April 27, 1943. A. W. BURWELL ET AL 2,317,666

LUBRICATION COMPOSITION

Filed May 8, 1940

Fig. 1.

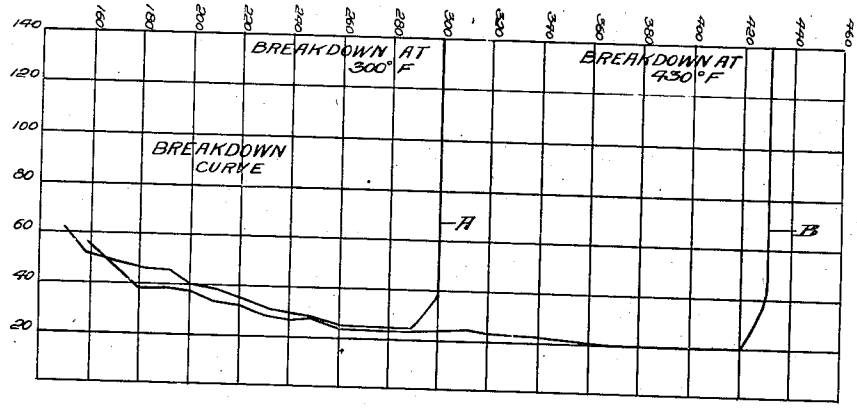


Fig. 2.

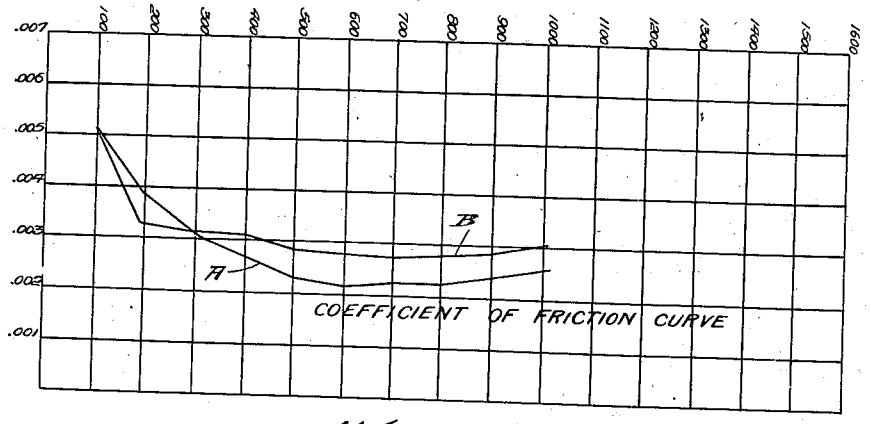
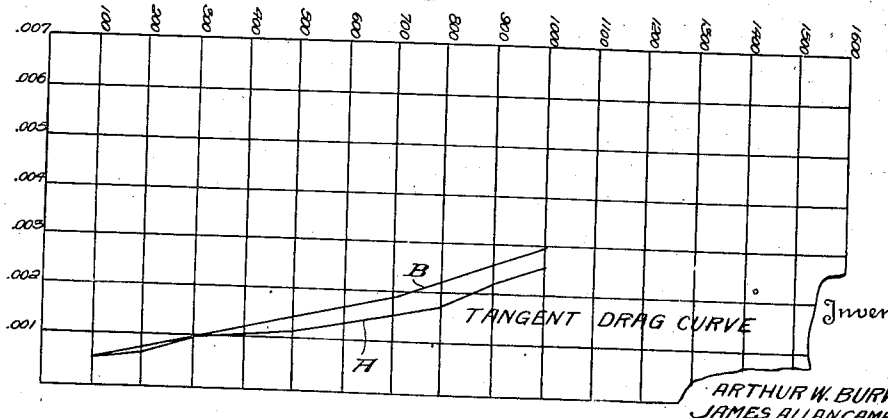


Fig. 3.



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UNITED STATES PATENT OFFICE

2,317,666

LUBRICATION COMPOSITION

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Application May 8, 1940, Serial No. 334,036

4 Claims. (Cl. 252—39)

This invention relates to the lubricating compositions art, and is particularly concerned with the provisions of lubricating compositions consisting essentially of lubricating oil and relatively small amounts of thio-alkyl derivatives of oxygenated saturated aliphatic compounds (alcohols, alcohol-ketones, ketones, hydroxy carboxylic acids, and alkyl esters of such acids, of relatively high molecular weights) derived from mineral hydrocarbonaceous mixtures (e. g., petroleum oils and/or waxes) by the controlled partial oxidation of the latter in liquid phase. The invention is concerned with processes for the production of such thio-alkyls, with the thio-alkyls per se, and with lubricating compositions containing such thio-alkyls.

It is known that some highly refined lubricating oils, more particularly paraffinic oils refined by selective solvent methods of refining, tend in use to form sludge and/or to acquire corrosive properties toward, for example, bearing metals with which they are in contact. Thus, it is known that some crankcase oils, initially free from corrosive constituents, in course of use develop corrosive properties towards copper-lead, cadmium-silver, and other bearing alloys, and form objectionable sludge in the presence of some metals. In the case of relatively high-speed Diesel engines it heretofore had been considered necessary to use only babbitt at the bearing alloy, because babbitt is less sensitive—than, say, copper-lead bearing alloy—to the corrosive action of the low molecular weight acids formed in the oil by oxidation of the latter in the crankcase, and from other decomposition products.

It is an object of the present invention to provide a thio-alkyl "additive" which, when added in small amount to a highly refined lubricating oil, prevents or delays sludge-formation and corrosives-formation therein during use. Another object of invention is the provision of lubricating oil compositions which can be used in the crankcases of internal combustion engines employing bearing alloys "sensitive" to corrosion.

U. S. Patent No. 1,863,004 to Arthur W. Burwell discloses improving the "oiliness" of crankcase oils by the incorporation therein of an oil-soluble addition material consisting essentially of a mixture of high-molecular-weight aliphatic oxygen-containing compounds including free saturated aliphatic carboxylic acids, said mixture being obtainable by the controlled, liquid-phase, partial oxidation of a mixture of hydrocarbons of mineral origin (e. g., petroleum wax or/and oil). Said patent discloses that the described oxidation procedure yields oxygen-containing compounds classifiable as "saponifiables" (typified by free saturated aliphatic carboxylic acids, and lactones and esters thereof) and "unsaponifiables" (typified by alcohols, alcohol-ketones and ketones), and that the "addition material" may consist exclusively of the "saponifiables" portion or may be composed of saponifiables in admixture with unsaponifiables. U. S. Patent No. 2,128,523 to Arthur W. Burwell discloses the prevention of corrosion of metal surfaces by filming them with a composition containing the aforesaid "unsaponifiables," and his Patent No. 2,110,078 discloses as an "oiliness agent" for lubricating Diesel engines a mixture of non-acidic, partially oxidized saturated aliphatic chain hydrocarbons of more than 5 carbon atoms each, including alcohols, alcohol-ketones, ketones, lactones and esters, produced by the Burwell oxidation process.

We have found that thio-alkyl products—compatible with refined mineral lubricating oils—having both sludge-inhibiting and corrosion-inhibiting properties, may be produced by treating with phosphorus hepta sulphide (P_4S_7), at an elevated temperature of the order of 250° to 300° F., the oxygenated hydrocarbons mixtures produced by the process described in the aforesaid Burwell Patents Nos. 1,863,004, 2,110,078 and 2,128,523. That is to say, we have found that these oxygenated hydrocarbons—which heretofore had been known to inhibit corrosion and/or to enhance "oiliness"—may have sludging-inhibiting properties conferred upon them by reacting them with phosphorus hepta sulphide under conditions to form thio-alkyls of the same, and that the resulting reaction products, when freed from components soluble in water, are trebly valuable "additives" for refined lubricating oils. The said additives are, in general mixtures of a plurality of sulphur-containing aliphatic compounds each of relatively high molecular weight (i. e., containing 6 or more carbon atoms to the molecule); these compounds may be broadly designated as "thio-alkyls," which term is here employed to embrace thio-ethers, thio-esters, thio-

ketones and polymers thereof, and
phidized oxidation products or and
carbons. The type reactions
lieved to be representable as
being in each instance an
from 6 to 24 carbon
whole numbers

(1)

(2)

(3)

Determination of sludge formation at completion of the Indiana test showed the following:

Sample #1—199.8 mg. per 10 gr. oil

Sample #2—111.9 mg. per 10 gr. oil

The above test demonstrated that the thio-alkyl mixture of Example III inhibited bearing corrosion in a bearing metal known to be very sensitive to corrosion and also materially retarded the rate of sludge formation. The neutralization value of Sample #2 at the end of the test was materially lower than that of the oil not containing the additive.

It should be noted, in connection with the foregoing, that the thio-ketones prepared from ketones containing from about 6 to about 24 carbon atoms per molecule have a relatively high sulphur content: in general, they show very desirable stability from the standpoints of temperature and further oxidation. By "further oxidation" we refer to the normal oxidation of hydrocarbon oils in use in the crankcase, the progress of which oxidation is retarded by presence of the thio-alkyl compounds of the present invention. Also, it is noted that the thio-ester products of the type "4" reaction above given have a relatively high sulphur content. Our researches tend to indicate that a direct relationship may exist between the relative sulphur contents of the thio-alkyls and their anti-oxidant effects.

As was indicated in reactions "3" above, the thio-ketone

$$\begin{matrix} R{-}C{=}S \\ | \\ R' \end{matrix}$$

is susceptible, under mild oxidizing conditions, to condensation or polymerization to a cyclic trimer (represented in "3"), which latter is even more stable than the thio-ketone. The trimer may be formed in one or another of a plurality of ways; e. g., when a crankcase lubricant containing an addition of the thio-ketone is subjected to the oxidizing conditions present in the crankcase during operation of the automotive engine. The trimer shares with the parent thio-ketone the properties of depressing sludge formation, preventing or retarding corrosion of bearing alloys, and increasing the "oiliness" of the lubricant.

Example IV

The starting material was a product produced by oxidizing Sharples wax, by the Burwell process, to a saponification equivalent of between 100 and 130, subjecting a portion of the resulting oxidation mass, including both saponifiable and unsaponifiable oxygen-containing compounds, to esterification treatment with methyl alcohol whereby to convert all the esterifiable components of the mass to methyl esters, and removing all water-absorbing materials from the treated mass.

100 parts by weight of the starting material just described was intimately mixed with 10 parts by weight of phosphorus hepta sulphide. These proportions were selected because experience had shown that an excess of unreacted P_4S_7 would remain at the end of the reaction, and hence that the concentration was suitable for completion of substitution of sulphur in the starting material. The mixture was maintained at a temperature of 300° F. for 2 hours, with constant stirring. By the end of the heating and stirring period all visible evidence of reaction had disappeared. The reaction mixture was strained through a very fine sieve, the strained material was washed with successive amounts of hot water, until no free phosphoric acid remained in the material and the wash water was neutral to alk-acid indicator paper, and the washed product was dried.

Example V

The procedure of Example IV was duplicated using, instead of the starting material described therein, the esterified product of the following:

A portion of the oxidation mass described in Example IV was treated with aqueous sodium hydroxide solution under conditions to insure saponification of the saponifiable constituents thereof. The resulting soaps were separated from the unsaponifiable constituents, the so-separated soaps were decomposed by treatment with a mineral acid whereby the organic acids of the soaps were freed, and the free organic acids were recovered. The recovered free organic acids were esterified, in known manner, with methyl alcohol, and the resulting esters were salted out in order to free them from any residual free acid.

By the end of the two-hour treatment of the above mixture of esters with P_4S_7 all visible evidence of reaction had disappeared. The reaction mixture was then strained, neutralized by washing with dilute sodium carbonate solution, washed with water, and dried as described in Example IV.

Indiana oxidation tests of lubricating oils containing small amounts (e. g., 1% by weight) of the sulphidized products of Examples IV and V demonstrated that the latter tend to inhibit corrosion of delicate bearing metals, and to retard formation of sludge, under the conditions of use of the oil in the engine crankcase. In these two connections, the product of Example IV showed greater inhibiting action (both as to corrosion and as to sludge formation) than did the product of Example V. Moreover, friction tests demonstrated that the sulphidized products of Examples IV and V enhanced the oiliness of the oils to which they were added in small amounts.

Example VI

An oil containing the sulphidized product of Example IV was further tested, for tangent drag, coefficient of friction, and breakdown, as described below and with reference to the accompanying drawing, in which Fig. 1 is a graph representing breakdown characteristics of two oils; Fig. 2 is a graph representing changes of coefficients of friction in the two oils; and Fig. 3 is a graph representing changes in tangent drag in the two oils.

The oil selected for the test was a standard lubricating oil known in the trade as "Texas Ursa." 1% by weight of the sulphidized product of Example IV was incorporated in one portion of the "Ursa" oil to yield sample "B." Sample "A" was a comparison sample and consisted of the "Ursa" oil without additive.

Breakdown tests on samples A and B

The samples were tested in a lubarometer equipped with bronze bearing elements; the journal speed was 500 ft./min. and the pressure was maintained constant at 1,000 lbs./sq. in. During the continuance of the test the temperature and power requirements were observed at regular intervals. In each case the test was continued until the lubricating oil film between the rotating shaft and the bearings ruptured. From the be-

ginning of the test to incipient breakdown of Sample A at about 290° F. the power requirements of the two were closely similar. Sample A showed complete breakdown at 300° F. However, Sample B did not show incipient breakdown until a temperature of about 420° F. had been reached, with complete breakdown at 430° F.: between 290° F. and 420° F. the power requirements in the case of Sample B did not rise (with increasing temperature) but remained between 26 and 20 watts net.

The breakdown test readings are represented in curves A and B of Fig. 1 of the accompanying drawing.

Coefficient of friction, and tangent drag, tests on Samples A and B

Figs. 2 and 3 represent the determination of coefficient of friction, and tangent drag, respectively, tests of Samples A and B. For these tests, the lubarometer was run at a journal speed of 500 ft./min. and the temperature was maintained constant at 212° F., while the bearing pressure was progressively increased through the range between 100 and 1,000 lbs./sq. in. The observed coefficients of friction, by 100 pound increments in pressure, were as follows:

Pressure	A	B
100	.0050	.0050
200	.0039	.0033
300	.0032	.0032
400	.0027	.0031
500	.0023	.0029
600	.0022	.0028
700	.0022	.0028
800	.0023	.0028
900	.0024	.0029
1000	.0026	.0030

The tangent drag values in pounds per square inch, through the same range, were as follows:

Pressure	A	B
100	0.50	0.50
200	0.75	0.70
300	0.95	0.95
400	1.10	1.20
500	1.18	1.45
600	1.32	1.70
700	1.55	1.90
800	1.75	2.25
900	2.20	2.60
1000	2.60	3.00

It is to be understood that instead of the esterification agent (methyl alcohol) described in Examples IV and V above there may be employed ethyl alcohol, propyl alcohol or other similar esterification agent for converting the esterifiable acidic bodies to alkyl esters. Instead of sodium carbonate solution, described in Example V, we may reduce the acidity of the product (e. g., remove the phosphoric acid, which is one of the reaction products) by washing the P_4S_7-treated material with an aqueous solution of another mild alkali.

It is to be understood, also, that thio-ether products, equivalent to that described in Example V, may be produced by treating a mixture of the free acids with P_4S_7 and thereafter esterifying the acidic groups of the resulting thio-ether compounds with a suitable esterifying agent (e. g., with methyl or ethyl alcohol).

We have found, also, that the aforesaid free acids may be treated with P_4S_7 as above described and salts, e. g., calcium salts, produced from the resulting acidic thio-ethers (or, that salts, e. g., calcium salts, of the free acids may be produced and the salts treated with P_4S_7), whereby to produce anti-corrosive lubricity-increasing additives for lubricating oils and anti-corrosive ingredients of greases. Thus, calcium soaps of the P_4S_7-treated free acids are valuable additives for lubricating oils used in high-speed Diesel engines: their presence in such oils inhibits the sticking of the piston rings and the development of "varnish" on cylinder and piston walls, and retards or limits formation of sludge in the oils.

The production of calcium salts of the carboxylic acid thio-ethers above described is illustrated below:

EXAMPLE VII

The starting material was a product obtained by the oxidation of crude scale wax by the Burwell process. The total reaction product from the oxidation was utilized and consists of a mixture of carboxylic acids, alcohols, alcohol-ketones, lactones, esters and the like.

100 parts by weight of the starting material just described was intimately mixed with 10 parts by weight of phosphorus heptasulphide. The mixture was heated to a temperature of 300° F. and maintained at that temperature with constant mechanical agitation for a period of 2 hours. At the end of this time all visual evidence of reaction had ceased. The reaction product was then strained through a very fine mesh screen to remove solid aggregates, and the strained material was washed with successive amounts of hot water until the wash water was neutral to a sensitive indicator paper. The product was then dried.

The saponification value of the starting material was 107 mg. per gr. KOH and the saponification value of the dried reaction product was 92 mg. per gr. KOH.

100 parts by weight of this reaction product was then mixed with 412 parts of petroleum lubricating oil. To this was added 8 parts by weight of calcium hydroxide which had previously been dispersed in 15 parts of water. The mixture was heated to about 205° F. and maintained at that temperature for about 3 hours, with constant stirring. At the end of this period the temperature was gradually increased until a temperature of about 270° F. was attained; at this point all the water had been expelled. The mass was then cooled. When a small portion of this final product was thoroughly mixed with previously neutralized ethyl alcohol a very definite alkaline reaction was observed. Analysis of the product showed an equivalent of 1.79% $CaSO_4$ in the mass.

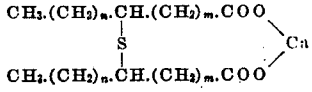
The resulting calcium soap concentrate, which was roughly equivalent to a 20% concentrate of the calcium soap of the sulphidized reaction product, was readily soluble in several types of hydrocarbon lubricating oils in amounts equivalent to 10% of the starting oxygenated-hydrocarbon material.

A lubricating oil composition particularly desirable for use as a Diesel engine lubricant consists essentially of a solution of the aforesaid calcium soap concentrate in a petroleum hydrocarbon lubricating oil (e. g., a high viscosity index petroleum hydrocarbon lubricating oil), the calcium soap content of which composition amounts to from about 0.5 to about 3.0% by weight.

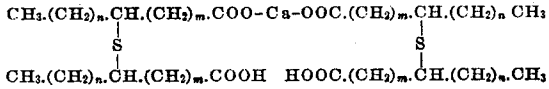
The mineral lubricating fraction employed in preparing such a composition may vary from a

low viscosity naphthalene-base oil to an extremely viscous paraffinic base oil which has been subjected to drastic selective solvent refining treatment. In a plurality of cases involving use of oils within this range, it has been demonstrated that the addition of a calcium salt of the type above described effected substantial decreases in sludge formation and corrosion of bearing alloys.

It is to be noted, relative to the above example descriptive of a normal calcium soap of the di-carboxylic salt of an aliphatic thio-ether, which calcium soap is believed to have the formula



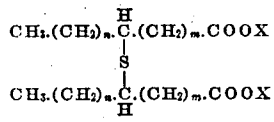
that it is equally possible, by suitable alteration in the relative amount of calcium hydroxide employed in the reaction, for two molecules of the di-carboxylic acid compound so to react as to form an acid salt of the type.



It is to be observed from the foregoing that the reaction with P_4S_7 may be carried out either (*a*) with the total oxidation mass which includes acids, alcohols, alcohol-ketones, ketones, ester and lactones or (*b*) with any desired fraction of the total oxidation mass which may, by suitable known manipulation, be separated therefrom.

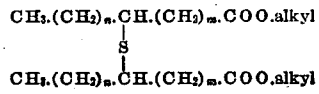
We claim:

1. A lubricating composition consisting essentially of a lubricating oil and an oil-soluble compound having the formula



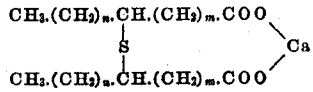
wherein *n* and *m* are whole numbers whose sum is not less than 12 and not greater than 48, and X stands for a substituent of the group consisting of hydrogen, an alkyl radical and a metallic salt-forming group.

2. A lubricating composition consisting essentially of a lubricating oil and an oil-soluble compound of the formula



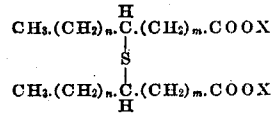
where *m* and *n* are whole numbers whose sum is not less than 12 and not greater than 48.

3. A lubricating composition consisting essentially of a lubricating oil and an oil soluble compound of the formula

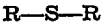


wherein *n* and *m* are whole numbers whose sum is not less than 12 and not greater than 48.

4. A lubricating composition consisting essentially of a lubricating oil and an oil-soluble mixture of a plurality of different thio-alkyl compounds produced by reacting with phosphorus hepta sulphide, a mixture of oxygenated saturated aliphatic hydrocarbons, including alcohols, ketones, and carboxylic acid compounds, derived from a petroleum hydrocarbon mixture by controlled partial oxidation thereof, said thio-alkyl compounds including compounds of the formulae



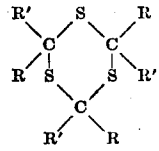
wherein *n* and *m* are whole numbers whose sum is not less than 12 and not greater than 48, and X stands for a substituent of the group consisting of hydrogen, an alkyl radical and a metallic salt-forming group,



wherein R is an alkyl radical containing from 6 to 24 carbon atoms,



wherein R and R′ are alkyl radicals each containing from 6 to 24 carbon atoms, and



wherein R and R′ are alkyl radicals each containing from 6 to 24 carbon atoms.

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