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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 including heavy duty oils for truck, bus, airplane and marine gasoline and diesel engines. More specifically, the 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, and 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 other which will appear hereinafter are accomplished by providing a hydrocarbon lubricating oil composition containing a new class of additive compounds derived from an inexpensive raw material, namely, tall oil pitch, which compounds have detergent and other desirable properties, as above mentioned. The most desirable feature of this new class of additive compounds is noted in its ability to assist in preventing the deposition

of hard deposits due to sludge formation in the oil, particularly at elevated temperatures.

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 percent [1]	40.9
Lignin percent	about 10.0
Other unsaponifiables percent	19.3
Ash percent	0.37
Water percent	0.0

[1] Free and esterified.

In our copending United States patent application Serial No. 335,606, filed February 6, 1953, we have disclosed the extraction and removal of the lignin-containing fraction of tall oil pitch and the use of the refined tall oil pitch, per se, or mixtures thereof with various unsaturated ester waxes or compounds containing the same, as reactants with phosphorus sulfides in the preparation of products which are oil soluble and comprise excellent improvement agents for hydrocarbon lubricating oils.

We have now found that the tall oil pitch may be used as such without refining, if in admixture with other materials, such as unsaturated ester waxes, or compounds containing the same, if such mixtures are within certain critical proportional ranges to be disclosed hereinafter. These mixtures may be reacted with phosphorus sulfides to yield reaction products which have improved oil solubility characteristics and comprise excellent improvement agents for hydrocarbon lubricating oils.

It is not essential that the tall oil pitch be used in admixture with pure unsaturated ester waxes such as octadecyl oleate, cetyl linoleate, tetradecyl oleate, and the like and it has been found that compounds containing such unsaturated ester waxes may be used in lieu thereof. 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 unsaturated ester waxes in the mixture may cover a wide range and may be in such minor amounts as at least 25% by weight or may be in such major amounts as approximately 95–99% by weight depending on the requirements of the particular situation. The percentages of the tall oil pitch may also vary within wide ranges and may be in such minor amounts as approximately 1.5% by weight but should not be present in amounts greater than approximately 75% by weight. Should that value be exceeded, then the neutralized reaction product of such a mixture and phosphorus sulfide will lose its oil solubility characteristics which are essential for its use as a hydrocarbon lubricating oil additive.

As used herein, the term "ester wax" is intended to cover esters of higher fatty acids with sterols, or with higher aliphatic alcohols having at least 14 carbon atoms in the molecule.

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 phosphorus sulfides or may be employed in partially or completely saponified form, depending on the circumstances of the particular situation.

Of the several phosphorus sulfides, phosphorus sesqui-

sulfide has been selected to be the preferred 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, tall oil pitch may be mixed with the selected ester wax, or a blend of two or more ester waxes, and the mixture may be reacted either as such or in partially or completely saponified form with the required amount of the selected sulfide of phosphorus. The reactants may be heated with constant agitation to an elevated temperature sufficient to promote the chemical reaction and preferably then 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 of phosphorus selected and the chemical composition and nature of the particular 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 ester wax and 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° C. to about 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 or not, 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 ester wax and the tall oil pitch and the phosphorus sulfide may then be neutralized, such as with metallic oxides or hydroxides or with other suitable reactive compounds 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.

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

A mixture of 100 grams of tall oil pitch, 100 grams of wool grease, 20 grams of butanol and 6 grams of sodium hydroxide in 15 ml. of water was heated on a steam bath for one hour. To this reaction mixture, 10½ grams of zinc chloride in 15 ml. of water were added and the reaction mixture heated for an additional ½ hour. After removing the volatile materials by heating the reaction mixture on a steam bath under vacuum, 15 grams of phosphorus sesquisulfide were added. The reaction mixture was then heated to 110–120° C. and blown with air, whereupon an exothermic reaction set in. The air-blowing was continued at such a rate as to maintain the temperature at 120–130° C. After 1½ hours, the exothermic reaction ceased, as evidenced by a decrease in the reaction mixture temperature. An increased rate of air blowing could not increase or even maintain the previously obtained reaction mixture temperature. The reaction mixture was then heated for an additional ½ hour at 120° C. while blowing with air. To this reaction mixture, 400 grams of oil, 4 grams of zinc oxide, and 5 ml. of 50% methanol were added and the reaction refluxed for ½ hour. To this was then added 20 grams of barium oxide and 10 ml. of methanol. After refluxing for 15 minutes, the reaction mixture became free of hydrogen sulfide and the volatiles were removed on a steam bath under vacuum. This material was then filtered through a "Hyflo" pre-coated steam-heated filter. The resulting material was soluble in all proportions when diluted with oil and had excellent detergent properties.

Example 2

To 125 grams of tall oil pitch and 75 grams of sugar cane oil was added 20 grams of butanol and 6 grams of sodium hydroxide in 10 ml. of water. This reaction mixture was heated at 100° C. for approximately one hour, after which 10½ grams of zinc chloride in 12 ml. of water were added and the heating continued for an additional ½ hour. Volatile materials were removed by heating the reaction mixture to 120° C. under vacuum, after which 15 grams of phosphorus sesquisulfide was added and the reaction mixture blown with air, whereupon an exothermic reaction set in. A reaction temperature of 120–130° C. was maintained for one hour by controlling the rate of air blowing. Air blowing was continued for an additional ½ hour after the exothermic reaction had ceased, while holding the temperature at 130° C. by the application of heat from an external source. To the reaction mixture was then added 400 grams of oil, 4 grams of zinc oxide and 10 ml. of 50% methanol, followed by heating at 100° C. for ½ hour. To this reaction mixture was then added 30 grams of barium oxide and 15 ml. of methanol, and the reaction mixture was refluxed for approximately ½ hour until the reaction mixture was hydrogen sulfide free. Volatile materials were removed by vacuum stripping on a steam bath, after which 20 grams of "Hyflo" were added and the reaction mixture filtered through a steam-heated "Hyflo" pre-coated filter to yield a material which, when dissolved in oil, gave a clear oil solution.

Example 3

180 grams of tall oil pitch and 220 grams of sugar cane oil were mixed directly with 30 grams of phosphorus pentasulfide in finely divided form (without any prior saponification step). The reaction mixture was heated with agitation to 110° C. whereupon an exothermic reaction started, thereby obviating the necessity of applying additional external heat. The exothermic reaction was substantially complete in approximately 3½ hours, after

which the temperature was maintained at 120° C. by the renewed application of external heat for about 30 minutes. The remainder of the procedure followed that set forth in Example 1. The final product had excellent oil solubility characteristics and possessed superior detergent, anti-oxidant and corrosion-inhibiting properties.

Example 4

150 grams of tall oil pitch, 50 grams of wool grease, 20 grams of butanol, and 6 grams of sodium hydroxide in 15 ml. of water were mixed and heated on 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 by heating the reaction mixture on a steam bath under vacuum. To the stripped material, 15 grams of phosphorus sesquisulfide was added and, after heating to 120° C., the mixture was blown with air. 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, and 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. This resulting material was soluble in all proportions when diluted with oil, and possessed properties similar to those exhibited by the product of Example 4.

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 compounds containing various other suitable reactive metals may be used, preferably the other alkaline earth metals, magnesium, calcium and strontium. Among the various other metal neutralizing 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 thus increase the effective service life of engines using oils containing such compositions. The commercial and economic value of these detergent compositions is particularly commendable in view of the comparative inexpensiveness of tall oil and tall oil pitch.

Although we have described but a few specific examples of our invention, we consider the case 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 mixture comprising from about 1% to 75% by weight of a member of the group consisting of tall oil pitch, partially saponified tall oil pitch, and completely saponified tall oil pitch and at least 25% by weight of a member of the group consisting of an unsaturated ester wax, a partially saponified unsaturated ester wax, and a completely saponified unsaturated ester wax.

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 mixture comprising from about 1% to 75% by weight of a member of the group consisting of tall oil pitch, partially saponified tall oil pitch, and completely saponified tall oil pitch and at least 25% by weight of 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 neutralizing the reaction product with a suitable 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 mixture comprising from about 1% to 75% by weight of a member of the group consisting of tall oil pitch, partially saponified tall oil pitch, and completely saponified tall oil pitch and at least 25% by weight of a member of the group consisting of an unsaturated ester wax, a partially saponified unsaturated ester wax, and a completely saponified unsaturated ester wax in the presence of a free oxygen-containing gas and at a temperature sufficient to promote such a reaction, and neutralizing the reaction product with a member of the group consisting of metal oxides and hydroxides.

4. A lubricating 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 a phosphorus sulfide with a mixture comprising from about 1% to 75% by weight of a member of the group consisting of tall oil pitch, partially saponified tall oil pitch, and completely saponified tall oil pitch and at least 25% by weight of 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 neutralizing the reaction product with a suitable reactive metal compound.

5. A lubricating 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 from about 1% to 75% by weight of a member of the group consisting of tall oil pitch, partially saponified tall oil pitch, and completely saponified tall oil pitch and at least 25% by weight of a member of the group consisting of an unsaturated ester wax, a partially saponified unsaturated ester wax, and a completely saponified unsaturated ester wax in the presence of a free-oxygen containing gas and at a temperature sufficient to promote such a reaction, and neutralizing the reaction product with a member of the group consisting of metal oxides and hydroxides.

6. A lubricating composition comprising a predominating amount of a hydrocarbon lubricating oil having dissolved therein from 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 from about 1% to 75% by weight of a member of the group consisting of tall oil pitch, partially saponified tall oil pitch, and completely saponified tall oil pitch and at least 25% by weight of a member of the group consisting of an unsaturated ester wax, a partially saponified unsaturated ester wax, and a completely saponified unsaturated ester wax, in the presence of a free-oxygen containing gas and at a temperature sufficient to promote such a reaction, and neutralizing the reaction product with a member of the group consisting of metal oxides and hydroxides.

7. 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 from about 1% to 75% by weight of a member of the group consisting of tall oil pitch, partially saponified tall oil pitch, and completely saponified tall oil pitch and at least 25% by weight of a member of theg roup consisting of an unsaturated ester wax, a partially saponified unsaturated ester wax, and a completely saponified unsaturated ester wax, and neutralizing the reaction product with a suitable reactive metal compound.

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