Patented Jan. 1, 1952 2,580,430

UNITED STATES PATENT OFFICE

2,580,430

CATALYZED SULFIDE-HYDROCARBON REACTION PRODUCTS AND METHOD OF MAKING SAME

Everett C. Hughes, Cleveland Heights, and John D. Bartleson, Cleveland, Ohio, assignors to The Standard Oil Company, Cleveland, Ohio, a corporation of Ohio

No Drawing. Application August 24, 1946, Serial No. 692,930

19 Claims. (Cl. 252—32.7)

1

The present invention relates to improvements in lubricants and has specific reference to the treatment of hydrocarbons with a phosphorus sulfide to form lubricants and lubricant additives having improved properties, especially with reference to the inhibition of oxidation and manifestations resulting therefrom.

Hydrocarbon-phosphorus sulfide reaction products have desirable lubricant properties and are frequently incorporated in lubricating oils to improve the strength of the lubricating film, impart anti-oxidant effects, and for other purposes. Various methods of manufacture have been proposed with the object of increasing the phosphorus and sulfur content of the hydrocarbon and establishing a phosphorus and sulfur bond of the desired type so as to enhance the lubricant properties to an extent permitting the use of smaller amounts of the compound for incorporation in the more or less inferior oils. The problem of chemically binding desired proportions of phosphorus and sulfur to the saturated hydrocarbons such as paraffinic and naphthenic materials, has been particularly difficult to solve.

It is an object of the present invention to provide an agent which in itself is useful as a lubricant, and which will inhibit in marked degree, acid and sludge formation, oxidation, and other common types of lubricant deterioration occurring under operating conditions.

A further object is to provide a lubricating oil containing this agent as an additive.

A further object is to provide an addition agent for lubricants containing a high percentage of phosphorus and sulfur, and having superior anti-oxidant qualities.

A further object is to provide an improved method of manufacture of lubricants and lubricant additives, providing a compound superior in the above respects.

A further object is to provide as a lubricant or lubricant additive a saturated hydrocarbon material having a higher percentage content of phosphorus and sulfur than a product obtained by the usual method.

Still a further object is to provide an improved method of manufacture of phosphorus-sulfur lubricants and lubricant additives, employing relatively saturated hydrocarbons as the base material.

Other objects and advantages will be apparent from the following detailed description of the invention.

In accordance with the present invention, hydrocarbons are treated with a phosphorus sulfide in the presence of a catalytic agent from the active metal and metalloid halide group. The

2

reaction products of the invention are characterized by high solubility in lubricating oils and greases and are particularly valuable as additives for lubricants such as the so-called extreme pressure lubricants, and also as additives for lubricating oils to improve the corrosion, lacquer, sludge, viscosity increase, and other like characteristics of the lubricant. In addition, the metal derivatives formed from these products have these desired properties, and are especially suitable when a lubricant having increased detergency is desired.

It has been found that the base material employed in carrying out the invention may comprise a hydrocarbon from any source. In its broadest application, the advantages of the invention result from the treatment of the preferred hydrocarbon base material with a phosphorus sulfide, in the presence of the active halide catalyst.

The invention is applicable broadly to the treatment of hydrocarbon oils such as mineral oils or mixtures thereof, and for more ready commercial application, is useful in the treatment of, for example, petroleum distillates and lubricating residuums, oils produced by various polymerization methods, acid treated oils and solvent extracted oils. Oils modified by sulfurizing or chlorination may be employed as the base material, or as the lubricant body for incorporation of the product of the invention as an additive.

The invention has particular utility however in the treatment of the more saturated hydrocarbons which under ordinary conditions of reaction combine with phosphorus sulfides in much less degree than the relatively unsaturated hydrocarbons. Thus, for example, excellent results are obtained employing paraffinic or naphthenic hydrocarbons or mixtures thereof, ranging in carbon atom content from 10 to 40 carbon atoms, an example of which is a so-called solvent extracted oil. Saturated hydrocarbon base materials are found to possess inherently desirable lubricant properties which are further improved by the incorporation therein of a phosphorus-sulfur constituent.

Of the phosphorus sulfides used as the reactant, phosphorus pentasulfide is preferred, because it is more readily available commercially and is economical. For this reason, phosphorus pentasulfide is employed in the illustrative examples of the invention to follow.

The quantity of phosphorus pentasulfide employed in carrying out the reaction may be in the order of from a fraction of one percent to about twenty percent by weight based upon the weight of the base hydrocarbon material employed. The upper limit is dictated by economic considerations, the nature of the hydrocarbon

employed and the properties desired in the final product, and is not indicative of the scope of the invention in a limiting sense.

The reaction of the hydrocarbon base material and phosphorus pentasulfide constituent is carried out in the presence of an active halide catalyst. Halides of elements including non-metals such as boron, and metals such as aluminum, are particularly effective, and these are preferred. Other halide catalysts are effective in more or less degree, and may include, for example, $FeCl_3$, $ZnCl_2$, $SnCl_4$ and other halide compounds. The "halide catalysts" are well known and well defined as a group and the art recognizes the scope of this definition. They are sometimes also referred to as a Friedel-Crafts catalyst because they are often used in catalyzing that reaction.

The quantity of the halide agent employed preferably may range from 0.05% to 10.0%. Amounts in excess of 10% may be employed but achieve little practical result in terms of improvement of the reaction compared to the additional cost, and in some instances may undesirably modify the final oil product.

The halide catalyst employed in the reaction has the effect of increasing the percentage of phosphorus and sulfur incorporated in the hydrocarbon, over that obtained by carrying out the reaction in the absence of the catalyst, particularly when a saturated hydrocarbon base material is employed. The halide catalyst has the added desirable effect of coagulating sludge and other residual solids formed during the reaction, thus facilitating filtration of the reaction product and increasing the product yield.

The reaction is carried out at an elevated temperature ranging between 250° F. and 600° F., the preferred temperature being about 375° to 425° F.

The reaction may be carried out at atmospheric pressure. However, elevated pressures may be employed. The reaction may be completed in the presence of air, or in an atmosphere of inert gas such as nitrogen.

The time of reaction may fall within an extended range, being a function of temperature, the amount of components to be reacted, mixing of the components during the reaction, etc. Employing atmospheric pressures and a reaction temperature within the prescribed range, it has been found that a reaction time of approximately one hour is ample to carry the reaction to completion, although it may extend to as much as six hours under some circumstances.

When the reaction is complete, the liquid reaction product is treated to remove sludge components which may have formed, by settling, centrifuging or mechanical filtering.

Where it is desired that the lubricant or lubricant additives of the invention have pronounced qualities of detergency, they may be converted to their metal derivatives by methods well known to the art. For example, the compound may be reacted with one or more metal yielding compounds in the form of sulfides, oxides or hydroxides, which may further comprise an alkali metal, or an alkaline earth compound such as barium, calcium and strontium, or higher metals. These or other metals should be selected with reference to the proposed use of the additive compound and the properties of detergency and/or oiliness desired in it. The heavier metals have excellent surface corrosion inhibition characteristics.

The reaction of the additive compound to produce the metal derivative thereof may be in accordance with known practice, wherein an amount of a reactable metal compound is added sufficient either to partially or completely react with the additive compound, as desired. Also ammonia or amines or other nitrogenous base may be used as well as carbides and cyanamides. Alcohols can be used to form the corresponding esters. These are all compounds which combine with or replace acid hydrogen.

The mixture preferably is reacted at a temperature ranging between 200° F. and 400° F., with stirring, one to a few hours. The presence of water desirably accelerates the reaction. The reaction product is settled and filtered to remove any residual solids, and any water content remaining may be removed by any usual method. The metal or other derivatives may be employed by themselves as additives for a lubricating oil, or a small amount added to the P_2S_5-solvent extracted oil additive, and are particularly useful in either case as detergents.

In some instances, it may be desirable to increase further the sulfur content of the additive compound. This may be accomplished by the inclusion of elemental sulfur or a material yielding elemental sulfur under the reaction conditions present in the reaction mixture. Reference to a reaction with the sulfide is not to exclude also a reaction with sulfur. The amount of sulfur employed depends on the degree of sulfurization desired in the final additive product. An excellent high sulfur constituent additive is derived by employing 25 to 75% sulfur by weight of the phosphorus pentasulfide. The sulfur preferably is added to the reaction mixture, carrying out the sulfurizing reaction simultaneously with the reaction with the sulfide in the presence of the halide catalyst. However, the additive compound may be sulfurized further with elemental sulfur as a step subsequent to the phosphorus sulfide-hydrocarbon reaction in the presence or absence of the catalyst.

The improved lubricant or lubricant additive compounds of the invention are characterized by markedly higher anti-oxidant qualities than a hydrocarbon-phosphorus sulfide compound formed of the same base material but in the absence of the halide catalysts.

The amount of the additive to be mixed with an oil, grease or other lubricant will depend upon factors of expense, the intended use of the lubricant, and the characteristics of the oil or grease. Oils having a marked tendency to oxidize or corrode metals require larger amounts of the additive. In general, for a lubricating oil, an effective concentration range may comprise between 1% and 10% by weight, the preferred concentration being approximately 2%. With some oils, the additive in amounts as low as a fraction of a percent shows marked improvement. The extreme upper range is dictated by economic considerations, and since the reaction product is itself a lubricant there is no inoperative upper limit.

The invention may be further illustrated by the following examples and tables of tests of lubricants containing the new composition of the invention, pointing out some of the advantages thereof. It is to be understood that these examples are intended only as practical illustrations fully disclosing the practice of the invention, and are not to be construed as limiting the scope thereof as defined in the claims.

EXAMPLE I

A typical component reaction charge may comprise 270 grams of solvent extracted oil, 30 grams of P_2S_5 and 3 grams of anhydrous $AlCl_3$ as the halide catalyst. The ingredients are mixed and heated to 500° F. and maintained at this temperature for one hour, with agitation. The reaction mass is then filtered to remove sludge constituents. The liquid product analyzed 3.40% sulfur and 1.90% phosphorus.

EXAMPLE II

270 grams of solvent extracted oil is mixed with 30 grams of P_2S_5 and the mixture saturated with BF_3 at room temperature. The mixture is charged to a stirred bomb and reacted therein for one hour at 500° F. The reaction mass is then filtered. The liquid product analyzed 4.15% sulfur and 2.24% phosphorus.

To illustrate comparatively the value of the products of the invention as additives for lubricants, a lubricating oil consisting of a solvent extracted oil was combined with a number of additives representative of the invention, and the oil tested according to laboratory test procedures for evaluating the service stability of oils, as published in Industrial and Engineering Chemistry, Analytical Edition, vol. 17, No. 5, May 1945, pages 302–309.

Essentially the laboratory test equipment consists of a vertical, thermostatically heated, large glass test tube, into which is placed a piece of steel tubing of about one-third its length and of much smaller diameter. A piece of copper-lead bearing strip is suspended within and from the upper end of the steel tube by a copper pin, and an air inlet is provided for admitting air into the lower end of the steel tube in such a way that in rising the air will cause the oil present to circulate. The test tube is filled with an amount of the oil to be tested which is at least sufficient to submerge the metals.

The ratios of surface active metals to the volume of oil in an internal combustion test engine are nearly quantitatively duplicated in the test equipment. In the "Standard" test the temperature used is approximately the average temperature of the crankcase. The rate of air flow per volume of oil is adjusted to the same as the average for a test engine in operation. Of the catalytic effects those due to iron are the most important. They are empirically duplicated by the addition of a soluble iron salt. Those due to lead bromide are duplicated by its addition. In the "Standard" test, 0.012% of iron salt is added; and in the "Iron Tolerance" test this is increased to 0.05%. The duration of the test is adjusted to that usually used in engine type tests. As is shown by the data in the papers referred to, the laboratory tests have been correlated with engine tests and the properties of the oil in an engine may be determined from the result of the laboratory tests.

The results given in the following tables were obtained from tests using:

A 160 cubic centimeter sample of the lubricant composition
70 liters of air per hour
100 square centimeters of steel surface
4.4 square centimeters of copper-lead surface
1.0 square centimeter of copper surface
0.10% by weight of lead bromide powder
0.05% soluble iron calculated as Fe_2O_3 (ferric 2-ethyl hexoate in C. P. benzene)

The "Iron Tolerance" tests are run at 280° F. for 36 hours. The used oil was sufficient to enable the determination of all of the usual oil tests, viz. isopentane insolubles, viscosity, acid number, etc.

The data in the following tables show the results obtained in testing the new lubricant additives by the tests described.

Tests on a solvent extracted oil base stock, and a lubricating composition containing this oil and a number of additives were run under the "Iron Tolerance" test conditions. For purposes of comparison, and to indicate more fully the advantages of the invention, tests were performed on a P_2S_5-hydrocarbon product formed in the absence of a halide catalyst (column 2), on a reaction product of a halide catalyst on a solvent extracted oil in the absence of P_2S_5 (column 5), and and on a sample of solvent extracted oil (column 1).

The following results are fully illustrative:

Table

[Solvent extracted oil—60 min. reaction at 500° F., 10% P_2S_5 by weight.]

	(1)	(2) P_2S_5	(3) P_2S_5	(4) P_2S_5	(5) No P_2S_5
Description		No catalyst	$AlCl_3$	BF_3	1% $AlCl_3$
Oil	SEO	SEO	SEO	SEO	SEO
Additive from Example No.			#1	#2	
Conc. of Additive by Weight	0%	2%	2%	2%	2%
Sludge-Pentane Insolubles (Mgms.)	206.4	52.7	18.9	8.5	54.05
Acid Number	14.5	5.0	2.6	3.0	10.2
Viscosity Increase (SUS)	1095	467	342	165	1155

These data show the unusual improvement imparted to lubricants in every previously indicated characteristic, by the lubricant additives of the invention. It is to be noted that a solvent extracted oil base comprising essentially saturated hydrocarbon materials was employed in conducting these tests. This oil is an inherently better grade of oil in many respects and heretofore has been relatively difficult to combine with phosphorus and sulfur. The advantages of the products of the invention are even more fully realized when the products are employed with ordinary base stock lubricants, having substantial amounts of more reactive hydrocarbon constituents, or the base material employed in carrying out the invention comprises a relatively more reactive hydrocarbon.

The marked improvement of the products of the invention prepared in the presence of halide catalysts, over phosphorus pentasulfide-hydrocarbon reaction products prepared in accordance with the usual methods in the absence of a halide catalyst, specifically with regard to type of sludge formation, acid number, and viscosity increase, is clearly indicated by these tests.

The neutral or partially neutralized derivatives of the products of the invention are particularly useful where increased oiliness and/or detergency is desired in the lubricant product. It will be obvious to one skilled in the art that the products of the invention may be employed as lubricants or as component parts of lubricants in accordance with the invention, as set forth in the following claims.

The expression "consisting essentially of" as used herein is intended to refer to the components which are essential to the composition,

namely the mineral lubricating oil and the additive in accordance with the invention, and the expression does not exclude other components from the composition which do not render it unsuitable for lubricant purposes.

We claim:

1. The reaction product of a saturated hydrocarbon oil and an amount within the range of about one to about twenty percent by weight of a phosphorus sulfide reacted in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250° to about 600° F. so as to produce a lubricant.

2. The metal derivative of the reaction product set forth in claim 1 selected from the group consisting of alkali metal and alkaline earth metal derivatives.

3. A lubricant consisting essentially of a mineral lubricating oil and the reaction product of a saturated hydrocarbon oil and an amount within the range of about one to about twenty percent by weight of a phosphorus sulfide reacted in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250° to about 600° F. so as to produce a lubricant and containing reacted elemental sulfur.

4. A lubricant consisting essentially of a mineral lubricating oil and the metal derivative selected from the group consisting of alkali metal and alkaline earth metal derivatives of the reaction product of a saturated hydrocarbon oil and an amount within the range of about one to about twenty percent by weight of phosphorus pentasulfide reacted in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250° to about 600° F. so as to produce a lubricant.

5. A lubricant consisting essentially of a mineral lubricating oil and the reaction product of a saturated hydrocarbon oil and an amount within the range of about one to about twenty percent by weight of a phosphorus sulfide reacted in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250° to about 600° F. so as to produce a lubricant.

6. A lubricant consisting essentially of a mineral lubricating oil and the reaction product of a saturated hydrocarbon oil and an amount within the range of about one to about twenty percent by weight of phosphorus pentasulfide reacted in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250° to about 600° F. so as to produce a lubricant.

7. A lubricant consisting essentially of a mineral lubricating oil and the reaction product of a solvent extracted oil and an amount within the range of about one to about twenty percent by weight of phosphorus pentasulfide reacted in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250° to about 600° F. so as to produce a lubricant.

8. A lubricant consisting essentially of a mineral lubricating oil and the metal derivative selected from the group consisting of alkali metal and alkaline earth metal derivatives of the reaction product of a solvent extracted oil and an amount within the range of about one to about twenty percent by weight of phosphorus pentasulfide reacted in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250° to about 600° F. so as to produce a lubricant.

9. As a lubricant additive the reaction product of a saturated hydrocarbon oil and an amount within the range of about one to about twenty

percent by weight of a phosphorus sulfide in the presence of not over 10% of aluminum chloride at a temperature in the range of about 250° to about 600° F. so as to produce an additive for improving a mineral lubricating oil.

10. As a lubricant additive the reaction product of a saturated hydrocarbon oil and an amount within the range of about one to about twenty percent by weight of a phosphorus sulfide in the presence of not over 10% of boron trifluoride at a temperature in the range of about 250° to about 600° F. so as to produce an additive for improving a mineral lubricating oil.

11. A lubricating composition consisting essentially of a major portion of a lubricating oil and an amount to inhibit the oxidative deterioration of the oil of the reaction product of a saturated hydrocarbon oil and an amount within the range of about one to about twenty percent by weight of a phosphorus sulfide reacted in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250° to about 600° F. so as to produce an additive for improving a mineral lubricating oil.

12. A lubricating composition consisting essentially of a major portion of a lubricating oil, and an amount to inhibit the oxidative deterioration of the oil of the reaction product of a saturated hydrocarbon oil and an amount within the range of about one to about twenty percent by weight of phosphorus pentasulfide reacted in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250° to about 600° F. so as to produce an additive for improving a mineral lubricating oil.

13. A method of producing a lubricant additive comprising reacting a saturated hydrocarbon oil with an amount within the range of about one to about twenty percent by weight of a phosphorus sulfide in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250° to about 600° F. so as to produce a lubricant.

14. A method of producing a lubricant additive comprising reacting a saturated hydrocarbon oil with an amount within the range of about one to about twenty percent by weight of phosphorus pentasulfide in the presence of not over 10% of a halide catalytic agent at a temperature in the range of about 250° to about 600° F. so as to produce a lubricant.

15. A method of producing a compound for use as an additive with a lubricating oil comprising reacting a saturated hydrocarbon oil with an amount within the range of about one to about twenty percent by weight of a phosphorus sulfide in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250° to about 600° F. so as to produce an additive for improving a mineral lubricating oil, and separating the reaction product from residues formed during the reaction.

16. A method of producing a compound suitable for use as an additive with a lubricating oil comprising reacting a solvent extracted oil base with an amount within the range of about one to about twenty percent by weight of phosphorus pentasulfide in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250° to about 600° F. so as to produce an additive for improving a mineral lubricating oil and separating the reaction product from the residues formed during the reaction.

17. A method of producing a lubricant additive comprising reacting a saturated hydrocarbon oil

with an amount within the range of about one to about twenty percent by weight of a phosphorus sulfide and elemental sulfur in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250° to about 600° F. so as to produce a lubricant.

18. A method of producing a lubricant additive comprising reacting a saturated hydrocarbon oil with an amount within the range of about one to about twenty percent by weight of a phosphorus sulfide in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250° to about 600° F. so as to produce a lubricant, and reacting at least part of the reaction product with a metal selected from the group consisting of alkali metals and alkaline earth metals.

19. The metal derivative selected from the group consisting of alkali and alkaline earth metal derivatives of the reaction product of a saturated hydrocarbon oil and an amount within the range of about 1 to about 20% by weight of phosphorus pentasulfide reacted in the presence of not over 10% of a halide catalyst at a temperature in the range of about 250 to about 600° F. so as to produce a lubricant.

EVERETT C. HUGHES.
JOHN D. BARTLESON.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,176,884	Butz et al.	Oct. 24, 1939
2,316,087	Gaynor et al.	Apr. 6, 1943
2,367,468	Mixon et al.	Jan. 16, 1945
2,398,429	Hughes	Apr. 16, 1946
2,449,934	Giammaria	Sept. 21, 1948
2,456,336	Smith et al.	Dec. 14, 1948
2,476,812	Buckmann et al.	July 19, 1949