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SYNTHETIC LUBRICANT

William E. Garwood, Haddonfield, Francis M. Seger, Pitman, and Alexander N. Sachanen, Woodbury, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

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This invention has to do with synthetic lubricants and, more particularly, has to do with a process for preparing a new and novel class of synthetic lubricants from certain normal, alpha mono-olefins and sulfur.

As is well known to those familiar with the art, hydrocarbons have been sulfurized by various means to develop products useful as lubricants or suitable for use as adjuvants. Considerable attention has been directed to sulfurization of olefins, in view of the known ease of reaction between sulfur and unsaturated materials. Generally, the products prepared by sulfurizing olefins contain relatively large amounts of sulfur, are dark in color and are characterized by a relatively low viscosity index and/or high pour point, all of which properties limit their utility. For example, such products are effective for use in cutting oils or even as cutting oils per se, but are not suitable for use as lubricants for internal combustion engines.

In all of the prior art, however, there has been no reported success in the preparation of stable synthetic lubricants of low sulfur content, high viscosity index and low pour point. It has now been discovered that certain mono-olefins can be polymerized with sulfur under well-defined conditions to form successfully synthetic lubricants having the aforesaid desirable properties. In the process of this invention normal, alpha mono-olefins having from about 6 carbon atoms to about 14 carbon atoms are reacted with sulfur at temperatures within the range of about 550 to 750° F., the quantity of sulfur so reacted being from about 0.01 mol (atomic weight) to about 0.15 mol and, preferably less than 0.05 mol, per mol of olefin.

REACTANTS

As indicated above, the mono-olefins of this invention are normal or straight-chain alpha, mono-olefins and contain from about 6 to about 14 carbon atoms. Such mono-olefins are normally liquid at temperatures of the order of 20–25° C. Illustrative of such olefins are: hexene-1, octene-1, decene-1, dodecene-1, tetradecene-1, and the like. Preferred of such olefins, however, are those having from 8 to 12 carbon atoms, with decene-1 forming particularly outstanding synthetic lubricants. It will be clear from the foregoing examples that an alpha olefin may also be referred to as a 1-olefin.

Not only may the mono-olefins of the aforesaid character be used individually in this invention, but they may also be used in admixture with each other. In addition, olefin mixtures containing a substantial proportion of such mono-olefins may be used. Preferred of such mixtures are those containing a major proportion of a 1-olefin or of 1-olefins. Representative of such mixtures are those obtained by the cracking of paraffin waxes and other paraffin products, and those obtained from the Fischer-Tropsch and related processes. These hydrocarbon mixtures may contain, in addition to the 1-olefin or 1-olefins, such materials as: other olefins, paraffins, naphthenes and aromatics.

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In contrast to the foregoing normal, alpha mono-olefins, other olefins provide substantially lower yields of lubricants when reacted with sulfur, and these lubricants are normally of much lower quality than are those prepared from the 1-olefins defined above. Typical olefins (not the aforesaid 1-olefins of preferred chain length) providing less desirable synthetic lubricants when reacted with sulfur, under the conditions of the present process, are: butene-1, triisobutylene, 2-ethylhexene-1 and octene-2.

Polymerization and concurrent sulfurization of the aforesaid normal, alpha mono-olefins is effected with elemental sulfur. Also contemplated herein, however, are the related materials: selenium and tellurium, which provide excellent synthetic lubricants in the process of this invention. Selenium and tellurium may replace sulfur in part or in entirety, and mixtures of two or all three of said substances may be used. It will be noted that each of these substances is in class VI—B of Mendelejeff's Periodic Table, with atomic weights ranging from 32 to 128.

In view of the availability and low cost of sulfur, and particularly in view of the outstanding character of the oils obtained therewith, sulfur is particularly preferred herein. It is on this basis that the following discussion and illustrative examples are directed to polymerizations involving sulfur.

REACTION CONDITIONS

Polymerization of the aforesaid 1-olefins is effected under critical conditions. Temperature must be maintained within the range of about 550° F. to about 750° F., and preferably between about 600° F. and about 700° F. Critical also is the proportion of sulfur used with the 1-olefin, from about 0.01 mol to about 0.15 mol of sulfur being used for each mol of 1-olefin. As shown hereinafter, the interrelation of 1-olefin, temperature and proportion of reactants provides the particularly outstanding synthetic lubricants. When either of these factors falls without the lim-

its defined above, substantially inferior lubricants are formed or lubricants are obtained in but small yield.

Polymerization is generally complete in from 1 to 20 hours, with the higher reaction temperature being used for the shorter reaction periods, and with the lower reaction temperatures being used for the longer reaction periods. Ten hours has been found to be an effective time interval with temperatures of the order of 650° F.

Pressures ranging from atmospheric to 4000 pounds per square inch, most frequently about 500 pounds, characterize the polymerization. It is desirable to use sufficient pressure to maintain the reactants in liquid state.

It will be understood, of course, that the polymerization is aided by providing mixing of the reactants. This may be provided by using various agitating means which are well known in the art. At the reaction conditions, the reactants are mutually soluble and homogeneity is readily attained.

EXAMPLES

In order to illustrate the principles of this invention, the results of a series of typical, and non-limiting, polymerizations are set forth in tabular form in Table I below. These polymerizations were carried out in a rocking-type bomb (American Instrument Co.). The reactants were charged to the bomb, the free space was swept with nitrogen, and the bomb was heated to the desired temperature for the desired length of time. Thereafter, the bomb was cooled and discharged. The contents of the bomb were vacuum topped to remove unreacted hydrocarbons and products of low molecular weight. It should be noted that the reaction times, recited as "time, hours" in Table I, represent the time intervals during which the bomb was maintained at the desired temperature, and do not include the time intervals necessary to heat the bomb and its contents to the desired temperature, and do not include the time intervals necessary to cool the bomb after heat to the bomb has been discontinued. Normally, about 1½ hours are required to raise the temperature of the bomb to about 650° F.; similarly, several (about 8) hours are required for the bomb to cool to room temperature after being maintained at 650° F. for ten hours.

The reaction or polymerization products discharged from the bomb, or other reaction vessel, were topped and filtered as in the runs shown in Table I. To distinguish the polymerization products from the distillate fractions thereof, the refined oils are identified as "residual oils." The latter term identifies the oils from which unreacted materials and products of intermediate boiling range have been separated.

All of the tests and analyses to which the residual oils in Table I were subjected are well known standard tests. In this connection, it will be noted that the designation "N. N." refers to the neutralization number, which is a measure of the acidity of the oil. The abbreviation "K. V. at 210° F., Cs." is used to identify the kinematic viscosity (of the residual oils) at 210° F., measured in centistokes.

Table I

Run No.	Influence of Olefin Structure			Influence of Reaction Temperature			
	1	2	3	4	5	6	7
Olefin	Octene-1	Octene-2	2-Ethyl Hexene-1	Decene-1	Decene-1	Decene-1	Decene-1.
Parts by Weight	336	336	336	280	280	280(X2.5)	280.
Molar Proportion	3	3	3	2	2	2(X2.5)	2.
Sulfur:							
Parts by Weight	2	2	2	2	2	2(X2.5)	2.
Molar Proportion	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625(X2.5)	0.0625.
Temperature, °F	655	650	655	510	600	652	702.
Time, Hrs.	10¼	10½	10¼	10	10	10¼	3.
Max. Pressure, p. s. i. g.	350	700	850	175	100	425	750.
Residual Oil:							
Yield, Percent [1]	8.9	5.3	2.1	6.74	15.2	26.4	16.0.
K. V. @ 210° F., Cs.	3.61	3.62	4.97	4.30	3.69	3.59	3.31.
V. I.	91.8	77.7	60.5	148	142	128	117.5.
Pour Point, °F	<−30	<−30		<−35	<−30	−20	−15.
N. N.				1.0	0.3	0.2	0.1.
Specific Gravity				0.8524	0.8378	0.8383	0.8498.
Color (Lovibond)						20	52.
Sulfur, Per Cent				4.17	2.37	1.16	1.41.

Run No.	Influence of Sulfur Concentration					
	8	9	10	11	12	13
Olefin	Decene-1	Decene-1	Decene-1	Octene-1	Butene-1	Tri isobutylene.
Parts by Weight	280	280	280	280	142	332.
Molar Proportion	2	2	2	2.5	2.63	2.
Sulfur:						
Parts by Weight	2	16	1	0.15	16	16.
Molar Proportion	0.0625	0.5	0.031	0.005	0.5	0.5.
Temperature, °F	652	653	604	600	500	500.
Time, Hrs.	10¼	10	10¼	10	10	10.
Max. Pressure, p. s. i. g.	425	150	200	950	500	<100.
Residual Oil:						
Yield, Per Cent [1]	26.4	25.6	11.4	10.4	5.7	Copper Gasket Corroded During Reaction Black Tar Left in Bomb.
K. V. @ 210° F., Cs.	3.59	2.92	3.37	4.01	Black Tar.	
V. I.	128	84.8	133	120.5		
Pour Point, °F	−20	<−30	<−30	<−35		
N. N.	0.2	0.2	0.1	0.1		
Specific Gravity	0.8383	0.8822	0.8319	0.8324		
Color (Lovibond)	20	350	1.7	60		
Sulfur, Per Cent	1.15	4.58	1.70	0.18		

[1] Based upon original charge materials; reaction product distilled to a maximum temperature of 200° C. at 2 mm. to remove intermediate products.

From the data in Table I above, it will be seen, in runs 1, 2 and 3, that a substantially larger yield of synthetic oil is obtained from octene-1 (a normal, alpha mono-olefin) than from either octene-2 or 2-ethylhexene-1. Further, the viscosity index (V. I.) of the synthetic oil from octene-1 is appreciably higher than the viscosity indices for the oils prepared from octene-2 or 2-ethylhexene-1.

Runs 4 through 7, inclusive, demonstrate the critical nature of the reaction temperature. At a temperature of 502° F. (run No. 4) a synthetic oil is obtained in relatively small yield and has a high sulfur content. When the temperature is maintained within the range of 600–702° F. (runs 5–7), synthetic oils are obtained in substantially larger yields than in run 4 at 510° F. and the sulfur content of the synthetic oils is at a desirable level.

Runs 8 and 9 indicate the influence of the proportion of sulfur, for when a larger proportion than contemplated herein is used the viscosity index falls and the yield decreases somewhat.

Runs 10 and 11 represent two additional synthetic oils, illustrative of the invention.

Runs 12 and 13 further illustrate the interrelation of olefin structure, reaction temperature and concentration of sulfur. For example, in run 12, the olefin used is butene-1 and the reaction temperature is only 500° F.; the product was a black tar. In run 13, the olefin was triisobutylene and the temperature of reaction only 500° F.; again a black tar was formed.

That the residual oils illustrated above in Table I are characterized by a high degree of stability is revealed by the results of a catalytic oxidation test for the oil of run 6. In this test 6.5 feet of No. 14 (Brown and Sharpe gauge) iron wire (15.6 square inch), 6.2 inches of No. 18 (B. & S.) copper wire (0.78 square inch), 3.33 inches of No. 12 (B. & S.) aluminum wire (0.87 square inch), a ¼ inch square of $\frac{1}{16}$ inch lead sheet ($^1/_{16}$ square inch), and 25 ccs. of the test oil were placed in a glass test tube, heated to 260° F. and air blown therethrough at the rate of 10 liters per hour for 40 hours.

Changes in the characteristics of the oil and effect of the oil upon the lead sheet were reported. The results of this test with the residual oil of run 6, and with a SAE–10 solvent-refined Pennsylvania motor oil, are shown in Table II below.

Table II

	N. N.	K. V. at 210° F., Cs.	Percent Vis. Incr.	Pb Loss, mgms.
Reference Oil	16	12.91	125	235
Oil of Run 6	0.9	3.77	5.0	46.1

The test data set forth in Table II clearly indicate the high degree of stability which characterizes the oils contemplated herein.

As will be evident from the data presented above in Tables I and II, the polymerization products of this invention are highly desirable lubricants per se. They are also of considerable value as blending agents for other lubricating oils. In view of the inherent stability of the synthetic oils, they impart stability to the oils with which they are blended. So also, they impart desirable viscosity index (V. I.) and pour point characteristics to the oils in combination therewith, for, as indicated above, they have advantageous viscosity index and pour point properties. In short, the synthetic oils find utility in "upgrading" other lubricants. Typical oils with which the synthetic oils may be blended are mineral oils such as are normally used in internal combustion and turbine engines. When so blended, the synthetic oils may comprise the major proportion of the final blended oil, or may even comprise a minor proportion thereof. For example, although used only in the amounts of the order of 1 to 10 per cent, the synthetic oils improve the stability of mineral oils, such as SAE 10 and 20 Pennsylvania type oils.

One or more of the individual properties of the synthetic lubricants of this invention may be further improved by incorporating therewith a small, but effective amount, of an addition agent such as an antioxidant, a detergent, an extreme pressure agent, a foam suppressor, a viscosity index (V. I.) improver, etc. Antioxidants which may be used are well-known in the art, and are generally characterized by phosphorus, sulfur, nitrogen, etc. content; representative of such materials is a phosphorus- and sulfur-containing reaction product of pinene and P_2S_5. Typical detergents which may be so used are metal salts of alkyl-substituted aromatic sulfonic or carboxylic acids, as illustrated by diwax benzene barium sulfonate and barium phenate, barium carboxylate of a wax-substituted phenol carboxylic acid. Extreme pressure agents are well known; illustrating such materials are numerous chlorine and/or sulfur containing compositions, one such material being a chlornaphtha xanthate. Silicones, such as dimethyl silicone, may be used to illustrate foam suppressing compositions. Viscosity index improving agents which may be used are typified by polypropylenes, polyisobutylenes, polyacrylate esters, and the like.

Contemplated also as within the scope of this invention is a method of lubricating relatively moving surfaces by maintaining therebetween a film consisting of any of the aforesaid oils.

It is to be understood that the foregoing description and representative examples are non-limiting and serve to illustrate the invention, which is to be broadly construed in the light of the language of the appended claims.

We claim:

1. The method of preparation of a viscous oil, which comprises: polymerizing, at a temperature between about 550° F. and about 750° F., for a period of time from about twenty hours to about one hour, respectively, a normal, alpha mono-olefin having from about 6 to about 14 carbon atoms, in the presence of an elemental substance selected from the group consisting of sulfur, selenium and tellurium, the molar ratio of said substance to said olefin being from about 0.01 to about 0.15.

2. The method of preparation of a viscous oil, which comprises: polymerizing, at a temperature between about 550° F. and about 750° F., for a period of time from about twenty hours to about one hour, respectively, a normal, alpha mono-olefin having from about 6 to about 14 carbon atoms, in the presence of sulfur, the molar ratio of sulfur to said olefin being from about 0.01 to about 0.15.

3. The method of preparation of a viscous oil, which comprises: polymerizing, at a temperature between about 600° F. and about 700° F., for a period of time from about twenty hours to about one hour, respectively, a normal, alpha mono-olefin having from about 6 to about 14 carbon atoms, in the presence of sulfur, the molar ratio of sulfur to said olefin being from about 0.01 to about 0.15.

4. The method of preparation of a viscous oil, which comprises: polymerizing, at a temperature between about 550° F. and about 750° F., for a period of time from about twenty hour to about one hour, respectively, a normal, alpha mono-olefin having from about 8 to about 12 carbon atoms, in the presence of sulfur, the molar ratio of sulfur to said olefine being from about 0.01 to about 0.15.

5. The method of preparation of a viscous oil, which comprises: polymerizing decene-1 in the presence of sulfur, at a temperature between about 550° F. and about 750° F., for a period of time from about twenty hours to about one hour, respectively, the molar ratio of sulfur to decene-1 being from about 0.01 to about 0.15.

6. A viscous oil obtained by: polymerizing, at a temperature between about 550° F. and about 750° F., for a period of time from about twenty hours to about one hour, respectively, a normal, alpha mono-olefin having from about 6 to about 14 carbon atoms, in the presence of an elemental substance selected from the group consisting of sulfur, selenium and tellurium, the molar ratio of said substance to said olefin being from about 0.01 to about 0.15.

7. A viscous oil obtained by: polymerizing, at a temperature between about 550° F. and about 750° F., for a period of time from about twenty hours to about one hour, respectively, a normal, alpha mono-olefin having from about 6 to about 14 carbon atoms, in the presence of sulfur, the molar ratio of sulfur to said olefin being from about 0.01 to about 0.15.

8. A viscous oil obtained by: polymerizing, at a temperature between about 600° F. and about 700° F., for a period of time from about twenty hours to about one hour, respectively, a normal, alpha mono-olefin having from about 6 to about 14 carbon atoms, in the presence of sulfur, the molar ratio of sulfur to said olefin being from about 0.01 to about 0.15.

9. A viscous oil obtained by: polymerizing, at a temperature between about 550° F., and about 750° F., for a period of time from about twenty hours to about one hour, respectively, a normal, alpha mono-olefin having from about 8 to about 12 carbon atoms, in the presence of sulfur, the molar ratio of sulfur to said olefin being from about 0.01 to about 0.15.

10. A viscous oil obtained by: polymerizing decene-1 in the presence of sulfur at a temperature between about 550° F. and about 750° F., for a period of time from about twenty hours to about one hour, respectively, the molar ratio of sulfur to decene-1 being from about 0.01 to about 0.15.

11. A viscous oil obtained by polymerizing decene-1 in the presence of sulfur at about 650° F. for about 10 hours, the molar ratio of sulfur to decene-1 being about 0.03.

12. A viscous oil obtained by polymerizing decene-1 in the presence of sulfur at about 600° F. for about 10 hours, the molar ratio of sulfur to decene-1 being about 0.03.

13. A viscous oil obtained by polymerizing decene-1 in the presence of sulfur at about 700° F. for about 3 hours, the molar ratio of sulfur to decene-1 being about 0.03.

WILLIAM E. GARWOOD.
FRANCIS M. SEGER.
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