Patented Apr. 22, 1947

2,419,325

UNITED STATES PATENT OFFICE

2,419,325

LUBRICATING COMPOSITION

John M. Musselman, South Euclid, Ohio, assignor to The Standard Oil Company, Cleveland, Ohio, a corporation of Ohio

No Drawing. Application November 13, 1945, Serial No. 628,382

13 Claims. (Cl. 252—32.7)

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It has been suggested to add oxidized petroleum acids to lubricating oil in an effort to increase the oiliness. While affording some result in this direction, the oxidation acids have had the very serious drawback of greatly accelerating the breakdown of the oil, particularly if elevated temperatures were involved. In accordance with the present invention it now becomes possible to attain the desired advantages of oxidized petroleum material with in addition a remarkable stability and other properties not heretofore regarded as possible with such starting material.

To the accomplishment of the foregoing and related ends, the invention, then, comprises the features hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative however, of but a few of the various ways in which the principle of the invention may be employed.

The invention will be best understood by reference to an illustrative example:

Paraffin wax is oxidized under pressure to yield an oxidation product comprising hydroxy acids. Desirably, this is separated into saponifiable and non-saponifiable fractions, and the further procedure is carried out with the saponifiable fraction, although where preferred the non-saponifiable diluent material may be left in. Phosphorus pentasulphide is reacted upon the oxidation product by heating to a temperature above thiophosphate formation, i. e., at least about 275° F. and preferably to around 300° F. An exothermic reaction takes place and it is generally not necessary to exceed a temperature above 425° F. It is particularly desirable to employ such an amount of phosphorus pentasulphide as requisite to supplant the oxygen of the compound with sulphur. In other words the amount of the phosphorus pentasulphide should be such that the sulphur therein is stoichiometrically sufficient to replace all of the oxygen in the oxygenated hydrocarbon. The amount of the sulphide to be used can be calculated readily, depending on the oxygenated hydrocarbon and its oxygen content. About 20 percent of phosphorus pentasulphide is satisfactory for an oxidized paraffin wax having about 7% oxygen. The amount generally falls within the range of 14 to 30 per cent for oxygenated

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hydrocarbons having 5 to 10% oxygen. A sludge is separated from the product and a major portion of the phosphorus, usually around at least 75% preferably 90 to 95% of that in the phosphorus sulphide, goes off in the sludge (probably in combination with the oxygen from the oxygenated hydrocarbon), while the major portion of the sulphur, usually at least 75% and preferably 90% of that in the original pentasulphide is in combination with the oxidation product. The nature of the phosphorus in the reaction product is not known, but it does not appear to be present as a thiophosphate because the phosphorus content is materially reduced upon reaction with an alkali in the manner described subsequently.

The reaction is carried out simply by mixing the reaction ingredients in the proportions stated at the temperature stated. Preferably the pentasulphide is added in increments to a kettle containing the oxygenated hydrocarbon and the reaction mass is stirred. It is completed in 1 to 4 hours when the exothermic reaction subsides. By next subjecting the material to air-blowing, residual odors may be eliminated.

Then, if desired, the material may be converted into a metal compound, and for instance from the saponification number of the material the required amount of lime for saponification is indicated and may be added. It is advisable that the product so formed be around 9–11 pH value. The product has outstanding lubricating and stabilizing properties and ability to maintain metal surfaces in clean polished condition. If desired, only a part of the product of the reaction product of the pentasulphide with the oxygenated hydrocarbon may be converted into the metal compound so as to form a mixture of the initial reaction product and the metal compound thereof.

The initial reaction product of the phosphorus sulphide and the oxygenated hydrocarbon, or the metal compound formed therefrom may be incorporated in a mineral lubricating oil in various amounts to improve the properties of the lubricating oil depending upon the particular purpose for which the oil is to be used. In general an amount of at least 0.1 per cent will be used. Inasmuch as the reaction products are lubricants themselves there is no upper limit but in general the amount will not exceed 10 per cent.

Other oxidized petroleum materials may be used instead of oxidized paraffin wax, as for instance oxidized petrolatum, oxidized gas oil, partially or fully oxidized motor oils or the product thereof, oxidized polymers of butylene or isobutylene and other olefins, naphthenic acids, or other oxygenated hydrocarbons derived by oxidizing petroleum hydrocarbons and containing oxygen capable of being displaced with sulphur by reaction with a sulphide of phosphorus. The oxidation may be carried out in the liquid or vapor phase, as in the case of the oxidation of paraffin wax discussed earlier, and in a manner well known in the art. (See chapter 36 of Ellis: The Chemistry of Petroleum Derivatives.) These oxidation products used in accordance with the inventions are liquids or solids, preferably having a boiling point above the temperature of the reaction with the sulphide so as to avoid the use of pressure during the reaction, and comprise mixtures of acids, alcohols, esters, aldehydes, ketones, lactones and similar oxygen containing hydrocarbon compounds. These mixtures are very complex and possess unique properties which are not inherent in any single constituent thereof. The oxidation product may be separated into a saponifiable fraction as in the case of oxidized paraffin wax, or the non-saponifiable portion may be left in.

The neutralization or saponification of the product from the reaction of phosphorus pentasulphide and oxidized petroleum may be effected also by other bases, such as aluminum, tin, zinc, lead, magnesium, barium, potassium, sodium, ammonia, amines, or a mixture of two or more of them, such as calcium and barium, aluminum and calcium, etc.

As illustrating the characteristics of the present compounds, comparisons in operating results with an untreated oil, an oil containing paraffin oxidation acid, an oil containing the calcium salt of paraffin oxidation acid, and an oil containing a compound in accordance with the present invention, may be noted: The testing engine was an Ethyl Gasoline Corporation test engine and it was operated in accordance with Procedure IV, namely, running at 1200 revolutions per minute, with sump temperature 300° F., and jacket temperature 212° F., and an iron catalyst in the amount of 0.1%, F_2O_3 as iron naphthenate. The fuel was a high octane gasoline containing 3 cc. of lead tetraethyl per gallon. The operating results being—

	S. A. E. 20 Mid-Continent Oil	Same plus 3% oxidized paraffin	Same plus 3% calcium salt of oxidized paraffin	Same plus 3% calcium salt of reaction product
Hours Operation	20	20	20	60.
Per cent Sludge	5.0	7.0	8.0	0.9.
Acid number	2.5	2.0	1.9	0.6.
Viscosity Increase	150	270	228	94.
Mg. lacquer per sq. dem. piston	60.0	85.0	69.0	0.
Condition of Engine	Light sludge	Heavy sludge	Heavy sludge	No sludge.

For a continuous running test of twenty hours, it is thus seen that the original oil had a life of actually less than twenty hours for satisfactory lubrication, and that the addition of oxidized paraffin or of the calcium salt of oxidized paraffin did not materially aid, while the metal salt of the reaction product gave outstandingly good performance.

As illustrative of the properties of the initial reaction product before its conversion into a

metal compound, the following example is also included:

An oxidized paraffin wax, available under the name of "Alox 152" was reacted with 25% phosphorus pentasulphide, which amount is that theoretically required to replace the oxygen in this oxidized paraffin wax. The reaction was carried out at 300° F. for one hour. The reaction product was separated from the sludge. The reaction product was found, upon analysis, to contain 1.87% phosphorus and 9.92% sulphur. It was tested in accordance with procedure IV explained earlier, with the following results, using the identical oil in each instance.

Amount of Additive	4.5%	None
Length of Run ... hrs.	30	20
Sludge ... per cent.	2.0	10
Acid Number	2.5	7.5
Viscosity Increase	190	1,003
Skirt Number	0.0	6.5
Demerit Reading	2.1	16.9

The reaction products of the invention are to be distinguished from reaction products obtained by reacting elemental sulphur and compounds yielding sulphur, such as sulphur halides, with oxygen containing compounds, since in such a reaction the oxygen is not replaced in the manner in which it is in accordance with the invention. The reaction products of the invention are also to be distinguished from the use of other sulphides in smaller amounts less than that in which the sulphur of the sulphide is the stoichiometric equivalent of the oxygen to be replaced. All such reaction products are inferior to the reaction product of the invention and not the equivalent thereof.

I claim:

1. A new lubricating oil composition of matter comprising a major portion of a lubricating oil and an amount of an additive sufficient to improve the stability of the lubricating oil, said additive comprising the metal compound of the reaction product of an oxygenated petroleum hydrocarbon boiling above the hereinafter named reaction temperature and an amount of phosphorus pentasulphide within the range of 14 to 30% and at least stoichiometrically sufficient to supplant the oxygen of the oxygenated petroleum hydrocarbon with sulphur, reacted at a temperature within the range of 275 to 425° F. to form a reaction product separable from a sludge comprising the major part of the phosphorus in the pentasulphide, and subsequently converted into said metal compound.

2. A new lubricating oil composition of matter comprising a major portion of a lubricating oil and an amount of an additive sufficient to improve the stability of the lubricating oil, said additive comprising the alkaline earth metal compound of the reaction product of an oxygenated petroleum hydrocarbon boiling above the hereinafter named reaction temperature and an

amount of phosphorus pentasulphide within the range of 14 to 30% and at least stoichiometrically sufficient to supplant the oxygen of the oxygenated petroleum hydrocarbon with sulphur, reacted at a temperature within the range of 275 to 425° F. to form a reaction product separable from a sludge comprising the major part of the phosphorus in the pentasulphide, and subsequently converted into said alkaline earth metal compound.

3. A new lubricating oil composition of matter comprising a major portion of a lubricating oil and an amount of an additive sufficient to improve the stability of the lubricating oil, said additive comprising the metal compound reaction product of an oxidized paraffin wax and an amount of phosphorus pentasulphide within the range of 14 to 30% and at least stoichiometrically sufficient to supplant the oxygen of the oxidized paraffin wax with sulphur, reacted at a temperature within the range of 275 to 425° F. to form a reaction product separable from a sludge comprising the major part of the phosphorus in the pentasulphide, and subsequently converted into said metal compound.

4. A new lubricating oil composition of matter comprising a major portion of a lubricating oil and an amount of an additive sufficient to improve the stability of the lubricating oil, said additive comprising the alkaline earth metal compound of the reaction product of an oxidized paraffin wax and about 20% phosphorus pentasulphide reacted at a temperature of about 300° F., said amount of phosphorus pentasulphide and said temperature resulting in a reaction product separable from a sludge comprising the major part of the phosphorus in the pentasulphide, and subsequently converted into the alkaline earth metal compound.

5. A new lubricating oil composition of matter comprising a major portion of a lubricating oil and an amount of an additive sufficient to improve the stability of the lubricating oil, said additive comprising the calcium compound of the reaction product of an oxidized paraffin wax and about 20% phosphorus pentasulphide, reacted at a temperature of about 300° F., said amount of phosphorus pentasulphide and said temperature resulting in a reaction product separable from a sludge comprising the major part of the phosphorus in the pentasulphide, and subsequently converted into the calcium compound.

6. A new lubricating oil composition of matter comprising a major portion of a lubricating oil and an amount of an additive sufficient to improve the stability of the lubricating oil, said additive comprising the reaction product of an oxygenated petroleum hydrocarbon boiling above the hereinafter named reaction temperature and an amount of phosphorus pentasulphide within the range of 14 to 30% and at least stoichiometrically sufficient to supplant the oxygen of the oxygenated petroleum hydrocarbon with sulphur, reacted at a temperature within the range of 275 to 425° F. to form a reaction product separable from a sludge comprising the major part of the phosphorus in the pentasulphide.

7. A new lubricating oil composition of matter comprising a major portion of a lubricating oil and an amount of an additive sufficient to improve the stability of the lubricating oil, said additive comprising the reaction product of an oxidized paraffin wax and an amount of the phosphorus pentasulphide within the range of 14 to 30% and at least stoichiometrically sufficient to

supplant the oxygen of the oxidized paraffin was with sulphur, reacted at a temperature within the range of 275 to 425° F. to form a reaction product separable from a sludge comprising the major part of the phosphorus in the pentasulphide.

8. A new lubricating oil composition of matter comprising a major portion of a lubricating oil and an amount of an additive sufficient to improve the stability of the lubricating oil, said additive comprising the reaction product of an oxidized paraffin wax and about 20% phosphorus pentasulphide, reacted at a temperature of about 300° F., said amount of phosphorus pentasulphide and said temperature resulting in a reaction product separable from a sludge comprising the major part of the phosphorus in the pentasulphide.

9. An additive effective in small amounts for improving the stability of a lubricating oil, comprising the metal compound of the reaction product of an oxygenated petroleum hydrocarbon boiling above the hereinafter named reaction temperature and an amount of phosphorus pentasulphide within the range of 14 to 30%, and at least stoichiometrically sufficient to supplant the oxygen of the oxygenated petroleum hydrocarbon with sulphur, reacted at a temperature within the range of 275 to 425° F. to form a reaction product separable from a sludge comprising the major part of the phosphorus in the pentasulphide, and subsequently converted into said metal compound.

10. An additive effective for improving the stability of a lubricating oil, comprising the alkaline earth metal compound of the reaction product of an oxygenated petroleum hydrocarbon boiling above the hereinafter named reaction temperature and an amount of phosphorus pentasulphide within the range of 14 to 30% and at least stoichiometrically sufficient to supplant the oxygen of the oxygenated petroleum hydrocarbon with sulphur, reacted at a temperature within the range of 275 to 425° F. to form a reaction product separable from a sludge comprising the major part of the phosphorus in the pentasulphide, and subsequently converted into said alkaline earth metal compound.

11. An additive effective for improving the stability of a lubricating oil, comprising the calcium compound of the reaction product of an oxidized paraffin wax and about 20% phosphorus pentasulphide reacted at a temperature of about 300° F., said amount of phosphorus pentasulphide and said temperature resulting in a reaction product separable from a sludge comprising the major part of the phosphorus in the pentasulphide, and subsequently converted into said calcium compound.

12. An additive effective for improving the stability of a lubricating oil, comprising the reaction product of an oxygenated petroleum hydrocarbon boiling above the hereinafter named reaction temperature and an amount of phosphorus pentasulphide within the range of 14 to 30% and at least stoichiometrically sufficient to supplant the oxygen of the oxygenated petroleum hydrocarbon with sulphur, reacted at a temperature within the range of 275 to 425° F. to form a reaction product separable from a sludge comprising the major part of the phosphorus in the pentasulphide.

13. A new composition of matter, suitable for use as an addition agent to improve the characteristics of lubricating oil, comprising the reaction product of an oxidized paraffin wax re-

acted at a temperature within the range of 275 to 425° F. and with stoichiometrically sufficient phosphorus pentasulphide to supplant oxygen of the oxygenated petroleum hydrocarbon with sulphur and to separate the major part of the phosphorus from the reaction product.

JOHN M. MUSSELMAN.

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