United States Patent

[11] 3,607,748

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[21] Appl. No. **803,397**
[22] Filed **Feb. 28, 1969**
[45] Patented **Sept. 21, 1971**

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[54] **SULFUR CONTAINING HYDROCARBON COMPOSITION**
6 Claims, No Drawings

[52] **U.S. Cl.** **252/48.2,** 252/48.6, 252/55, 260/125
[51] **Int. Cl.** **C10m 1/38**
[50] **Field of Search** 252/48.2, 48.6, 55; 208/3; 260/125, 139

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ABSTRACT: Compositions which exhibit improved oxidation resistance and process for producing such compositions prepared by treating an oxidized hydrocarbon material with hydrogen sulfide. The preferred oxidized hydrocarbon material is an oxidized mineral oil which has been oxidized with oxygen, preferred air.

SULFUR CONTAINING HYDROCARBON COMPOSITION

This invention relates to hydrocarbon compositions having improved oxidation resistance and to a process for preparing such compositions and more particularly to lubricating oil composition having improved oxidation resistance.

The use of automobiles and other types of machines and apparatus which are operated through widely varying temperature ranges require lubricating oils, greases and other fluids which are resistant to oxidation. The oxidation of fluids particularly lubricating oils adversely affects properties of such oils such as viscosity, lubricating characteristics and corrosion tendency of the oil toward metallic members in contact with such oil. Thus, oxidation of an oil can produce sludge, deposits, and corrosion of metal parts present in a machine or apparatus such as an internal combustion engine thereby adversely affecting the functioning of such parts.

It is therefore an object of this invention to improve the oxidation resistance of lubricating oil compositions.

It has now been found that a hydrocarbon composition having improved oxidation resistance is prepared by the process which comprises (1) oxidizing a hydrocarbon material with an oxidant optionally in the presence of an oxidation promoting catalyst and (2) contacting said oxidized hydrocarbon material from step (1) with hydrogen sulfide.

The compositions of this invention are prepared by contacting a hydrocarbon material with an oxidizing amount of an oxidant optionally in the presence of an oxidation promotion catalyst for a time sufficient to effect oxidation of at least a part of the hydrocarbon material. The oxidized hydrocarbon material from step (1), is then contacted with hydrogen sulfide in an amount sufficient to incorporate sulfur into the hydrocarbon material from process step (1). By the use of the term "at least a part" it is meant that oxidation step (1) preferably produces increases in oxygen content of the hydrocarbon material of from about 0.10 wt. percentage to about 10.0 wt. percentage more preferably from about 0.25 wt. percentage to about 3.0 wt. percentage. The material from process step 1 is then contacted with hydrogen sulfide, preferably within the range of from about 0.1 moles to about 5 moles, more preferably from about 0.5 moles to about 2 moles of hydrogen sulfide per mole of oxygen incorporated in the oxidized hydrocarbon material, for a time sufficient to incorporate sulfur into step 1 material. In general sulfur is incorporated on a mole basis of from about 0.25 moles to about 1 mole more preferably from about 0.5 moles to about 1 mole per mole of oxygen incorporated into the oxidized hydrocarbon material.

As is apparent from the foregoing, oxidation step (1) is a mild oxidation whereby only a part of the hydrocarbon material is oxidized, which term oxidized hydrocarbon material from step (1) is used herein to include both oxidized and unoxidized hydrocarbon materials which remain after process step (1). The unoxidized hydrocarbon material merely acts as a diluent for the preparation of the compositions of this invention. In general the compositions of this invention have incorporated therein from about 0.10 percent sulfur to about 10 percent sulfur, more preferably from about 0.20 percent sulfur to about 2.5 percent sulfur on a weight basis. As stated above the unoxidized hydrocarbon material acts as a diluent in both process steps (1) and (2) and in general is present in the compositions of this invention on a weight basis of at least about a major amount more preferably greater than about 80 percent. Thus, a lubricating oil composition is prepared which can be used optionally with other additives or additional mineral oil, as a lubricating oil composition for an internal combustion engine.

In carrying out process step (1), an oxidant is utilized such as oxygen (including air and activated oxygen), ozone, organic peroxides, organic hydroperoxides and organic peracids, optionally in the presence of a metal catalyst.

The concentration of oxidants is usually dependent upon the increase in oxygen content which is to be obtained during the oxidation step such as oxygen content increases as set forth above. In general air rates of from about 500 to 20,000 preferably from about 1,000 to 5,000 standard cubic feet (s.c.f.) per barrel of hydrocarbon material and a liquid hourly space velocity, (volume of feed per volume of catalyst per hour, L.H.S.V.) of from about 0.2 to about 10 more preferably from about 0.5 to about 6 are utilized. In the case of ozone, organic peroxides, organic hydroperoxides and organic peracids a concentration of oxidant generally within the range of from about 0.2 to about 10 moles of oxidant per mole of oxygen incorporated into the hydrocarbon material is utilized more preferably from about 1.5 to about 4 moles of oxidant. It is preferred to use an excess of both air and other types of oxidants above that needed to incorporate the actual number of moles of oxygen (representing the oxygen increase) into the hydrocarbon material, preferably up to about 100 percent excess oxidant. The preferred oxidant which is utilized in carrying out process step (1) is oxygen (preferably as air). When a catalyst is employed, it is preferred to use a catalyst concentration varying from about 0.0001 to about 10 wt. percent based upon the weight of the hydrocarbon material and still more preferably from about 0.10 to about 10 wt. percent, the catalyst being used at that concentration which is sufficient to promote the effectiveness of the oxidant. The temperature utilized in carrying out oxidation step (1) can vary over a wide range and in general a temperature of from about 28° F. to about 450° F. is utilized, depending upon the oxidant, although higher and lower temperatures can be utilized. In general the oxidant contacts the hydrocarbon material for a time generally within the range of from about 15 minutes to about 24 hours preferably from about one-half hour to about 20 hours. The time that is utilized of necessity depends upon the nature of the hydrocarbon material and the type of oxidant. In the case of a gas, the time can vary over a wide range depending upon the particular amount of gas such as oxygen or ozone which is passed into the reaction mixture, that is the rate of introduction of oxygen or ozone into the hydrocarbon material. In general when utilizing oxygen, a temperature within the range of from about 100° F. to about 650° F., preferably within the range of from about 200° F. to about 400° F. is utilized. When ozone is utilized as the oxidant, a low temperature such as from 20° F. to about 125° F. is utilized. The quantity of oxidant utilized in the oxidation step can be obtained during the time utilized for the oxidation step. Process step (1) in general is carried out from atmospheric pressure up to 20 atmospheres although pressures above 25 atmospheres for example up to about 100 atmospheres can be utilized.

The hydrocarbon material which has been subjected to an oxidation step is then contacted with hydrogen sulfide. The hydrogen sulfide process step can be carried out in the presence of the catalyst although the presence of a catalyst is not necessary for preparing the compositions of this invention. By the use of the term "interaction with hydrogen sulfide" is meant that process step (2) can be carried out either in the absence or presence of a catalyst. Typical catalysts which can be utilized are bauxite and the oxides and sulfides of iron, copper, nickel, aluminum and manganese. These metal compounds can be employed alone or on a suitable carrier such as activated alumina, silica, silica gel or silica-alumina composites. In general a temperature of from 100° F. to about 800° F. preferably from about 200° F. to about 400° F.; pressures of from about 10 to about 1,000 p.s.i.g. preferably 14 to about 300 p.s.i.g.; liquid hourly space velocities (L.H.S.V.) of from about 0.1 to about 10 preferably from about 0.5 to about 2.0 volumes of feed per volume of catalyst per hour; and hydrogen sulfide rates of from about 250 to about 20,000 preferably from about 1,000 to about 6,000 standard cubic feet (s.c.f.) per barrel of hydrocarbon material are utilized in the hydrogen sulfide contact step.

The organic oxidants include by way of example hydrocarbon peroxides, hydroperoxides and hydrocarbon peracids wherein the hydrocarbon radicals in general contains from about 1 to about 30 carbon atoms per peroxide linkage. With

respect to the hydrocarbon peroxides and hydrocarbon hydroperoxides, it is particularly preferred that such hydrocarbon radical contain from 4 to 30 carbon atoms per peroxide linkage and more particularly from 4 to 16 carbon atoms per peroxide linkage. With respect to the hydrocarbon peracids the hydrocarbon radical which is attached to the carbonyl carbon in general contains from 1 to about 12 carbon atoms more preferably from about 1 to about 8 carbon atoms. It is intended that the term organic peracid includes by way of definition performic acid.

In addition it is contemplated within the scope of this invention that the organic oxidants can be prepared in situ, that is the peroxide, hydroperoxide or peracid can be generated in the hydrocarbon material and such organic oxidant is contemplated for use within the scope of this invention.

Typical examples of hydrocarbon radicals are alkyl such as methyl, ethyl, butyl, t-butyl, 3-methyl-1-pentyl-n-octyl and those aliphatic radicals which represent the hydrocarbon portion of a middle distillate or kerosene, cycloalkyl radicals such as cyclopentyl, alkylated cycloalkyl radicals such as mono and polymethylcyclopentyl radicals, aryl and cycloalkyl substituted alkyl radicals such as phenyl and alkylphenyl substituted alkyl radicals examples of which are benzyl, methylbenzyl, caprylbenzyl, phenylethyl, phenylpropyl, naphthylmethyl, naphthylethyl, aryl radicals such as phenyl, and naphthyl, alkaryl radicals such as xylyl, alkylphenyl and ethylphenyl.

Typical examples of oxidants are hydroxyheptyl peroxide, cyclohexanoneperoxide, t-butyl peracetate, di-t-butyl diperphthalate, t-butyl perbenzoate, methylethylketone peroxide, dicumyl peroxide, t-butyl hydroperoxide, di-t-butylperoxide, p-menthane hydroperoxide, pinane hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide and cumene hydroperoxide, organic peracids, such as performic acid, peracetic acid, trichloroperacetic acid, perbenzoic acid and perphthalic acid.

The catalysts which can be utilized to promote the oxidation of the hydrocarbon material vary with the particular oxidant. The particularly preferred catalysts for use with air are potassium sulfate promoted vanadium oxide on silica, vanadium oxide plus molybdenum oxide on silica promoted with magnesium oxide, aluminum vanadate, vanadium oxide such as when prepared by hydrolysis of butyl vanadate with water in the presence of a porous catalyst carrier, vanadium oxide, silver oxide, vanadium oxide and stannic oxide on pumice, and tin vanadate on asbestos. Examples of catalysts which can be utilized with ozone, organic peroxides, organic hydroperoxides and organic peracids are metals such as titanium, zirconium vanadium, tantalum, chromium, molybdenum and tungsten, the most preferred catalyst metals being titanium, vanadium, and molybdenum.

These catalysts for the oxidation and hydrogen sulfide contact steps can be incorporated into the process system by any means known to those skilled in the art, and can be either a homogeneous or heterogeneous catalyst system. The catalysts can be incorporated by a variety of means and by the use of a variety of carriers. The particular catalyst carrier which is utilized can be for example, a support medium or an anion (including complex formation) which is attached to the metal (e.g. a ligand). Illustrative ligands include halides, organic acids, alcoholates, mercaptides, sulfonates and phenolates. These metals may be also bound by a variety of complexing agents including acetyl acetonates, amines, ammonia, carbon monoxide and olefins, amongst others. The metals may also be introduced in the form of organometallics including "ferrocene"-type structures. The various ligands illustrated above which are utilized solely as carriers to incorporate the metal into the process system, in general have an organic radical attached to a functional group such as the oxygen atom of carbonyloxy group of the acid, the oxygen of the alcohol, the sulfur of the mercaptan, the $-\overset{O}{\overset{\|}{S}}-O-$ of the sulfonate, the oxygen of the phenolic compound and the nitrogen of the amines. The organic radical attached to the aforedescribed functional groups can be defined as a hydrocarbon radical and in general can contain from 1 to about 30 carbon atoms. Typical examples of hydrocarbon radicals are set forth above.

The metals contained on the heterogeneous catalyst can include individual or combinations of metals. These metals can be suspended on a suitable material, for example alumina, silica (or combinations of both) as well as activated clays or carbon, amongst others. The modes of contacting whereby the catalytic effect may be achieved may include slurry-bed reactions or fixed-bed reactor.

The hydrocarbon materials which are particularly suitable for preparing the compositions of this invention can be by way of example distillate oils and deasphalted residual oils. In addition such distillates or deasphalted residual oils which have been subjected to a solvent extraction process are particularly desirable as starting materials. These hydrocarbon materials are solvent refined in order to remove aromatic hydrocarbons from the distillates or deasphalted residual oils. Conventional solvent extraction techniques for obtaining such hydrocarbon materials (e.g. mineral oils) are well known in the art and selective solvents such as furfural, phenol, N-methyl-2-pyrrolidone, liquid SO_2, nitrobenzene, and dimethylformamide can be utilized as the selective solvent. The preferred hydrocarbon oils are obtained from the raffinate phase after removal of solvent. Thus, raffinates obtained by the selective solvent extraction of such distillates or deasphalted residual oils, for example raffinates obtained by the solvent extraction of lubricating oil distillates from naphthenic base crudes, mixed base or paraffinic base crudes, particularly mineral oils obtained from raffinate solutions resulting from the extraction of lube fractions to give high viscosity index (at least about 85) raffinates are particularly useful.

Examples of suitable raffinate solutions are those obtained by extracting lubricating oil distillates to produce lubricating oil raffinates having a viscosity of at least about 200 SUS at 100° F., such as so-called 200, 250, 380 and heavy distillates. Expressed another way, the raffinate should comprise hydrocarbons having an average molecular weight above about 300, although raffinate solutions obtained in the production of so-called bright stock, by the solvent extraction of short residues, generally after deasphalting, where the molecular weights are greater than 500, are suitable also, e.g. (bright stock raffinate phases).

The invention can be better appreciated by the following nonlimiting examples.

EXAMPLE 1

To a 2 liter rocking autoclave is charged 581 grams of a solvent neutral oil (kinematic viscosity of 20.6 cs. at 100° F. 4.0 cs. at 210° F. and a sulfur content of 0.05 wt. percent), together with 50 grams of a potassium sulfate promoted vanadium oxide (10.0 wt. percent) on silica catalyst. The pressure is increased to 300 p.s.i.g. with air at ambient temperature after which the temperatures is increased to 300° F. and maintained for a period of 3 hours. The temperature is reduced to ambient temperature and the pressure to atmospheric. The pressure is increased to 200 p.s.i.g. with hydrogen sulfide at ambient temperature and the temperature is increased to and maintained at 300° F. for a period of 3 hours. The temperature is reduced to ambient temperature and the pressure to atmospheric. The composition after removal of the catalyst has a kinematic viscosity of 21.8 cs. at 100° F., 4.15 cs. at 210° F., a sulfur content of 0.17 wt. percent and a pour point of −5° F.

EXAMPLE 2

To a 2 liter rocking autoclave is charged 525 grams of a solvent neutral oil (kinematic viscosity 69.1 cs. at 100° F., 8.1 cs. at 210° F. a sulfur content of 0.13 wt. percent) together with 46 grams of a silver oxide (10 wt. percent) on alumina

catalyst. The pressure is increased to 300 p.s.i.g. with air at ambient temperature after which the temperature is increased to 200° F. and maintained for a period of 2 hours. The temperature is reduced to ambient temperature and the pressure to atmospheric. The pressure is increased to 25 p.s.i.g. with hydrogen sulfide at ambient temperature and the temperature is increased to and maintained at 300° F. for a period of 6 hours. The temperature is reduced to ambient temperature and the pressure to atmospheric. The product after removal of the catalyst has a kinematic viscosity of 68.3 cs. at 100° F., 8.13 cs. at 210° F., a sulfur content of 0.21 wt. percent, and a pour point of +10° F.

EXAMPLE 3

To a 2 liter rocking autoclave is charged 550 grams of a solvent neutral oil (Kinematic viscosity of 20.6 cs. at 100° F., 4.0 cs. at 210° F. and a sulfur content of 0.05 wt. percent). The pressure is increased to 300 p.s.i.g. with air at ambient temperature after which the temperature is increased to 375° F. and maintained for a period of 4 hours. The temperature is reduced to ambient temperature and the pressure to atmospheric. To the oil is added 40 grams of silver oxide (10 wt. percent) on alumina and the pressure is increased to 200 p.s.i.g. with hydrogen sulfide. The temperature is increased to 350° F. and maintained for a period of 3 hours. The temperature is reduced to ambient temperature and the pressure to atmospheric. The composition is then separated from the catalyst by filtration.

EXAMPLE 4

To a 2 liter rocking autoclave is charged 500 grams of a solvent neutral oil (kinematic viscosity of 20.6 cs. at 100° F., 4.0 cs. at 210° F. and a sulfur content of 0.05 wt. percent). The pressure is increased to 350 p.s.i.g. with air at ambient temperature after which the temperature is increased to 325° F. and maintained for a period of 6 hours. The temperature is reduced to ambient temperature and the pressure at atmospheric. The pressure is increased to 300 p.s.i.g. with hydrogen sulfide at ambient temperature and the temperature is increased to 300° F. and maintained for a period of 8 hours. The temperature is reduced to ambient temperature and the pressure to atmospheric. The composition after removal of the catalyst has a kinematic viscosity of 22.0 cs., at 100° F., and 4.00 cs. at 210° F.

EXAMPLE 5

To a 2 liter rocking autoclave is charged 550 grams of a solvent neutral oil (kinematic viscosity of 20.6 cs. at 4.0 cs. at 210° F. and a sulfur content of 0.05 wt. percent), together with 50 grams of a copper, chromium on alumina catalyst. The pressure is increased to 300 p.s.i.g. with air at ambient temperature after which the temperature is increased to 300° F. and maintained for a period of 3 hours. The temperature is reduced to ambient temperature and the pressure to atmospheric. The catalyst is removed from the oil and the pressure is increased to 200 p.s.i.g. with hydrogen sulfide at ambient temperature. The temperature is increased to 300° F. and maintained for a period of 10 hours. The temperature is reduced to ambient temperature and the pressure to atmospheric. The composition after removal of the catalyst has a kinematic viscosity of 21.8 cs. at 100° F., and 4.20 cs. at 210° F.

EXAMPLE 6

To a 2 liter rocking autoclave is charged 581 grams of a solvent neutral oil (kinematic viscosity of 20.6 cs. at 100° F., 4.0 cs. at 210° F. and a sulfur content of 0.05 wt. percent), together with 50 grams of a potassium sulfate promoted vanadium oxide on silica catalyst. The pressure is increased to 300 p.s.i.g. with air at ambient temperature after which the temperature is increased to 300° F. and maintained for a period of 3 hours. The temperature is reduced to ambient temperature and the pressure to atmospheric. To the autoclave is added 6.5 grams of carbon disulfide and the temperature is increased to and maintained at 300° F. for a period of 3 hours. The temperature is reduced to ambient temperature and and the pressure to atmospheric. The composition after removal of catalyst has a kinematic viscosity of 20.5 cs. at 100° F., 4.00 cs. at 210° F., a sulfur content of 0.40 wt. percent and a pour point of −5° F.

As indicated previously the compositions of this invention usually have sulfur present in amounts ranging from about 0.10 percent to about 10 percent, more preferably from about 0.20 percent to about 2.5 percent by weight. The optimum amounts for a particular application depend to a large measure on the type of surface to which the lubricating composition is to be subjected. Thus for example lubricating compositions for use in gasoline internal combustion engines may contain from about 0.25 to about 2.5 by weight of sulfur whereas lubricating compositions for use in gears and diesel engines may contain as much as 10 wt. percent sulfur or even more.

This invention contemplates also the presence of other additives in the lubricating compositions. Such additives include, for example, detergents of ashless and ash-containing type, viscosity index improving agents, pour point depressing agents, antifoam agents, extreme pressure agents, rust-inhibiting agents, and oxidation and corrosion inhibiting agents.

The nonash containing detergents are exemplified by an oil-soluble, acylated nitrogen composition characterized by the presence within its structure of a hydrocarbon-substituted polar group selected from the class consisting of acyl, acylimidoyl, and acyloxy radicals wherein the substantially hydrocarbon substituent contains at least about 50 aliphatic carbon atoms and a nitrogen-containing group characterized by a nitrogen atom attached directly to said relatively polar group.

The ash-containing detergents are exemplified by oil-soluble neutral and basic salts of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, or organic phosphorus acids characterized by at least one direct carbon-to-phosphorous linkage such as those prepared by the treatment of an olefin polymer (e.g. polyisobutene having a molecular weight of 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium, and barium.

Extreme pressure agents, corrosion-inhibiting and oxidation-inhibiting agents are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulfides and polysulfides such as benzyl disulfide, bis-sulfurized sperm oil, sulfurized alkylphenol, phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with turpentine or metal oleate; phosphorus esters including principally dihydrocarbon and trihydrocarbon phosphites such as dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, metal thiocarbonmates, such as zinc dioctyl-dithiocarbamate, and barium heptylphenyl dithiocarbonmate: Group II metal phosphorodithioates such as zinc dicyclohexylphosphorodithioate zinc dictylphosphorodithioate, barium di(heptylphenyl) phosphorodithioate, cadmium dinonylphosphorodithioate, and zinc salt of a phosphorodithioic acid produced by the reaction of phosphorus pentasulfide with an equimolar mixture of isopropyl alcohol and n-hexyl alcohol.

The lubricating compositions may also contain metal detergent additives in amounts usually within the range of about 0.1 percent to about 20 percent by weight. In some applications such as in lubricating marine diesel engines the lubricating compositions may contain as much as 30 percent of a metal detergent additive. They may also contain extreme pressure addition agents, viscosity index improving agents, and pour

point depressing agents, each in amounts within the range of from about 0.1 percent to about 10 percent. The improved oxidation resistance of the compositions of this invention were determined by means of a test designed to indicate the oxidation resistance of a lubricating oil in service. The measure of oxidation resistance is determined by the varnish forming characteristics of the lubricating oil composition. In this test a weighed glass cylinder is immersed in a sample of the test oil maintained at 350° F. and agitated by a centrifugal mixer. Copper baffles are also immersed in the test oil to act as oxidation catalysts. After 13 hours the test is terminated and the glass cylinder removed, washed with gasoline, dried and reweighed. The amount of varnish deposited on the cylinder is the difference between the initial and final weights of the cylinder.

Table I summarizes the result obtained in the above test.

TABLE I

	Deposits 350° F. mgs.
Untreated solvent neutral oil from Example 1	149
Untreated solvent neutral oil from Example 2	113
Solvent sulfurized solvent neutral oil from Example 1	38
Solvent sulfurized solvent neutral oil from Example 2	38
Solvent sulfurized solvent neutral oil from Example 6	339

The results listed in Table I demonstrate the outstanding effectiveness of the compositions of this invention. Thus the amount of deposits formed using the sulfurized compositions, Examples 1 and 3, are considerably less than the unsulfurized (untreated) solvent neutral oil and considerably less than the carbon desulfide treated solvent neutral oil. Thus, the lubricating oil compositions of this invention exhibit improved oxidation compositions when subjected to an oxidation environment. As stated above, the compositions of this invention can be bonded together with other additives and lubricating oils to produce lubricating oil compositions which find utility for use in internal combustion engines. In addition, a method for improving the oxidation resistance of lubricating oil compositions has been discovered and such invention includes the treatment of an oxidized lubricating oil with hydrogen sulfide.

While this invention has been described with respect to various specific examples and embodiments it is to be understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

We claim:

1. A hydrocarbon lubricating oil composition of improved oxidation resistance prepared by the process comprising first contacting a hydrocarbon of lubricating oil viscosity with an oxidant selected from the group consisting of oxygen containing gas, ozone, organic peroxides, organic hydroperoxides and organic peracids at a temperature between about 28 and 450° F. under a pressure between about 1 and 100 atmospheres to form a first resultant hydrocarbon lubricating oil composition having an oxygen content of between about 0.1 and 10 wt. percent, subsequently second contacting said first resultant composition with hydrogen sulfide at a temperature between about 100 and 800° F. under a pressure between about 10 and 1000 p.s.i.g. to form a hydrocarbon lubricating oil composition having an oxygen content of between about 0.1 and 10 wt. percent and a sulfur content of between about 0.1 and 10 wt. percent.

2. A composition in accordance with claim 1 wherein said oxidant is air.

3. A composition in accordance with claim 1 wherein said first and second contacting is conducted in the presence of an oxidation promoting catalyst.

4. A composition in accordance with claim 3 wherein oxidant is air and said catalyst is potassium sulfate promoted vanadium oxide on silica.

5. A composition in accordance with claim 3 wherein said oxidant is air and said catalyst is silver oxide on alumina.

6. A composition in accordance with claim 3 wherein said oxidant is air and said catalyst is copper, chromium on alumina.