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TALL OIL PITCH-PHOSPHORUS SULFIDE REACTION PRODUCT AND METALLIC SALTS AS DISPERSANTS FOR LUBRICATING OILS

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The present invention relates to compositions for use in lubricating oils, particularly those of the type known as crankcase oils for internal combustion engines, and more particularly to such compositions for use in heavy duty oils for truck, bus, airplane and marine gasoline and diesel engines. More specifically, the present invention is concerned with improving agents or chemical additives for lubricating oils to increase the effective service life of engines using such oils under all types of operating conditions.

These additives are oil soluble and act as dispersants or anti-sludge agents to prevent the formation of hard sludge deposits due to sludge formation in the oil particularly at elevated temperatures and thereby to maintain engine cleanliness. Additionally, these additives are effective to reduce oxidation or deterioration of the oil and inhibit or mitigate the normal corrosive action of such oils, or the decomposition products thereof, on metallic parts.

When conventional mineral lubricating oils are subjected to high operating temperatures, especially for extended periods of time, as in heavy duty service, they tend to decompose and form complex and objectionable oxidation and decomposition products. Under the high temperature conditions prevailing in an engine, these decomposition products polymerize to form lacquer-like deposits on or between the moving parts of the engine, causing them to wear rapidly or to stick. Even larger quantities of polymerization products remain dispersed in the partly oxidized crankcase oil and are readily precipitated to form a sludge when the engine cools or when fresh oil is added to the engine. These precipitated sludges become caked on the heated metal surfaces and cut down the effective life of the engine by preventing proper functioning of the parts thereof, such as by hindering proper ring action, as well as causing bearing failures by blocking the passages of small diameter through which the lubricating oil normally flows to the bearings.

The principal objects of the present invention are to provide a lubricating oil composition capable of heavy duty service under varying operating conditions, which composition possesses excellent detergent properties, is resistant to oxidation and sludge formation, is non-corrosive to metallic parts or alloy bearings, is free from lacquer formation and ring-sticking tendencies as well as fouling or oil passage-blocking characteristics.

Another object of the present invention is to provide new and superior lubricating oil additives from available and inexpensive raw materials.

These objects and others which will appear hereinafter are accomplished by providing a hydrocarbon lubricating oil containing a new class of additive compounds derived from an inexpensive raw material, namely tall oil pitch, which compounds have the above-mentioned detergent and other desirable properties.

Tall oil pitch is the residue or still bottoms resulting from the distillation of tall oil and comprises a tarry substance separated as pitch from the resin acids-fatty

acids components thereof. It is a dark-brown, almost solid material having the following characteristics and properties which are illustrated by but not limited to the following analysis of a typical sample:

Color (Gardner—50% in benzene)	>18
Saponification No	124.9
Acid No	70.4
Iodine No	167.4
Rosin acids (Wolff method, percent)	29.8
Total fatty acids,[1] percent	40.9
Lignin, percent (about)	10.0
Other unsaponifiables, percent	19.3
Ash, percent	0.37
Water, percent	0.0

[1] Free and esterified.

We have found that tall oil pitch, however, possesses constituents which are either of such an unreactive or insoluble nature that they interfere seriously with the use of such a raw material in the preparation of desirable lubricating oil additives. Without being bound to the particular theory here advanced, it is believed that these interfering materials comprise the ligneous matter present in tall oil pitch up to 10% or more.

Inasmuch as the ligneous materials have been found to be substantially insoluble in saturated aliphatic hydrocarbon solvents, or a mixture of several of the lighter constituents of petroleum, such as petroleum ether, the separation and practically complete removal thereof is possible by dissolving the tall oil pitch in hexane (or pentane, or heptane), for example, and then filtering and discarding the insoluble ligneous residue. The filtrate containing the hexane-soluble fraction may then be evaporated to leave a residue comprising lignin-free refined tall oil pitch capable of use in accordance with the present invention in the preparation of oil-soluble detergents for lubricating oils.

We have found that tall oil pitch, once these interfering materials have been removed, constitutes a desirable raw material for the preparation of lubricating oil additives.

As a more specific aspect of the present invention, we have further found that tall oil pitch, when refined as above-described, either by itself, or in admixture with compounds containing or consisting of unsaturated ester waxes, may be reacted with phosphorus sulfides to form reaction products which comprise excellent improvement agents for hydrocarbon lubricating oils.

As used herein, therefore, the term "refined tall oil pitch" refers to a tall oil pitch which has been refined by partially or completely removing the objectionable interfering ligneous matter. It is not necessary that the ligneous matter be removed by the above-described method involving a hexane extraction of tall oil pitch but other refining methods may be used such as, for example, removal of the ligneous matter from tall oil prior to distillation.

As mentioned above, the refined tall oil pitch may be used by itself in the reaction with the phosphorus sulfide, or it may be used in admixture with various unsaturated ester waxes, such as cetyl oleate, octadecyl linoleate, tetradecyl oleate, and the like.

As used herein, the term "ester-wax" is intended to cover esters of higher fatty acids with sterols, or higher aliphatic alcohols having at least 14 carbon atoms in the molecule. It is not essential that such ester waxes be used in a pure form and it has been found that compounds containing ester waxes may be satisfactorily used. For example, such materials as sugar cane oil, sperm oil, wool grease, and the like, which contain unsaturated ester waxes may be used. The percentages of such additional materials in the mixture may cover a wide range and may be in such minor amounts as approximately 1–5% by

weight or may be in such major amounts as approximately 95–99% by weight, depending on the requirements and circumstances of the particular situation.

It is not beyond the purview of the present invention to use mixtures of two or more of these unsaturated ester waxes, or the compounds containing the same, with the refined tall oil pitch.

It is further to be observed that the tall oil pitch, or mixtures thereof with the above-mentioned compounds, may be used as such in the reaction with the phosphorus sulfide or may be employed in partially or completely saponified form, depending on the circumstances of the particular situation.

Of the several available phosphorus sulfides, phosphorus sesquisulfide has been selected to be the preferred illustrative form for the purpose of describing the invention which will be set forth with particular reference thereto. However, this is not to be construed as limitative of the inventive concept involved and it is to be appreciated that the use of other sulfides has been found successful. For example, other sulfides of phosphorus, namely, the pentasulfide, P_2S_5, and the heptasulfide, P_4S_7, have been satisfactorily employed.

In order to prepare the oil soluble lubricant additives of the present invention, refined tall oil pitch either as such, or in partially or completely saponified form, may be mixed with the required amount of the selected sulfide of phosphorus, such as phosphorus sesquisulfide, for example, and heated with constant agitation to an elevated temperature sufficient to promote the chemical reaction. The mixture of reactants is then preferably blown with oxygen, whereupon an exothermic reaction will begin. This reaction is accompanied by the evolution of white fumes, presumably of oxides of phosphorus. The initial temperature of the reaction will naturally vary according to the specific sulfide or phosphorus selected and the chemical composition and nature of the particular refined tall oil pitch and has been found to be normally in the range of from 100° to 140° C.

This reaction is promoted or accelerated by the presence of the oxygen and the more intimate the contact between the oxygen and the sulfide of phosphorus and the refined tall oil pitch, the more effective is the promotion of the reaction. The oxygen may be supplied as such, or in form of air or other free oxygen-containing gas which may be blown, bubbled into or otherwise passed through the mixture of reactants at the desired elevated temperature. This reaction is exothermic and, once it has begun, it may be maintained at a desired temperature by the simple expedient of controlling the rate of passage of the free oxygen-containing gas through the mixture without the necessity of supplying any additional heat from an external source. For the purposes of this invention, it has been found preferable to control the amount of oxygen in such a way as to provide a temperature in the range of from about 120° to 130° C. Higher temperatures such as up to 150° C. or higher have been employed with successful results but the control over the reaction in such a case is less and the uniformity of the resulting product decreases, due probably to high losses of sulphur and phosphorus.

The conclusion of the reaction is indicated by a falling-off of the temperature of the reaction mixture and by the cessation of fuming, accompanied by an inability to increase such reaction temperature by increasing the rate of flow of oxygen through the mixture.

The employment of the oxygen during the reaction considerably shortens the reaction period and additionally accomplishes a more complete combination of the reactants, whereby the possibility of the presence of free sulfides is minimized and a product having better odor and physical appearance is produced. In order to determine if the reaction is complete, a test sample of the reaction mixture may be drawn and chilled down to 0° C. whereby any free sulfides, if present, will form a precipitate, indicating that the reaction has not been completed.

The reaction mixture of the refined tall oil pitch and the phosphorus sulfide may then be neutralized, such as with metallic oxides or hydroxides by the procedures hereinafter described, and the resulting neutralized product vacuum stripped of water, volatiles, etc. and then filtered to yield the desired finished product.

When the refined tall oil pitch is used in mixtures with other compounds consisting of or comprising ester waxes, the procedure substantially follows that set forth for refined tall oil pitch alone, with the temperature ranges and amounts of reagents varying to some extent. It is also to be observed that such is the compatibility of these constituents that each may be present in the mixture in such minor quantities on the order of 1–5% by weight or may be in such major quantities as 95–99% by weight. In view of the comparative inexpensiveness of refined tall oil pitch, it is to be appreciated that it will normally preferably comprise the predominating, or perhaps the only, constituent in such mixtures.

The invention will be further illustrated in greater detail by the following specific examples. It should be understood, however, that although these examples may describe in particular detail some of the specific features of the invention they are given primarily for purposes of illustration and the invention in its broader aspects is not to be construed as limited thereto.

Example 1

180 grams of refined tall oil pitch was mixed with 20 grams of butanol and 18 grams of sodium hydroxide in 50 ml. of water. This reaction mixture was heated on a steam bath for approximately one hour. 31.5 grams of zinc chloride dissolved in 30 ml. water was then added and the reaction mixture heated an additional half hour. The water and utanol were then removed under vacuum and 15 grams of phosphorus sesquisulfide was added. The reaction mixture was then heated to 110° C. and blown with air whereupon an exothermic reaction set in. The blowing of air was continued at such a rate so as to maintain the reaction temperature at 120–130° C. After 1½ hours, the exothermic reaction stopped and blowing was continued for an additional hour using external heat to maintain the temperature at 120° C. The reaction mixture was then diluted with 400 grams of oil and treated with 30 grams of barium oxide and 15 grams methyl alcohol. After refluxing for ½ hour, the reaction mixture became free of hydrogen sulfide and was then stripped under vacuum on the steam bath and filtered through a "Hyflo" pre-coated Buechner funnel. This product was soluble in oil in all proportions and had excellent detergent properties.

Example 2

A mixture of 360 grams of refined tall oil pitch, 40 grams butanol, 12 grams sodium hydroxide and 15 ml. of water was heated in a steam bath for one hour. To this reaction mixture was added 21 grams of zinc chloride in 30 ml. of water and heating was continued for an additional ½ hour. Volatile materials were then removed under vacuum on the steam bath. To this material, 30 grams of phosphorus sesquisulfide was added, and, the mixture, after heating to 120° C., was blown with air, whereupon an exothermic reaction set in. A temperature of 120°–130° C. was maintained by controlled air blowing for approximately one hour. After the exotherm had stopped, air blowing was continued for one hour while applying external heat and holding the temperature at 120° C. To this reaction mixture, after diluting with 800 grams of oil, was added 8 grams of zinc oxide and 8 ml. of 50% methanol. After refluxing for one hour, 30 grams of barium oxide and 30 ml. of methanol were added and the refluxing continued for another hour. The material became H_2S free at this point and was stripped

under a 10 mm. mercury vacuum to 100° C. The resulting mixture was then filtered through a "Hyflo" precoated steam-heated filter to give a product similar to that resulting from Example 1.

Example 3

To a mixture of 100 grams of the hexane-soluble portion of tall oil pitch and 100 grams of sugar cane oil was added 20 grams of butanol, 6 grams sodium hydroxide and 10 ml. of water. This reaction mixture was heated at 100° C. for approximately one hour. 10½ grams of zinc chloride in 12 ml. of water were then added and the heating continued for an additional ½ hour. Volatile materials were removed by vacuum stripping to 120° C. The reaction mixture was treated with 15 grams of phosphorus sesquisulfide and, after heating to 120° C. was air-blown for approximately one hour, causing an exothermic reaction to take place. After the exotherm had ceased, air blowing was continued for an additional ½ hour while maintaining the temperature at 120°–130° C. by the application of external heat.

To the reaction mixture were added 400 grams of oil, 4 grams of zinc oxide and 5 ml. of 50% methanol. After heating on a steam bath for ½ hour, 30 grams of barium oxide and 12 ml. of methanol were added and the heating continued for an additional ½ hour. The reaction mixture was free of hydrogen sulfide at this point and was vacuum stripped to 120° C. to remove volatile matter. 12 grams of a suitable diatomaceous earth filter aid were added and the product was filtered.

Example 4

400 grams of refined tall oil pitch and 30 grams of finely divided phosphorus pentasulfide were mixed directly (without any prior saponification reaction) and heated to about 110°–130° C. whereupon an exothermic reaction set in, which was substantially complete in approximately four hours. The remainder of the procedure followed that set forth in Example 1.

Example 5

A mixture of 150 grams refined tall oil pitch, 50 grams of wool grease, 20 grams butanol and 6 grams of sodium hydroxide were mixed in 15 ml. of water. This reaction mixture was heated in a steam bath for one hour. 10½ grams of zinc chloride and 15 ml. of water were then added and heating continued for an additional ½ hour. The volatile materials were then removed on a steam bath under vacuum. To the stripped material 15 grams of phosphorus sesquisulfide was added and, after heating to 120° C., air was blown into the mixture. An exothermic reaction took place for about one hour, after which blowing was continued for an additional ½ hour while maintaining a temperature of 120°–130° C. by the application of external heat. To the reaction mixture was then added 400 grams of oil, 4 grams of zinc oxide, 5 ml. of 50% methanol. The reaction mixture was then refluxed for ½ hour, after which 20 grams of barium oxide and 10 ml. of methanol were added. This reaction mixture became free of hydrogen sulfide after heating for ½ hour, after which it was stripped under vacuum on a steam bath to remove volatile materials. The reaction mixture was filtered through a steam-heated "Hyflo" pre-coated filter to yield an oil soluble product having excellent detergent properties.

It is to be appreciated that although the preceding examples involve the use of basic neutralizing compounds of barium and zinc, it is to be realized that other reactive metal compounds may be used, preferably of the other alkaline earth metals, magnesium, calcium and strontium. Among the various other metal compounds which have been employed in carrying out the invention are those of the salt-forming radicals nickel, cobalt, chromium, aluminum, tin, and others.

From the foregoing it is seen that we have provided novel detergent compositions suitable for use as improvement agents for hydrocarbon lubricating oils operative to assist in preventing the deposition of hard deposits due to sludge formation of the oil at elevated temperatures. These compositions are further valuable as anti-oxidants and corrosion inhibitors and increase the effective service life of engines using oils containing such compositions. The commercial and economic value of these detergent compositions is particularly commendable, primarily due to the relative inexpensiveness of tall oil pitch.

The quantities of these lubricating additives required for improving hydrocarbon lubricating oils will depend to a large extent upon the nature of the lubricating oil. Larger amounts will be required for those oils which are more susceptible to sludge formation, oxidation and the like. The improved effects of the compositions of the present invention have been observed when added in such small amounts as approximately 0.8% by weight and the upper limits are primarily set by economic or commercial factors. In any event, it has been found that up to 8.0% by weight or more may be added for improved results on any type of lubricant. In the event that the additives of the present invention are used in conjunction with other improving agents, it is, of course, apparent that the amounts required to stabilize the oil, or to avoid sludge formation, or prevent corrosion, will be less. In such cases, amounts as low as 0.2% by weight have been effective to provide the desired effect.

Although we have described but a few specific examples of our invention, we consider the inventive concept not to be limited thereby nor to the specific substances mentioned therein, but to include various other equivalent compounds of similar constitution as set forth in the claims appended hereto. It is understood that any suitable changes or variations may be made without departing from the spirit or scope of the inventive concept.

We claim:

1. A composition suitable for use as an improvement agent for hydrocarbon lubricating oils operative to assist in preventing the deposition of hard deposits due to sludge formation in the oil comprising as its essential ingredient a reaction product resulting from chemically reacting a phosphorus sulfide with a member of the group consisting of refined tall oil pitch, partially saponified refined tall oil pitch, and completley saponified refined tall oil pitch.

2. A composition suitable for use as an improvement agent for hydrocarbon lubricating oils operative to assist in preventing the deposition of hard deposits due to sludge formation in the oil comprising as its essential ingredient a neutralized reaction product resulting from chemically reacting a phosphorus sulfide with a member of the group consisting of refined tall oil pitch, partially saponified refined tall oil pitch, and completely saponified refined tall oil pitch, and then neutralizing the product of such reaction with a reactive metal compound.

3. A composition suitable for use as an improvement agent for hydrocarbon lubricating oils operative to assist in preventing the deposition of hard deposits due to sludge formation in the oil comprising as its essential ingredient a neutralized reaction product resulting from chemically reacting phosphorus sesquisulfide with a member of the group consisting of refined tall oil pitch, partially saponified refined tall oil pitch, and completely saponified refined tall oil pitch in the presence of a free-oxygen containing gas and at a temperature to promote such a reaction, and neutralizing the product of such reaction with a member of the group consisting of metal oxides and hydroxides.

4. A lubricating oil composition comprising a predominating amount of a hydrocarbon lubricating oil and a minor amount of a detergent composition operative to assist in preventing the deposition of hard deposits due to sludge formation in the oil, said detergent composition comprising as its essential ingredient a neutralized reaction product resulting from chemically reacting a phos-

phorus sulfide with a member of the group consisting of refined tall oil pitch, partially saponified refined tall oil pitch, and completely saponified refined tall oil pitch, and then neutralizing the product of such reaction with a suitable reactive metal compound.

5. A lubricating oil composition comprising a hydrocarbon lubricating oil having dissolved therein a detergent composition operative to assist in preventing the deposition of hard deposits due to sludge formation in the oil, said detergent composition comprising as its essential ingredient a neutralized reaction product resulting from chemically reacting phosphorus sesquisulfide with a member of the group consisting of refined tall oil pitch, partially saponified refined tall oil pitch, and completely saponified refined tall oil pitch in the presence of a free-oxygen containing gas and at a temperature to promote such a reaction, and neutralizing the product of such reaction with a member of the group consisting of metal oxides and hydroxides.

6. A lubricating oil composition comprising a predominating amount of a hydrocarbon lubricating oil and about 0.8% to about 8.0% by weight of a detergent composition operative to assist in preventing the deposition of hard deposits due to sludge formation in the oil, said detergent composition comprising as its essential ingredient a neutralized reaction product resulting from chemically reacting phosphorus sesquisulfide with a member of the group consisting of refined tall oil pitch, partially saponified refined tall oil pitch, and completely saponified refined tall oil pitch in the presence of a free-oxygen containing gas and at a temperature to promote such a reaction, and neutralizing the product of such reaction with a member of the group consisting of metal oxides and hydroxides.

7. A composition suitable for use as an improvement agent for hydrocarbon lubricating oils operative to assist in preventing the deposition of hard deposits due to sludge formation in the oil comprising as its essential ingredient a neutralized reaction product resulting from chemically reacting a phosphorus sulfide with a mixture comprising a material containing a member of the group consisting of an unsaturated ester wax, a partially saponified unsaturated ester wax, and a completely saponified unsaturated ester wax and a material of the group consisting of refined tall oil pitch, partially saponified refined tall oil pitch, and completely saponified refined tall oil pitch; and then neutralizing the product of such reaction with a reactive metal compound.

8. A lubricating oil composition comprising a hydrocarbon lubricating oil having dissolved therein a detergent composition operative to assist in preventing the deposition of hard deposits due to sludge formation in the oil, said detergent composition comprising as its essential ingredient a neutralized reaction product resulting from chemically reacting phosphorus sesquisulfide with a mixture comprising a material containing a member of the group consisting of an unsaturated ester wax, a partially saponified unsaturated ester wax, and a completely saponified unsaturated ester wax and a material of the group consisting of refined tall oil pitch, partially saponified refined tall oil pitch, and completely saponified refined tall oil pitch in the presence of a free-oxygen containing gas and at a temperature to promote such a reaction; and neutralizing the product of such reaction with a member of the group consisting of metal oxides and hydroxides.

9. A lubricating oil composition comprising a predominating amount of a hydrocarbon lubricating oil and about 0.8% to about 8.0% by weight of a detergent composition operative to assist in preventing the deposition of hard deposits due to sludge formation in the oil, said detergent composition comprising as its essential ingredient a neutralized reaction product resulting from chemically reacting phosphorus sesquisulfide with a mixture comprising a material containing a member of the group consisting of an unsaturated ester wax, a partially saponified unsaturated ester wax, and a completely saponified unsaturated ester wax and a material of the group consisting of refined tall oil pitch, partially saponified refined tall oil pitch, and completely saponified refined tall oil pitch in the presence of a free-oxygen containing gas and at a temperature to promote such a reaction; and neutralizing the product of such reaction with a member of the group consisting of metal oxides and hydroxides.

10. A process of preparing a composition suitable for use as an improvement agent for hydrocarbon lubricating oils operative to assist in preventing the deposition of hard deposits due to sludge formation in the oil comprising the steps of chemically reacting a phosphorus sulfide with a member of the group consisting of refined tall oil pitch, partially saponified refined tall oil pitch and completely saponified refined tall oil pitch, and then neutralizing the product of such reaction with a reactive metal compound.

11. A process of preparing a composition suitable for use as an improvement agent for hydrocarbon lubricating oils operative to assist in preventing the deposition of hard deposits due to sludge formation in the oil comprising the steps of chemically reacting a phosphorus sulfide with a mixture comprising a material containing a member of the group consisting of an unsaturated ester wax, a partially saponified unsaturated ester wax and a completely saponified unsaturated ester wax and a material of the group consisting of refined tall oil pitch, partially saponified refined tall oil pitch and completely saponified refined tall oil pitch; and then neutralizing the product of such reaction with a reactive metal compound.

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