

UNITED STATES PATENT OFFICE

2,500,163

SYNTHETIC LUBRICANTS

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No Drawing. Application October 29, 1948,
Serial No. 57,421

15 Claims. (Cl. 260—683.15)

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This invention has to do with a new and novel class of synthetic lubricants and with a method of preparing the same. More particularly, the invention relates to synthetic lubricants obtained by polymerization of normal, alpha mono-olefins in the presence of phosphorus sulfides.

As is well known to those familiar with the art, olefins have previously been polymerized and condensed, thermally or catalytically, to form products of varying character. Olefins have also been reacted at elevated temperatures with phosphorus sulfides, and with elemental phosphorus and sulfur, to form phosphorus- and/or sulfur-containing products. The latter products have been developed, for example, for use as additives for lubricating oils and the like. In the prior art, it has been indicated that olefins as a class may be so reacted to produce lubricating oil addition agents. There has been little emphasis upon the character of the olefins, although relatively short-chain iso-olefins, such as isobutylene, and polymers thereof, have received considerable attention. Long chain olefins, such as cetene (C₁₆) and melene (C₃₀) have also been mentioned, no distinction being made as to the position of the double bond. With regard to the phosphorus sulfide, and phosphorus and sulfur reactants, it has been disclosed that at least one per cent by weight of phosphorus sulfide, or corresponding quantity of phosphorus and sulfur, is necessary in order to form an effective addition agent. Temperatures necessary for reaction have been within the range of 200° F. to 500° F.

While the foregoing phosphorus- and sulfur-containing products have been effective in stabilizing lubricating oils when incorporated therein in minor proportions, as of the order of 0.5 to 10 per cent, such products have not been suitable for use as lubricants per se. They are generally rather acidic, as indicated by neutralization number determinations (N. N.), and some have poor viscosity and/or pour characteristics.

In contrast to prior art developments, it has now been discovered that synthetic lubricants of excellent character, particularly high viscosity

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index, low pour point and great stability, are formed by polymerizing certain normal, alpha mono-olefins in the presence of phosphorus sulfides, or elemental phosphorus and sulfur, under the critical and inter-related reaction conditions hereinafter described.

REACTANTS

As indicated above, the mono-olefin reactants of this invention are normal or straight chain alpha mono-olefins and contain from 5 to 18 carbon atoms. Such mono-olefins are normally liquid at temperatures of the order of 20–25° C. Illustrative of such mono-olefins are the following: pentene-1, octene-1, decene-1, dodecene-1, octadecene-1, and the like. Preferred however, of such olefins are those having from 8 to 12 carbon atoms, with decene-1 representing a particularly desirable olefin. 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; 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.

In many instances, in commercial operation, it will be found desirable to use technical grades of 1-olefins. Mixed olefinic materials derived from thermal cracking of hydrocarbon wax or from the Fischer-Tropsch process constitute satisfactory charging stocks. In this connection, it must be noted that it is suspected that substantially straight chain 1-olefins, that is, 1-olefins

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in which the length of the side chain (or chains) is short relative to the length of the main chain, and in which the side chain (or chains) is not adjacent to the terminal double bond, are also suitable, although less advantageous charge stocks for the purpose of the present invention. In view of the unavailability of such olefins, however, no test data can be adduced to confirm this suspicion.

That the character of the olefin reactant is critical is shown by several illustrative examples hereinbelow. For example, when a normal olefin having from 5 to 18 carbon atoms and having an interior double bond rather than a terminal double bond, is used, the product is obtained in low yield and is characterized in most instances by a low viscosity index and/or high corrosivity toward copper. Similar results are obtained with branched chain olefins having an interior double bond, and with branched chain 1-olefins in which a side chain is adjacent to the terminal double bond.

The phosphorus and sulfur reactant may be in the form of elemental phosphorus and elemental sulfur or in the form of a phosphorus sulfide. All of the phosphorus sulfides are contemplated herein, included among which are: P_3S_2 (or PS_2), P_4S_3 (or P_2S_3), P_4S_5 , P_2S_5 , P_4S_7 , P_4S_{10} , etc. Particularly advantageous in providing outstanding synthetic oils is P_2S_5 which represents the preferred reactant. When elemental phosphorus and elemental sulfur are used under the conditions of operation described below, it is most probable that a phosphorus sulfide or phosphorus sulfides are formed in situ. It will be understood that elemental phosphorus and/or elemental sulfur may be used with one or more of the phosphorus sulfides in the preparation of a synthetic oil.

REACTION CONDITIONS

The most critical reaction conditions, coupled with the specific character of the aforesaid reactants, are the proportions of the reactants and the reaction temperature.

It has been found that the proportion of phosphorus sulfide reacted with the 1-olefin reactant is critical and should be maintained below one per cent, by weight, of their combined weight. The proportion of phosphorus sulfide used falls within the range of from about 0.01 per cent to less than one per cent by weight of the olefin-phosphorus sulfide charge. When elemental phosphorus and sulfur are used in place of a phosphorus sulfide, the proportion of phosphorus will be of the order of 0.003 to 0.9 per cent by weight of the charge, and the proportion of sulfur will be from about 0.007 to 0.9 per cent of said charge, the total proportion of phosphorus and sulfur not exceeding 1 per cent. Correspondingly, when a small quantity of elemental phosphorus, preferably red phosphorus, is used with a phosphorus sulfide, the combined quantity of phosphorus and phosphorus sulfide will be less than one per cent by weight of the charge. A similar precaution is observed when elemental sulfur, or when both elemental sulfur and elemental phosphorus, are used with a phosphorus sulfide.

Specifically in regard to the proportions of reactants, it has been noted that when more than one per cent of a phosphorus sulfide, as P_2S_5 , is used, a product of relatively low viscosity index is obtained in low yield. The influence of

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the proportions of reactants is demonstrated by several illustrative examples shown hereinbelow.

With regard to reaction temperature, it has been found that the temperature should be above 600° F. and below 750° F. When temperatures below 600° F. are used, the yield of product is generally low, and the product is characterized by a relatively high degree of corrosivity to copper and other metals as indicated by neutralization number determinations. When temperatures of 750° F. and greater are used, the yield is again low, and the product is of low viscosity index and has poor color. Most advantageous results are obtained with reaction temperatures between about 640° F. and about 700° F.

Other reaction conditions to be considered in forming the lubricants contemplated herein are pressure and reaction time. The pressure to be used is not particularly critical. It may range from about 100 to about 4000 pounds per square inch, or even higher.

Reaction time varies inversely with temperature. Satisfactory products and satisfactory yields of the same may be obtained with reaction times as short as one hour or less and as long as twenty hours. With higher temperatures, as those approaching the upper limit of 750° F., shorter reaction periods are used; correspondingly, with lower temperatures, as those of the order of 625° F., longer reaction periods are used. Preferably, the time is in the neighborhood of 10 hours at 625–650° F., and about 3 hours at 700–725° F.

EXAMPLES

In order to illustrate the principles of this invention, the results of a series of typical, and non-limiting, condensations are set forth in tabular form in Table I below. These condensations were carried out in rocking-type bombs (American Instrument Co.). The reactants were charged to the bombs, which were then heated to the desired temperature for the desired length of time. Thereafter, the bombs were cooled, and discharged. The contents of the bombs were vacuum topped to remove unreacted hydrocarbon materials. It should be noted that the reaction times, recited as "Time, hours" in Table I, represent the time intervals during which the bombs were maintained at the desired temperature, and do not include the time intervals necessary to heat the bombs and their contents to the desired temperature, and do not include the time intervals necessary to cool the bombs after heat to the bombs has been discontinued. In general, about 2 hours are required to raise the temperature from 60–08° F. to 640° F., and about 10 hours to cool thereafter to 60–80° F., in runs such as shown in Table I.

The condensation products discharged from the bombs, or other reaction vessels, were vacuum topped and filtered, as in the runs shown in Table I. To distinguish the condensation 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.

TABLE I

Run No.	1	2	3	4	5	6
Olefin	Octene-1	Octene-2	2-Ethyl Hexene-1	Decene-1	Decene-1	Decene-1
Parts by Weight	336	336	336	280	280	700
Molar Proportion	3.0	3.0	3.0	2.0	2.0	5.0
Phosphorus Sulfide	P ₂ S ₅	P ₂ S ₅	P ₂ S ₅	P ₂ S ₅	P ₂ S ₅	P ₂ S ₅
Parts by Weight	1	1	1	6	0.15	2
Per cent by Weight	0.3	0.3	0.3	2.1	0.05	0.3
Molar Proportion	0.0045	0.0045	0.0045	0.027	0.0007	0.009
Phosphorous						
Parts by Weight						
Per Cent by Weight						
Molar Proportion						
Sulfur						
Parts by Weight						
Per Cent by Weight						
Molar Proportion						
Temperature, °F	650	645	650	505	600	640
Time, Hrs	10	10	9½	10	10	10
Max. Pressure, p. s. i. g.	2600	3200	1600	100	100	350
Residual Oil:						
Parts by Weight	163	10	18	26	10	132
Yield, Per Cent	48.5	3.0	5.3	9.0	3.6	18.9
Viscosity @ 100° F., Cs.	9.72	18.43	15.97	62.97	17.94	7.22
Viscosity @ 210° F., Cs.	2.57	3.70	3.07	8.21	3.93	2.12
V. I.	104.7	92	26.5	107	133	101.5
Pour Point, °F	< -30	< -30	< -30	< -20	< -35	< -30
Specific Gravity	0.8260			0.9613		0.8227
N. N.	0.1	5.5	0.1	23.5	2.5	2.4
Color (Lovibond)	4					54
Per Cent Phosphorus	0.001		< 0.001	6.65		0.11
Per Cent Sulfur	0.50		0.25	12.16		0.38

Run No.	7	8	9	10	11
Olefin	Decene-1	Decene-1	Decene-1	Decene-1	Decene-1
Parts by Weight	350	350	280	400	250
Per Cent by Weight	2.5	2.5	2.0	2.86	2.0
Phosphorous Sulfide	P ₂ S ₅	P ₂ S ₅	P ₂ S ₅		
Parts by Weight	1	3.5	0.8		
Per Cent by Weight	0.3	1.0	0.3		
Molar Proportion	0.0045	0.016	0.0036		
Phosphorous				Red	Red.
Parts by Weight				1	1
Per Cent by Weight				0.2	0.4
Molar Proportion				0.031	0.031
Sulfur				Flowers	Flowers.
Parts by Weight				3	2
Per Cent by Weight				0.7	0.7
Molar Proportion				0.094	0.062
Temperature, °F	700	703	750	615	700
Time, Hrs.	3	3	3	10	3
Max. Pressure, p. s. i. g.	300	800	1100	1500	900
Residual Oil:					
Parts by Weight	73.1	41	27	201.2	38
Yield, Per Cent	20.8	11.5	9.6	49.8	13.4
Viscosity @ 100° F., Cs.	8.99	11.09	16.12	7.33	14.70
Viscosity @ 210° F., Cs.	2.42	2.69	3.23	2.21	3.21
V. I.	98	83.7	57.2	119.6	87.3
Pour Point, °F	< -30	< -30	< -30	-10	< -30
Specific Gravity	0.8333			0.8222	0.8639
N. N.	0.3	0.2	0.2	0.1	21.7
Color (Lovibond)	11	110	500	2.3	575
Phosphorus	0.20	90.002	0.013	0.005	1.34
Per Cent Sulfur	0.51	0.49	0.13	1.01	1.48

¹ Ramsbottom carbon Residue 0.02.

² Ramsbottom carbon Residue 0.07.

From the data set forth in Table I above, several observations may be made. Run 1 indicates that a synthetic oil of excellent quality may be prepared by reacting octene-1 with P₂S₅ under the conditions described above, namely, 650° F. and less than one per cent by weight of P₂S₅. The lubricant obtained in run 1 is obtained in a yield of 48.5 per cent; it has a V. I. of 104.7, a pour point of less than -30° F., an N. N. of only 0.1, and a Lovibond color of only 4. In contrast, run 2 shows an oil product obtained by reacting octene-2, which is not a normal, alpha mono-olefin, with P₂S₅ under substantially the same conditions. The yield in run 2 is only 3.0 per cent and the product has considerable acidity, as indicated by an N. N. of 5.5. Also in contrast with run 1 is run 3, wherein 2-ethyl hexene-1 is used. Here again, the olefin is not a normal, alpha mono-olefin. In run 3, the yield is again low, only 5.3 per cent, and the V. I. is but 26.5.

Runs 4 through 9 show oil products obtained from decene-1 and P₂S₅. In run 4, the reaction

temperature is only 505° F., below the prescribed minimum temperature, and the quantity of P₂S₅ is 2.1 per cent by weight, greater than the prescribed maximum quantity. With such conditions in run 4, the oil product is obtained in relatively low yield, 9.0 per cent, and has a high degree of acidity, as shown by an N. N. of 23.5. Run 5 was also carried out with a low temperature, only 600° F., with the result that the product was obtained in very low yield, 3.6 per cent. In comparison with runs 4 and 5, run 6 shows reaction conditions within the prescribed limits: 640° F. and 0.3 per cent by weight of P₂S₅. The yield of product in run 6 was 18.9 per cent, with the product characterized by the following desirable properties: V. I., 101.5; pour point, less than -30° F.; N. N., 2.4; Lovibond color, 54.

Run 7 also illustrates the invention, showing an oil obtained at 700° F. The oil product, in comparison with the desirable oil product of run 6, has a slightly lower V. I., but a much lower degree of acidity (N. N.=0.3) and better color.

Run 8 demonstrates again the effect of an excessive quantity of P_2S_5 . In contrast with run 7, the oil product of run 8 is obtained in lower yield, only 11.5 per cent; has a substantially lower V. I., only 83.7; and is of excessively dark color, 110. Run 9 reveals the effect of high temperature at the upper limit of the range described above. At 750° F., the yield is low, 9.6 per cent; the viscosity index is but 57.2; and the color is again very dark, 500.

Runs 10 and 11 demonstrate the production of oil products from phosphorus and sulfur, rather than a phosphorus sulfide. Under the conditions of reaction, however, it is probable that a phosphorus sulfide or more than one such sulfide is formed. Run 10 is illustrative of the invention, with an excellent oil product being formed therein. Run 11, however, is conducted with an excessive quantity of phosphorus and sulfur, the sum being greater than one percent. Contrasting runs 10 and 11, it will be noted that the yield of run 10 is 49.8 per cent and that of run 11 only 13.4 per cent. The V. I. of the oil product of run 10 is 119.6, substantially greater than that of run 11, namely, 87.3. Further, the acidity of the oil of run 10 is negligible, only 0.1 N. N.; whereas, the oil of run 11 has an N. N. of 21.7. The great difference between the two oils is also revealed by color determinations, 2.3 for the oil of run 10 compared with 575 for the oil of run 11.

Referring further to the results provided in Table I, it will be noted that the oils of runs 1, 6, 7 and 10, all of which illustrate the invention, have kinematic viscosities, at 210° F., of the order of 2.12–2.57 centistokes. Such oils, thereof, are below SAE 10 oils in viscosity and are excellently suited for use as break-in oils, blending stocks, cold climate lubricants and the like. Furthermore, the properties of the synthetic oils are such as to meet the requirements for turbo-jet lubricating oils. The latter oils, for example, should have low viscosity, low pour point and high viscosity index.

As a further note, on Table I, the molecular weight of the oil of run 6 was found to be 331 using cyclohexane as a solvent, and 313 using benzene as a solvent. This would indicate that the oil is predominantly comprised of dimers (molecular weight 280) and trimers (molecular weight 420) of decene-1.

A number of well-known tests were made on the residual oils shown in Table I, above, to determine their characteristics and usefulness. For example, the residual oil from run 6 was subjected to the copper strip test, which is a standard test for lubricants. The purpose of the copper strip test is to detect free sulfur and corrosive sulfur, the latter often being present as "loosely-bound" sulfur in an oil. In this test, 50

mls. of the oil to be tested are placed in a 100 mls. beaker along with a polished copper strip, about $\frac{1}{2}$ inch by 2 inches. The copper strip is bent into a V and so placed in the beaker that the flat surface thereof does not touch the bottom or sides of the beaker. The oil sample in the beaker completely covers the copper strip. The beaker, containing oil sample and copper strip, is placed in an electric oven for the required period of time. Thereafter, the beaker is removed from the oven and the copper strip is removed from the beaker. The strip is washed with petroleum ether and then is examined for corrosion. After 24 hours at 100° C., the copper strip subjected to the residual oil from run 6 was only slightly stained, the color being designated "brassy." The oil sample was light and there was no sludge therein. This result is comparable to that normally realized with an SAE-10 solvent refined Pennsylvania motor oil subjected to the same test. This test, then, demonstrates that the sulfur present in the oil is firmly bound and that no free sulfur is present in the oil.

In sharp contrast to the oil of run 6 in the copper strip test, the oil of run 4 fails badly in this test. With only 0.5 per cent of the oil of run 4 blended with the aforesaid SAE-10 motor oil, under the same conditions, the copper strip was black, and the oil blend was dark in color and contained some sludge. Such results clearly indicate that the oil of run 4 is highly corrosive and unstable. It will be noted that the oil of run 4 has an N. N. of 23.5, whereas the oil of run 6 has an N. N. of only 2.4; further, the oil of run 4 contains 12.16 per cent sulfur, as compared with only 0.38 per cent for the oil of run 6.

The stability of the oils of this invention is revealed by the results of a catalytic oxidation test, to which were subjected several of the residual oils shown in Table I, above. 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. and S.) copper wire (0.78 square inch), 3.33 inches of No. 12 (B. and S.) aluminum wire (0.87 square inch), a $\frac{1}{4}$ inch square of $\frac{1}{4}$ inch lead sheet ($\frac{1}{4}$ square inch), and 25 cc. 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, sludge formed, and effects of oil on the copper coil and on the lead sheet were reported. On the basis of these changes, the residual oils were rated as compared with a SAE-10 solvent refined Pennsylvania motor oil subject to the same test. The results of these tests and of the comparisons with SAE-10 Pennsylvania oil are reported in Table II below.

TABLE II
Catalytic oxidation test

Run No.	Penna. SAE 10W Oil	1	7	10
Analyses of Oil:				
N. N.	16.	0.4.	1.7.	0.9.
K. V. at 210° F., Cs.	12.91	2.83	2.50	2.46.
Per Cent Vis. Increase.	125.	10.1	5.7	11.3.
Sludge, Tube.	Nil.	Nil.	Nil.	Nil.
Copper Coil.	Dull Copper.	Dark Brown.	Dark Brown.	Dark Brown.
Lead Loss, Mgrs.	235.	11.9.	26.1.	36.2.
Rating:				
N. N.	Poor.	Good.	Good.	Good.
Vis. Increase.	do.	do.	do.	Do.
Sludge.	Good.	do.	do.	Do.
Lead Loss.	Very Poor.	do.	do.	Do.

From inspection of the results shown above in Table II, it will be seen that the new synthetic oils are equal to or better than SAE-10 Pennsylvania solvent refined motor oil in every respect.

As will be evident from the data presented above in Tables I and II, the condensation 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.

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 a detergent, an extreme pressure agent, a foam suppressor, a viscosity index (V. I.) improver, etc. 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 chlor-naphtha 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.

I claim:

1. The method of preparation of a viscous oil, which comprises: polymerizing, at a temperature above 600° F. and below 750° F., a normal, alpha mono-olefin having from 5 to 18 carbon atoms with a material selected from the group consisting of a phosphorus sulfide, elemental phosphorus with elemental sulfur, and mixtures thereof, the quantity of said material being less than one per cent by weight of the combined weight of said olefin and said material.

2. The method of preparation of a viscous oil, which comprises: polymerizing, at a temperature between about 640° F. and about 700° F., a normal, alpha mono-olefin having from 5 to 18 carbon atoms with a material selected from the group consisting of a phosphorus sulfide, elemental phosphorus with elemental sulfur, and mixtures thereof, the quantity of said material being less than one per cent by weight of the combined weight of said olefin and said material.

3. The method of preparation of a viscous oil, which comprises: polymerizing, at a temperature above 600° F. and below 750° F., a normal, alpha-mono-olefin having from 8 to 12 carbon atoms with a material selected from the group consisting of a phosphorus sulfide, elemental phosphorus with elemental sulfur, and mixtures thereof, the quantity of said material being less than one per cent by weight of the combined weight of said olefins and said material.

4. The method of preparation of a viscous oil, which comprises: polymerizing, at a temperature above 600° F. and below 750° F., a normal, alpha mono-olefin having from 5 to 18 carbon atoms with a material selected from the group consisting of a phosphorus sulfide, elemental phosphorus with elemental sulfur, and mixtures thereof, the quantity of said material being greater than about 0.01 per cent and less than one per cent by weight of the combined weight of said olefin and said material.

5. The method of preparation of a viscous oil, which comprises: polymerizing, at a temperature above 600° F. and below 750° F., a normal, alpha mono-olefin having from 5 to 18 carbon atoms with a phosphorus sulfide, the quantity of said sulfide being greater than about 0.01 per cent and less than one per cent of the combined weight of said olefin and said sulfide.

6. The method of preparation of a viscous oil, which comprises: polymerizing, at a temperature above 600° F. and below 750° F., a normal, alpha mono-olefin having from 5 to 18 carbon atoms with a mixture of elemental phosphorus and elemental sulfur, the quantity of said phosphorus and sulfur being greater than about 0.01 per cent and less than one per cent by weight of the combined weight of said olefin and said mixture.

7. A viscous oil obtained by: polymerizing, at a temperature above 600° F. and below 750° F., a normal, alpha mono-olefin having from 5 to 18 carbon atoms with a material selected from the group consisting of a phosphorus sulfide, elemental phosphorus with elemental sulfur, and mixtures thereof, the quantity of said material being less than one per cent by weight of the combined weight of said olefin and said material.

8. A viscous oil obtained by: polymerizing, at a temperature between about 640° F. and about 700° F., a normal, alpha mono-olefin having from 5 to 18 carbon atoms with a material selected from the group consisting of a phosphorus sulfide, elemental phosphorus with elemental sulfur, and mixtures thereof, the quantity of said material being less than one per cent by weight of the combined weight of said olefin and said material.

9. A viscous oil obtained by: polymerizing, at a temperature above 600° F. and below 750° F., a normal, alpha mono-olefin having from 8 to 12 carbon atoms with a material selected from the group consisting of a phosphorus sulfide, elemental phosphorus with elemental sulfur, and mixtures thereof, the quantity of said material being less than one per cent by weight of the combined weight of said olefin and said material.

10. A viscous oil obtained by: polymerizing, at a temperature above 600° F. and below 750° F., a normal, alpha mono-olefin having from 5 to 18 carbon atoms with a material selected from the group consisting of a phosphorus sulfide, elemental phosphorus with elemental sulfur, and mixtures thereof, the quantity of said material being greater than about 0.01 per cent and less than

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one per cent by weight of the combined weight of said olefin and said material.

11. A viscous oil obtained by: polymerizing, at a temperature above 600° F. and below 750° F., a normal, alpha mono-olefin having from 5 to 18 carbon atoms with a phosphorus sulfide, the quantity of said sulfide being greater than about 0.01 per cent and less than one per cent of the combined weight of said olefin and said sulfide.

12. A viscous oil obtained by: polymerizing, at a temperature above 600° F. and below 750° F., a normal, alpha mono-olefin having from 5 to 18 carbon atoms with a mixture of elemental phosphorus and elemental sulfur, the quantity of said phosphorus and sulfur being greater than about 0.01 per cent and less than one per cent by weight of the combined weight of said olefin and said mixture.

13. A viscous oil obtained by: polymerizing, at about 650° F. for about 10 hours, octene-1 in the presence of about 0.3 per cent of phosphorus pentasulfide.

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14. A viscous oil obtained by: polymerizing, at about 700° F. for about 3 hours, decene-1 in the presence of about 0.3 per cent of phosphorus pentasulfide.

15. A viscous oil obtained by: polymerizing, at about 615° F. for about 10 hours, decene-1 in the presence of about 0.2 per cent of phosphorus and about 0.7 per cent of sulfur.

WILLIAM E. GARWOOD.

REFERENCES CITED

The following references are of record in the file of this patent:

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Certificate of Correction

Patent No. 2,500,163

March 14, 1950

WILLIAM E. GARWOOD

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 4, line 58, for "60-08° F." read *60-80° F.*; columns 5 and 6, Table I, Run No. 4, line 24, for "< -20" read *-20*; same table, in the portion beginning with Run No. 7, second line under "Olefin", for "Per Cent by Weight" read *Molar Proportion*; tenth line under "Residual Oil", for "Phosphorus" read *Per Cent Phosphorus*; same line, Run No. 8, for "90.002" read *0.002*; column 9, line 13, for "poor" read *pour*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 26th day of December, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.