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**DETERGENT LUBRICANTS AND LUBRICATING OIL ADDITIVES AND PROCESS OF MAKING THE SAME****Harvey E. Alford, Amherst, Ohio, and John D. Bartleson, Franklin, Mich., assignors to The Standard Oil Company, Cleveland, Ohio, a corporation of Ohio**No Drawing. Application October 1, 1953,  
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This invention relates to lubricants and lubricating oil additives which have high detergent properties and zero ash content, and to a process of making the same.

It has been proposed heretofore to react a phosphorus sulfide such as phosphorus pentasulfide with various hydrocarbons including paraffins and cycloaliphatics for the purpose of producing a lubricating oil additive. The art recognizes that such reaction products are good additives and in general their effectiveness can be measured at least in part by their sulfur content.

It has also been proposed to prepare detergent-type lubricating oil additives by treating such reaction products with a base, especially a metal base, to form lubricants having improved detergent properties especially as to corrosion, lacquer, sludge, viscosity increase and the like characteristics. Such improved lubricants have a measurable and significant ash content which is approximately proportional to the detergent properties of such additives.

In U. S. Reissue Patent No. 23,676 to John D. Bartleson, there is described a process of treating solvent-refined hydrocarbon base lubricating oil stocks to impart detergency thereto. According to that process, the solvent-refined oil is reacted with a small amount of a phosphorus sulfide and then with a base, especially a metal base. The treatment may be carried out at elevated temperatures, and the products have an ash content which is associated with the detergency of the oil, and which may range from 0.1 to 0.5% by weight of the oil.

Under some circumstances it is thought that oil ash may lead to the formation of engine deposits, and accordingly it would be desirable to provide a detergent oil which has a very low or zero ash content. However, the preparation of such oils has not heretofore been described.

In accordance with the instant invention, organic amine bases are reacted with a phosphorus sulfide-treated solvent-refined hydrocarbon lubricating oil stock, and this reaction is carried out at a temperature above about 450° F. and preferably in the presence of oxygen. A product having a high alkaline number and excellent detergency is obtained, and this product does not have an ash content inasmuch as the product of course does not contain a metal and therefore does not form inorganic ash. Because of the absence of ash content, the products are quite different in an unexpected way from the products prepared in accordance with Reissue Patent No. 23,676.

The reaction products of the invention are to be distinguished from simple reaction products of phosphorus sulfides and organic amines. The amines in the instant

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invention's reaction function as bases to take up the acidity of the phosphorus sulfide-hydrocarbon stock reaction product, and do not react directly with the phosphorus sulfide. The direct reaction products of phosphorus sulfide and amines are acidic, and can be reacted with metal bases to reduce the acidity thereof. The reaction products of the instant invention are alkaline.

The products of the invention are primarily useful as detergent lubricating oils, but they can be used as lubricating oil additives to impart detergency to untreated or phosphorus sulfide-treated lubricating oils by diluting such oils therewith.

The reaction of the solvent-refined hydrocarbon base stock with the phosphorus sulfide, preferably phosphorus pentasulfide, can be carried out as set forth in the aforesaid Reissue Patent No. 23,676. Thus, the reaction may be conducted with direct admixture of the stock with the phosphorus pentasulfide or, if desired, by their admixture in the presence of a diluent which may be subsequently removed. Generally a diluent is not necessary. The reaction usually is complete in about ten hours or less time, generally from one to two hours. The reaction time is a function of the temperature, the amount of sulfide that is to react, the degree of subdivision of the reactants, the efficiency of mixing the reactants, and the like.

The hydrocarbon lubricating stock to which the process is applied is a solvent-extracted or solvent-refined oil, i. e., oils treated in accordance with conventional modern methods of solvent-refining lubricating oils. The oil may be a fluid hydrocarbon lubricating base stock having a viscosity at 100° F. of 10 to 500 centistokes, such as is used as the base for SAE Nos. 10 to 50 oils. It may be obtained as a distillate such as from petroleum, or from synthetic materials, and oils produced by cracking, polymerization, dehydrogenation and the like methods are also contemplated.

The solvent-refining process is well known and generally involves a physical separation of impurities from the oil by extraction with a solvent. Usually the solvent selected such as furfural, phenol, sulfur dioxide, etc., dissolves such constituents as aromatic, unsaturated and low viscosity index materials, and these are separated. A clay treatment may follow, but while this is desirable, it is not essential. Where necessary, a separate propane or the like deasphalting treatment may be used in conjunction with the solvent-refining.

The solvent-refined hydrocarbon lubricating stock is reacted with the phosphorus pentasulfide in a ratio within the range from about 0.1 to about 0.75% by weight, based on the weight of the stock, desirably about 0.25 to about 0.6%, and preferably about 0.4 to about 0.6%. Higher amounts of the pentasulfide give products which are inferior as to viscosity increase. Generally at least about 0.1% thereof should be used to achieve the desired result, although smaller amounts show some improvement.

The reaction of the solvent-refined hydrocarbon stock with the phosphorus pentasulfide can be carried out in the presence or absence of air or in an atmosphere of inert or non-deleterious gas such as nitrogen. It may also be carried out under pressure, such as the pressure generated when the reaction is carried out in a closed vessel due to the liberation of gases in the course of the reaction.

During the reaction, nitrogen or other inert gas can

be bubbled through the reaction mixture. This assists in the removal and dissipation of hydrogen sulfide, shifting the reaction towards the desired end product and thus shortening the time required to complete the reaction.

The reaction temperature varies with the hydrocarbon stock. Generally the treatment should be at least at 275° F. but should be below the temperature at which the reaction product would be decomposed. A temperature in the range of about 300 to about 450° F. is preferred in many cases. The reaction product preferably is centrifuged or filtered to remove by-products, sludge or other material. A volatile diluent, if present, can be removed by evaporation or distillation.

The solvent-refined phosphorus-pentasulfide-treated oil stock is then reacted with an organic amine base. The basicity of the amine is important, and the stronger amine bases are preferred. Tertiary amines do not react. The basicity of amines increases in the order primary < secondary while the reactivity decreases in the order primary > secondary and these considerations must be balanced in selecting the amine. The primary amines are preferred, but in general any primary and secondary amine containing up to 18 carbon atoms is operative. The amine should have a boiling point above the reaction temperature but those with lower boiling points can be used if the reaction is carried out under a superatmospheric pressure adequate to retain the amine in the reaction mixture. The amine can have one or more amino or imino nitrogen groups, and other polar groups such as hydroxy groups may be present as substituents on the carbon chain or ring.

Thus, a wide variety of amines can be employed and those which are useful would generally be described as coming within the general classes of aliphatic, cycloaliphatic, aromatic and mixed aromatic-aliphatic and mixed aromatic-alicyclic amines. Saturated, unsaturated and aromatic heterocyclic amines also are useful. In general, those amines having from 6 to 16 carbon atoms are preferred.

Exemplary operative amines are p-phenylene-diamine, 2-aminobenzenethiol, stearylamine, palmitylamine, indole, pyrrole, monoethanolamine, aniline, ethylenediamine, diethanolamine, diethylenetriamine, o-phenylenediamine, diphenylamine, pyrazole, imidazole, triazole, tetrazole, carbazole, phenoxazine, phentiazine, hexylamine, laurylamine, decylamine, butylamine, distearylamine, dinonylamine, dioctylamine, cyclohexylamine, cyclopentylamine, myristylamine, cetylamine, morpholine, trimethylenediamine and pentamethylenediamine.

The reaction with the amine is carried out at a temperature of 350° F. and above, and at some stage of the reaction the reaction mixture should be held at at least about 450° F. for a half hour or more. Reaction products obtained using temperatures below 450° F. throughout the reaction are generally unsatisfactory. Temperatures within the range from 450 to 550° F. are preferred but there is no upper limit except as may be established by the stability of the oil, of the amine and of the reaction product at elevated temperatures.

If air is brought into the reaction mixture during the reaction of the amine with the phosphorus sulfide-treated oil, a larger amount of amine will react, and the basicity of the product is increased. Possibly the acidity of the material reacting with the amine is increased, due to oxidation, so that more acid groups are made available for reaction with the amine. Therefore it is preferred to carry out the reaction with the amine in the presence of oxygen, such as would be provided by air or by oxygen itself or by oxygen diluted with other inert gases such as nitrogen or carbon dioxide. The amount of oxygen is not critical, the improvement increasing in proportion to the amount used. Amounts of air up to 6 liters per hour per 100 grams of reaction mixture have been found to give satisfactory results, but more could be used if desired.

The reaction will be continued under the conditions mentioned, preferably with the addition of air or oxygen as noted, until the desired alkalinity is obtained or until reaction is complete, as evidenced by no further increase in detergency and alkaline number. Usually two hours is sufficient, but in many instances a good reaction product is obtained after one hour of heating and longer heating times than two hours may be used without undue effect.

The amount of amine is not critical but a large enough amount of amine would be used to give an alkaline product. As little as 0.5 mole of amine per atomic weight of phosphorus in the reaction product can be used, but usually about two moles of amine per atomic weight of phosphorus in the reaction product being treated is preferred as this will produce a product having a high detergency under the appropriate temperature conditions. These amounts can however be widely varied and as much as eight moles of amine per atomic weight of phosphorus have been used.

In order to illustrate some of the advantages of the invention, but in no sense as a limitation thereof, the following specific examples are included.

In the examples the detergency of the oil was measured by a dispersancy test, which consists in determining the highest weight of carbon black which a solution of the oil in benzene will hold in suspension. This test is carried out as follows: A 5% by volume solution of the oil in benzene is prepared and 100 ml. of this solution is placed in a 100 ml. glass-stoppered graduate. 0.2 gram of carbon black is added and the graduate shaken for 15 seconds. The mixture then is observed in front of a light source for a break point which marks the interface between the settled carbon particles and the suspension, and which is seen as a thin layer of completely transparent liquid containing no carbon particles which travels down the graduate as the carbon particles settle. The graduate is allowed to stand for 5 minutes and the weight of carbon black increased by 0.2 gram additions each 5 minutes thereafter until a break point appears. The highest weight carbon black which does not produce a break point is recorded as a measure of the dispersancy.

#### EXAMPLES 1 TO 8

This set of examples shows the importance of the reaction temperature. The phosphorus pentasulfide-refined oil employed in these examples was obtained by reacting phosphorus pentasulfide (16 grams 0.4%) with hydrocarbon stock which was the blend of 88.5 parts of No. 300 solvent-extracted neutral oil (300 SSU at 100° F.) and 5 parts each of bright stocks of 78 and 250 SSU, respectively, at 210° F. These stocks were refined by furfural extraction, methyl ethyl ketone dewaxing and clay treating, and are a good grade of solvent-refined oil available on the market and typical of such an oil. These ingredients were reacted for 1 hour at 300° F. at atmospheric pressure in an open vessel while blowing nitrogen through the reaction mixture.

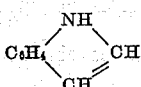
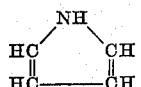
A. *Reaction temperature of 350° F.*—To the above reaction product was added 2 moles of amine (set forth in Table I) per atomic weight of phosphorus in the oil and these ingredients reacted with nitrogen stripping in an open vessel<sup>1</sup> for 2 hours at 350° F. Thereafter the detergency and the resistance of the product to hydrogen sulfide formation were determined and the appearance of the oil noted.

B. *Reaction temperature of 350–450° F.*—A second group of reaction products was obtained by reacting the phosphorus sulfide-refined oil prepared as described with 2 moles of the amine per atomic weight of the phosphorus atom for 2 hours at 350° F. and 1 hours at 450° F. with nitrogen stripping throughout the reaction in a system open to air<sup>1</sup>.

The results were as follows:

<sup>1</sup> About 6 liters of air/100 g. of oil/hr. is believed to have entered the reaction mixture.

Table I

Example No.	Amine	B. P., ° C.	Formula	Reaction Temperature, 350° F.		Reaction Temperature, 350-450° F.	
				Detergency, g. carbon black	H <sub>2</sub> S Formation	Detergency, g. carbon black	H <sub>2</sub> S Formation
1	Armeen 16 (cetylamine)	344°	C <sub>16</sub> H <sub>33</sub> NH <sub>2</sub>	0.2	-	4.4	-
2	Aniline	184.4°	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	0.2	+	1.2	+
3	Indole	253°		0.2	+	2.6	-
4	Monoethanolamine	171°	NH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> OH	0.2	+	1.4	+
5	p-Phenylenediamine	256°	C <sub>6</sub> H <sub>4</sub> (NH <sub>2</sub> ) <sub>2</sub>	0.2	+	4.8	-
6	2-Aminobenzenethiol	114°/11 mm.	NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SH	0.2	+	4.8	-
7	Pyrrole	131°		0.2	+	2.6	+
8	Ethylenediamine	116°	NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	0.2	+	1.4	-

The above results show that when the reaction with the amine is carried out at 350° F. throughout very little reaction occurred. The products had substantially no detergency and with two exceptions were unstable to formation of hydrogen sulfide. When the temperature was increased to 450° F. for 1 hour of the reaction the detergency of the oil was materially improved and the hydrogen sulfide formation reduced in most instances. Except for Example 1, all of the products were clear.

The amines of Examples 2, 4 and 8 are more volatile than the others, and very likely were at least partially removed from the reaction mixture during the reaction, which explains the lower detergency. Examples 3 and 7 are of secondary amines, which are less reactive.

#### EXAMPLES 9 TO 12

All of the preceding examples were prepared in the presence of air with nitrogen stripping. The following examples illustrate the effect of air on the course of the reaction. In these examples the phosphorus pentasulfide-refined oil was the same as in Examples 1 to 8. The amine was Armeen 16 and the amount was 2 moles per atom of phosphorus. Reaction was carried out for 2 hours at 350° F. and 1 hour at 450° F. with nitrogen stripping in a closed system in which the amount of air added per 100 grams of oil per hour was as noted in Table II below.

Table II

Example No.	Added Air, liters/100 g. oil/hr.	Detergency Test, g. carbon black	Color
9	0 <sup>1</sup>	0.6	Very light amber.
10	1	1.8	Amber.
11	2	3.2	Amber-red.
12	Open to air (about 6 liters/100 g. oil/hr.).	4.4	Red.

<sup>1</sup> However, 6 l./hr. of N<sub>2</sub> per 100 g. oil was bubbled through mixture.

It is evident that as the amount of air is increased the amount of reaction also increases. Slight reaction occurs when no air is added, even though the system is closed to the atmosphere, showing that the reaction proceeds in the absence of air. However, it proceeds to a much greater extent in the presence of air, and at the rate of 6 liters per 100 grams of oil per hour the detergency is at its highest for the examples reported. This obviously is not the upper limit of oxygen which can be incorporated in the reaction mixture.

The increase in detergency is obtained at the cost of a slight darkening in color.

The high detergency of the chemically-refined or finished lubricants of the invention is especially noteworthy inasmuch as the product contains no ash. Thus a detergent oil is provided which could not have any tendency to form deposits in the engine due to ash content of the oil. The products of the invention also are stable in most instances to liberation of hydrogen sulfide.

If desired, the improved lubricants of the invention can be used in blends together with other lubricants or other lubricant agents such as soap or the like in a grease.

An antioxidant can be added to oils treated by the invention. Any antioxidant can be used, such as dibutyl-p-cresol, sulfurized terpenes, dialkyl zinc dithiophosphates and tetramethyldiaminodiphenyl methane.

An agent for improving the clarity of the oil may be included, e. g., lauryl alcohol and the like. Agents for preventing foaming may also be included, e. g., tetraamyl silicate, an alkyl ortho-carbonate, ortho-formate or ortho-acetate, or a polyalkyl silicone oil.

In view of the foregoing disclosure, variations and modifications of the invention will be apparent to those skilled in the art and it is intended to claim such variations and modifications broadly except as do not come within the scope of the appended claims.

We claim:

1. A method of preparing detergent lubricating oil additives and lubricants which comprises reacting the product of the reaction of solvent-extracted lubricating oil stock consisting essentially of hydrocarbon material with an amount of phosphorus pentasulfide in the range of about 0.1 to about 0.75% by weight at a temperature in the range of about 275° to 450° F. with an organic amine base selected from the group consisting of primary and secondary amines having up to 18 carbon atoms in an amount to improve the detergency of the oil within the range from about 0.5 to about 8 moles per atomic weight of phosphorus in the reaction product at a temperature of at least 450° F. for at least one-half hour.

2. The method of claim 1 wherein the sulfide-treated stock is reacted at a temperature within the range from about 450° to about 550° F. with an amine in an amount in the range of about 0.5 to about 8 moles per atomic weight of phosphorus in the sulfide-treated oil.

3. Lubricants and lubricating oil additives obtained by the process of claim 1.

4. Lubricants and lubricating oil additives obtained by the process of claim 2.

5. The method of claim 1 wherein the amine is cetylamine.

6. The method of claim 1 wherein the amine is p-phenylenediamine.

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- 7. The method of claim 1 wherein the amine is 2-amino-benzenethiol.
- 8. The method of claim 1 wherein the amine is indole.
- 9. The method of claim 1 wherein the amine is pyrrole.
- 10. Lubricants and lubricating oil additives obtained by the process of claim 5.
- 11. Lubricants and lubricating oil additives obtained by the process of claim 6.
- 12. Lubricants and lubricating oil additives obtained by the process of claim 7.
- 13. Lubricants and lubricating oil additives obtained by the process of claim 8.
- 14. Lubricants and lubricating oil additives obtained by the process of claim 9.
- 15. The method of claim 1 wherein the reaction is carried out in the presence of oxygen.

- 16. Lubricants and lubricating oil additives obtained by the process of claim 15.
- 17. The method of claim 15 wherein the reaction is carried out in the presence of air.
- 18. Lubricants and lubricating oil additives obtained by the process of claim 17.

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