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LUBRICATING OIL ADDITIVES AND PROCESS OF MAKING SAME

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This invention relates to improved lubricating oil additives and to a method for their preparation. In one of its specific aspects it relates to a method for the catalytic oxidation of hydrocarbons to produce a lubricating oil additive.

It is common practice to add modifying agents to lubricating oils to control corrosion and/or oxidation tendencies of the oil. The lubricating oils employed in internal combustion engines are subjected to extreme temperatures and pressures, therefore it is desirable to control corrosion and oxidation characteristics of the oil subjected to these conditions. Compounds which have the desired effect upon the corrosion and oxidation characteristics of a lubricating oil usually adversely affect the sludge and piston varnish forming characteristics of the oil.

It has been found that controlled oxidation of certain selected fractions of lubricating oil produces a completely ashless material having excellent detergent properties when added to a lubricating oil. This detergent material substantially reduces the piston varnish formation tendencies of a lubricating oil with no adverse effects upon the results obtained by the other additive agents. The process for producing these detergent materials is described and claimed in my co-pending application Serial No. 304,659 filed August 15, 1952.

In at least one embodiment of this invention at least one of the following objects is obtained.

It is an object of this invention to provide a method for the catalytic oxidation of hydrocarbons.

It is another object to provide an improved method for preparing lubricating oil additives having detergent properties.

It is another object to provide an improved lubricating oil additive.

It is still another object to provide a method for the catalytic air oxidation of a lubricating oil fraction.

Other objects will be apparent to one skilled in the art upon reading this disclosure.

I have discovered that the addition of a small amount of the product obtained by reacting a phosphorus and sulfur containing compound with terpenes to a lubricating oil fraction reduces the reaction time required for air oxidation and results in an oxidized product having improved detergent properties.

Thus, according to the practice of this invention there is added to a lubricating oil undergoing air oxidation to produce a lubricating oil additive from 0.2 to 2.0, preferably 0.5 to 1.0 weight per cent of a product formed by reacting a phosphorus and sulfur containing compound with terpenes.

Phosphorus sulfides in general are applicable to the practice of this invention, however, phosphorus pentasulfide, P_2S_5 is preferred. The dicyclic terpenes are preferred for reaction with P_2S_5 for producing my oxidation catalyst; monocyclic terpenes and mixtures of dicyclic and monocyclic terpenes may be employed, also.

The catalysts employed in the practice of this invention are prepared by reacting a phosphorus and sulfur containing compound with terpenes. Illustrative of this reaction is that of P_2S_5 and pinene wherein these materials

are gently heated together at atmospheric pressure and with a maximum temperature of about 160° C. until the exothermic reaction is completed after which the product is recovered by distillation at reduced pressure, e. g. at 5 mm. pressure and a maximum temperature of 150° C.

The controlled oxidation of a lubricating oil fraction modifies the oil in at least four physical characteristics. These characteristics are as follows:

(1) An increase in the carbon to hydrogen weight ratio,
(2) An increase in oxygen content,
(3) An increase in molecular weight,
(4) And a decrease in solubility in propane under propane fractionation conditions.

The reaction can be followed and controlled by measuring the water formed, measuring the increase in viscosity and measuring the detergent activity by the carbon dispersion spot plate test because it has been found that all of these values increase during the course of the reaction.

The oxidation reaction is conducted at temperatures in the range 200 to 400° C., preferably 200 to 300° C. and at substantially atmospheric pressure, although higher pressures can be employed, with a gas comprising free oxygen.

The oxidation reaction is usually conducted according to this invention until from 15 to 50 per cent, preferably 25 to 40 per cent of the hydrocarbon has been oxidized. If more than 40 or 50 per cent of the hydrocarbon is oxidized substantial amounts of an oil insoluble product are formed which must be removed and if less than 15 to 25 per cent of hydrocarbon is oxidized the process is functioning below its optimum capacity. It has been found that the yield of detergent material can be controlled in the above range of 25 to 40 per cent by stopping the reaction when the viscosity of the oil has been raised to the range from 600 to 800 S. U. S. at 210° F.

The partially oxidized hydrocarbon oil produced by this process can be used as a detergent without additional concentration or purification. If desired the detergent material can be separated by removing the unreacted oil in a propane fractionation step. The detergent can be further purified by extraction with an alcohol such as isopropyl alcohol to provide an alcohol insoluble product.

The following examples are illustrative of the practice of this invention.

EXAMPLE I

A highly paraffinic lubricating oil fraction obtained from a Mid-Continent crude was blown with air at 250° C. and substantially atmospheric pressure until the viscosity had increased to approximately 700 S. U. S. at 210° F. from an original viscosity of 200 S. U. S. at 210° F.

A seecond portion of this lubricating oil, having incorporated therein 0.82 weight per cent of the product obtained by reacting P_2S_5 with terpenes,[1] was oxidized, under the same conditions of temperature and pressure to approximately the same viscosity.

The results of these tests are tabulated in Table I.

Table I

	Run 1	Run 2
Catalyst, wt. percent	None	0.82
Temp., ° C	250	250
Initial vis. S. U. S., 210° F	200	200
Final vis. S. U. S., 210° F	640	714
Spot plate Test, mm	30	50
Time required, hrs	21	16

[1] The P_2S_5-terpene reaction product used in the examples was Santalube 395–X, a commercial lubricating oil corrosion inhibitor.

EXAMPLE II

In testing the detergent properties of the additives of this invention, a solvent-refined Mid-Continent oil of lubricating grade was used. This oil had the following characteristics:

Gravity, API	30.3
Viscosity at 210° F., S. U. S	61.8
Viscosity index	98.0
Neutralization number	0.01

The ashless detergent was added to the above base oil and tested in a standard Lausen engine. This test consisted in placing 920 grams of the oil composition in the crank case of a single cylinder Lausen gasoline engine. The engine was 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 225° F. and an air-to-fuel ratio of 13.5:1. At the end of 60 hours' operation under these conditions the engine was stopped, disassembled, and the piston, crankcase and bearings examined. The piston varnish was rated on an arbitrary scale of 1 to 10 in which 10 represented a clean or perfect condition and 1 represented the dirtiest condition.

Tests were made according to the above procedure using the base oil in combination with a commercial corrosion inhibitor, Santalube 395–X, as well as the detergent additives. The uninhibited base oil is known to have a high bearing loss rating, for example in a test similar to the above described test the bearing loss was 870.8 milligrams and the piston varnish rating was 7.4. The addition of Santalube 395–X reduced the bearing loss to a satisfactory low level of 12 to 15 milligram but the piston varnish rating dropped to 3.0. The addition of the detergent additive of this invention raised the piston varnish rating to a satisfactory level with no determinable effect upon the bearing loss rating.

The piston varnish rating results of tests are compared in Table II below. A commercial corrosion inhibitor, Santalube 395–X, was used in each case.

Table II

	Piston Varnish Rating at 1.75 wt. percent
Detergent (no catalyst):	
Air oxidized at 250° C., propane insoluble fraction	5.8
Air oxidized at 300° C., propane insoluble fraction	5.2
Detergent (P_2S_5-terpene catalyzed):	
Air oxidized at 250° C., propane insoluble fraction	8.0
Air oxidized at 250° C., propane insoluble and isopropyl alcohol insoluble fraction	8.5

The results of the above tests show that the detergent produced by the P_2S_5-terpene reaction product is a superior detergent for use in lubricating oils.

Variations and modifications are possible within the scope of the disclosure of the present invention the essence of which is that the air oxidation of a lubricating oil fraction is catalyzed by the reaction product of P_2S_5 and a terpene and a product having superior detergent properties is thereby obtained.

I claim:

1. In a process for producing lubricating oil detergent additives by the oxidation, with a gas comprising free oxygen, of a lubricating oil fraction at a temperature above 200° C. the improvement which comprises catalyzing the oxidation reaction with the product obtained by reacting a phosphorus sulfide with a terpene whereby oxidation time is reduced and a superior additive is produced.

2. The method of claim 1 wherein the oxidation reaction is catalyzed by a product obtained by reacting phosphorus pentasulfide with pinene.

3. The method of claim 1 wherein the oxidation reaction is catalyzed by a product obtained by reacting phosphorus pentasulfide and a mixture of terpenes.

4. An improved lubricating oil detergent additive which comprises an oxidation product obtained by oxidizing, with a gas comprising free oxygen, a lubricating oil fraction at a temperature above 200° C. in the presence of a catalyst comprising a reaction product obtained by reacting a phosphorus sulfide with a terpene and recovering the oxidation product from a resulting mixture.

5. In a process for producing lubricating oil detergent additives by the air oxidation of a lubricating oil fraction the improvement which comprises blowing the oil with an oxygen containing gas at a temperature in the range 200 to 300° C. at substantially atmospheric pressure and in the presence of 0.2 to 2.0 weight per cent of a product obtained by reacting phosphorus pentasulfide and a terpene for a period of time sufficient to react from 15 to 50 weight per cent of the said oil.

6. The process of claim 5 wherein 0.5 to 1.0 weight per cent of a reaction product of phosphorus pentasulfide and pinene is employed.

7. The process of claim 6 wherein the oxygen containing gas is air.

8. In a process for producing lubricating oil detergent additives by the air oxidation of a lubricating oil fraction the improvement which comprises blowing said lubricating oil with air at a temperature in the range 200 to 300° C. at substantially atmospheric pressure and in the presence of from 0.5 to 1.0 weight per cent of a product obtained by reacting phosphorus pentasulfide and a mixture of terpenes for a period of time sufficient to react from 25 to 40 weight per cent of said oil.

9. A process for producing a lubricating oil detergent additive which comprises contacting a highly paraffinic lubricating oil fraction with a stream of air at a temperature above about 200° C. in the presence of the reaction product of a phosphorus sulfide and a terpene.

10. A process for producing a lubricating oil detergent additive which comprises contacting a highly paraffinic lubricating oil fraction with a stream of air, at a temperature above about 200° C. in the presence of about 0.2 to 2.0 weight per cent of a product formed by reacting phosphorus sulfide and a terpene, until about 15 to 50 per cent of the hydrocarbon oil has been oxidized; passing the product of said oxidizing step to a propane fractionating step; and recovering the propane insoluble product as the product of the process.

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