gas through the treated stock.

Following removal of hydrogen sulfide, the sulfurized hydrocarbon can be used as an additive without concentration or purification. However, if a product of improved quality and purity is desired, the oil containing the additive is treated with a suitable solvent which is a solvent for the non-sulfurized fraction but is not a solvent for the additive which has combined sulfur therein. Hydrocarbon solvents are preferred. A preferred method is to treat the sulfurized fraction with propane under propane fractioning conditions such that a firm plastic or brittle solid is obtained as the insoluble bottom fraction and a propane-soluble fraction is obtained as the overhead fraction. The firm plastic or brittle solid obtained as the bottom fraction is the additive concentrate of this invention. This concentrate should contain 2 to 10 percent by weight of combined sulfur, although

I prefer additives which contain 3 to 7.5 percent combined sulfur.

In compounding the improved oil compositions provided by this invention, the additive is added to the desired oil base in an amount sufficient to obtain the desired degree of improvement in general characteristics of the oil. This amount, accordingly, depends upon the characteristics of the lubricating oil itself as well as the conditions to which the composition is subjected in use. Ordinarily, I employ the additive in an amount representing at least 0.1 percent by weight of the entire composition. The amount used seldom exceeds 10 percent by weight of the entire composition. For a preferred range, amount in the range from 0.3 to 5 percent by weight are used. The base oil can be any oil of suitable grade and viscosity obtained by modern refining methods. The additive of this invention functions independent of other additives without materially altering the physical characteristics of the oil. Accordingly, the oil may contain other additives such as detergents, viscosity index improvers, for dispersing, etc.

In application Serial No. 304,659, filed August 15, 1952, now abandoned, of Whitney, a process of preparing additives having detergent and dispersant properties is disclosed. The process of Whitney comprises oxidizing a hydrocarbon stock in order to prepare an ashless detergent. The teaching of that disclosure may be combined with my invention, that is, sulfur can be added to the oil while it is being oxidized according to the method of Whitney.

The following examples represent specific embodiments of additives prepared according to the process of my invention. The amounts, temperatures, times, etc., should be considered as illustrative of the invention and not as unduly limiting. The neutralization number used in these examples represents the number of milligrams of potassium hydroxide required to neutralize 1 gram of the material.

Example I

About 7 pounds of a finished SAE 250 stock were charged to a reaction vessel equipped with a heating mantle, a thermometer and an agitator. The free space in the reaction vessel was blanketed with natural gas throughout the treatment. The oil was heated to 480° F. and powdered sulfur was added in 0.02 pound portions every 10 to 30 minutes. Each addition of sulfur caused considerable foaming with the evolution of hydrogen sulfide. At the end of 8 hours, 0.44 pound of sulfur had been added. The oil was then stripped of hydrogen sulfide with natural gas, this taking some 12 hours. After stripping, the viscosity of the oil was 347 SUS at 210° F. and the oil showed no discoloration of copper after 3.5 hours at 180° F. Over a period of 2.5 hours, an additional 0.22 pound of sulfur was added and the oil was again stripped of hydrogen sulfide for 12 hours. At this time the viscosity was 502 SUS at 210° F. Following stripping for an additional 7 hours the viscosity was 540 SUS at 210° F. The sulfur content was 1.2 percent by weight and the neutralization number was 0.03. A spot test of a lubricating composition, an SAE 30 stock containing the sulfurized oil in a concentration of 10 percent by weight, gave results indicating excellent detergency and also oxidation stability.

Example II

The sulfurized oil prepared as described in Example I was added to a base oil and tested in a high temperature Lauson engine test. The oil employed as a base oil was a solvent-refined Mid-Continent oil of lubricating grade having the following characteristics:

Gravity, API	30.3
Viscosity at 210° F	61.8 SUS
Viscosity index	98
Neutralization number	0.01

The detergent prepared as described in Example I was added to the base oil and tested in a standard Lauson engine. This test consists in placing 920 grams of the oil composition in the crankcase of a single cylinder Lauson gasoline engine. The engine is operated under a 1.2 H. P. load at 1600±20 R. P. M. maintaining a cooling jacket temperature of 300° F., an oil temperature of 225° F. and an air-to-fuel ratio of 13.5:1. At the end of 60 hours operation under these conditions the engine is stopped, disassembled, and the piston, crankcase and bearings are examined. The piston varnish was rated on an arbitrary scale of 1 to 10 with 10 representing a clean or perfect condition and 1 representing the dirtiest condition.

Results of this test are presented below together with comparative data for the base oil and base oil plus the commercial oxidation inhibitor Santolube 395X.

	Piston Varnish	Bearing Loss, mg.
Base Oil	6.0	182
Base Oil+0.82 wt. percent 395X	6.0	1.4
Base Oil+0.82 wt. percent 395X	6.3	3.4
Base Oil+3.5 wt. percent Sulfurized Oil	7.0	11.2

Example III

The following table presents aluminum block data on a base oil and on a blend of 95 percent base oil and 5 percent of the sulfurized 250 stock prepared as described in Example I.

ALUMINUM BLOCK DATA ON SULFURIZED 250 STOCK

Oil Tested	Base Oil	5% Sulfurized 250 Stock, 95% Base Oil
Evaporation loss	0.09	0.00
SUS_{100} new oil	1,196	1,304
SUS_{210} new oil	100.7	
VI new oil	101	
SUS_{100} used oil	1,256	1,371
Vis. increase, SUS	60	67
Vis. increase, percent	5.02	5.1
Neut. No. new oil	0.03	
Neut. No. used oil	0.11	0.08

Example IV

Two additives were prepared, one from a Kansas City SAE 20 stock and the second from an SAE 50 stock by treatment with 2 percent by weight of sulfur for a period of 1 hour at a temperature of 380 to 390° F. During this treatment carbon dioxide was bubbled through the oil in order to prevent oxidation. The treated product in each case was agitated with a caustic solution of sodium sulfide to effect removal of free sulfur. The oil was then washed with water and steamed, the water separated and the oil filtered. A third additive was prepared from an SAE 250 stock according to the method set forth in Example I. These additives were tested in a concentration of 3.5 percent by weight in the base oil described in Example II. They were tested according to the method described in Example II in a high temperature Lauson engine. The following results were obtained:

Additive	Conc, Wt. Percent	Piston Varnish	Bearing Loss, mg.
None		6.0	182
From SAE 20 stock	3.5	5.7	23.1
From SAE 50 stock	3.5	4.8	11.9
From SAE 250 stock	3.5	7.0	11.2

It is to be noted that the additive prepared according to this invention, that from the 250 stock, was equal to the additives prepared according to the method used in pre-

paring the additives from the 20 and 50 stocks with respect to corrosion inhibition. The additive prepared by the method of Example I possesses detergent properties while the additives prepared according to the other method caused, in one case, a decrease in the piston varnish rating, and in the other case, substantially the same rating as the base oil.

As many possible embodiments may be made of this invention without departing from the scope thereof, it is to be understood that all matter herein set forth is to be interpreted as illustrative and not as unduly limiting the invention.

I claim:

1. A process for producing a lubricant additive which comprises subjecting a petroleum hydrocarbon fraction having the properties

Refractive index n_D^{20}	1.495–1.515
Average molecular weight	700–900
Viscosity, SUS at 210° F	150–600
Viscosity index	80–110
Carbon atom content per molecule	50–70

to treatment with sulfur in an amount of 5 to 20% by weight based on the hydrocarbon at an elevated temperature sufficient to increase the viscosity; removing hydrogen sulfide after the reaction is complete; and recovering an additive having detergent and corrosion inhibiting properties, said additive containing 2 to 10% by weight of combined sulfur, being insoluble in propane and having a viscosity at least 1.5 times that of the original hydrocarbon.

2. A lubricant additive produced by treating with sulfur a petroleum hydrocarbon fraction having the properties

Refractive index n_D^{20}	1.495–1.515
Average molecular weight	700–900
Viscosity, SUS at 210° F	150–600
Viscosity index	80–110
Carbon atom content per molecule	50–70

at an elevated temperature sufficient to increase the viscosity; said additive being insoluble in propane, containing 2 to 10% by weight of combined sulfur and having a viscosity of at least 1.5 times that of the original hydrocarbon.

3. A lubricant composition comprising a major portion of lubricating oil and at least 0.1% by weight of additive produced by treating with sulfur a petroleum hydrocarbon fraction having the properties

Refractive index n_D^{20}	1.495–1.515
Average molecular weight	700–900
Viscosity, SUS at 210° F	150–600
Viscosity index	80–110
Carbon atom content per molecule	50–70

at an elevated temperature sufficient to increase the viscosity; said additive being insoluble in propane, containing 2 to 10% by weight of combined sulfur and having a viscosity of at least 1.5 times that of the original hydrocarbon.

4. A process for producing a lubricant additive which comprises subjecting a propane fractionated SAE 250, solvent extracted petroleum hydrocarbon fraction stock, to treatment with sulfur in an amount of 5 to 20% by weight based on the hydrocarbon at a temperature of 300 to 700° F. for 2 to 20 hours, the sulfur being added incrementally over the time of the reaction; removing hydrogen sulfide after the reaction with the sulfur is completed; and recovering a lubricant additive having detergent and corrosion inhibiting properties, said additive being insoluble in propane, containing 2 to 10% by weight of sulfur and having a viscosity of at least 1.5 times that of the original hydrocarbon.

5. A lubricant additive produced by treating with sulfur a propane fractionated, SAE 250 solvent extracted petroleum hydrocarbon fraction stock, said additive being insoluble in propane, containing 2 to 10% by weight of combined sulfur and having a viscosity of at least 1.5 times that of the original hydrocarbon.

6. A lubricant composition comprising a major portion of lubricating oil and at least 0.1% by weight of an additive produced by treating with sulfur a propane fractionated, SAE 250 solvent extracted petroleum hydrocarbon fraction stock, said additive being insoluble in propane, containing 2 to 10% by weight of combined sulfur and having a viscosity of at least 1.5 times that of the original hydrocarbon.

References Cited in the file of this patent

UNITED STATES PATENTS

1,929,955	Nelson	Oct. 10, 1933
2,227,691	Plummer	Jan. 7, 1941
2,356,843	Henry	Aug. 29, 1944