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COMPOUNDED LUBRICATED OIL

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1 Claim. (Cl. 252—33.6)

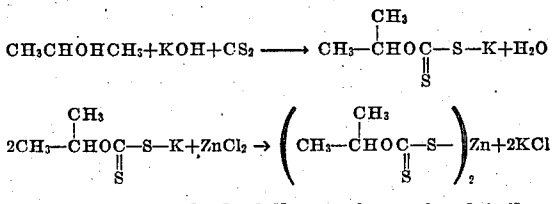
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This invention relates to a lubricating oil composition suitable particularly for use as a crankcase lubricant for internal combustion engines, improved as to stability and other properties by the addition of a novel improving agent.

The new addition agent for mineral lubricating oils used in accordance with the present invention is zinc isopropyl xanthate. This compound has been found to possess the property of inhibiting the oxidation and consequent development of corrosive properties in mineral lubricating oils to a very remarkable degree. The compound also promotes general engine cleanliness when oils containing it are used as crankcase lubricants for internal combustion engines, and it likewise reduces piston skirt varnish formation to a marked degree. This agent is likewise free from the corroding tendencies which have been observed when such well-known addition agents as metal derivatives of fatty acids, naphthenic acids, sulfonic acids, alcohols, phenols and the like have been used.

Generally the additive of the present invention is most advantageously blended with lubricating oil base stocks in concentrations between the approximate limits of 0.02% and 1% and preferably from 0.1% to 0.5%, although larger amounts may be used for some purposes. The exact amount of addition agent required for maximum improvement depends to a certain extent on the nature of the lubricating oil base stock and the general operating conditions of the engine in which the lubricating oil is to be employed.

The novel addition agent, zinc isopropyl xanthate, may conveniently be prepared by treating isopropyl alcohol with potassium or sodium hydroxide and carbon disulfide and reacting the resultant potassium salt with a soluble zinc salt in accordance with the following equations:



Example 1, which follows, shows in detail a method of preparing zinc isopropyl xanthate.

EXAMPLE 1

In a 3-liter 3-necked flask equipped with an air driven stirrer, reflux condenser, and dropping funnel, were intimately mixed 1200 cc. of 99%

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propanol-2 and 112 g. (2 mols) of KOH. To this stirred solution 152 g. (2 mols) of CS_2 was added over a period of one hour. The reaction was exothermic and frequent cooling with water was required to prevent the temperature from rising substantially above 20° C. After stirring for one hour the reaction mixture was filtered and the resulting yellow solid was placed in crystallizing dishes for drying on the steam bath. After 2 hours of such drying the product was placed in the vacuum oven overnight. 260 g. of a light yellow product consisting of potassium isopropyl xanthate was obtained (75% yield).

68.2 g. (0.5 mol) of $ZnCl_2$ was dissolved in 600 cc. of water acidified with 2 drops of hydrochloric acid. This solution was added, with stirring, to a solution of 174 g. (1 mol) of the potassium isopropyl xanthate prepared as described above in 2.5 l. of water. The resultant precipitate was filtered, washed with distilled water and then with methyl alcohol. It was then placed in a large evaporating dish to dry. 165 g. (98% yield) of a white, odorless, fine powder was obtained, consisting of zinc isopropyl xanthate.

In the following example are described tests of the corrosion inhibiting effect of zinc isopropyl xanthate as compared with other compounds which have been previously proposed as corrosion inhibitors for mineral lubricating oils.

EXAMPLE 2

Blends of various additives were made in a well refined solvent extracted paraffinic type mineral lubricating oil of S. A. E. 20 viscosity grade in 0.25% concentration by weight and submitted to a standard bearing corrosion test conducted as follows:

500 cc. of the oil was placed in a glass oxidation tube (13" long and 2⅝" diameter) fitted at the bottom with a ¼" bore air inlet tube perforated to facilitate air distribution. The oxidation tube was then immersed in a heating bath so that the oil temperature was maintained at 325° F. during the test. Two quarter sections of automotive bearings of copper-lead alloy of known weight having a total area of 25 sq. cm. were attached to opposite sides of a stainless steel rod which was then immersed in the test oil and rotated at 600 R. P. M., thus providing sufficient agitation of the sample during the test. Air was then blown through the oil at the rate of 2 cu. ft. per hour. At the end of each four-hour period the bearings were removed and were washed with naphtha and weighed to determine the amount of loss by corrosion. The bearings

were then repolished (to increase the severity of the test), reweighed, and then subjected to the test for an additional four-hour period. The cumulative weight losses of the two quarter sections of bearings used in a given test at the end of the various four-hour periods are given in Table I.

It will be seen from the test results that zinc ispropyl xanthate is much more effective as a corrosion inhibitor than are other xanthate salts and that it is also more effective than several other known types of sulfur-containing additives for lubricating oils.

Although in most instances the additive of the present invention will of itself impart sufficient improvement to lubricating oils to give very satisfactory results, still greater improvement may often be obtained by employing this addition agent in conjunction with additives of the detergent type such as metal soaps, metal phenates, metal alcoholates, metal phenol sulfides, metal organic-phosphates, thiophosphates, phosphites and thiophosphites, metal thiocarbamates, sulfur-treated metal phenates, reaction products of metal phenol sulfides and sulfides of phosphorus, and the like.

TABLE I

[Cumulative Bearing Weight Loss (mg./25 sq. cm. surface)]

Oil Blend	4 Hrs.	8 Hrs.	12 Hrs.	16 Hrs.	20 Hrs.	24 Hrs.	28 Hrs.	32 Hrs.	36 Hrs.	40 Hrs.	44 Hrs.	48 Hrs.
Base Oil	0	14	197									
Base Oil+0.25% tertiary amyl phenol sulfide	3	17	63	115								
Base Oil+0.25% barium salt of tert.-octyl phenol sulfide	5	30	36	110								
Base Oil+0.25% reaction product of phenol with sulfurized diisobutylene	0	0	0	1	53	269						
Base Oil+0.25% nickel ethyl xanthate	0	14	215									
Base Oil+0.25% nickel terposol xanthate [1]	0	12	210									
Base Oil+0.25% zinc isopropyl xanthate	0	0	0	0	0	2	2	2	2	2	2	

Oil Blend	53 Hrs.	57 Hrs.	61 Hrs.	65 Hrs.	69 Hrs.	73 Hrs.	78 Hrs.	82 Hrs.	86 Hrs.	90 Hrs.	94 Hrs.	98 Hrs.
Base Oil												
Base Oil+0.25% tertiary amyl phenol sulfide												
Base Oil+0.25% barium salt of tert.-octyl phenol sulfide												
Base Oil+0.25% reaction product of phenol with sulfurized diisobutylene												
Base Oil+0.25% nickel ethyl xanthate												
Base Oil+0.25% nickel terposol xanthate [1]												
Base Oil+0.25% zinc isopropyl xanthate	2	2	3	4	5	7	10	13	15	25	47	339

[1] Terposol=reaction product of alpha-terpineol+ethylene oxide.

In the following example are given data of comparative engine tests of the performance of a lubricating oil with and without addition of zinc isopropyl xanthate.

EXAMPLE 3

In the following engine performance tests, samples of an unblended oil, consisting of an extracted Coastal naphthenic oil of 60 seconds Saybolt viscosity at 210° F. and of a blend containing this oil with the addition of 0.25% of zinc isopropyl xanthate were tested in a Chevrolet engine run for 36 hours under the following conditions: 30 brake horsepower, 3150 R. P. M., 245° F. oil temperature, and 200° F. water jacket temperature. At the end of each test the individual parts of the engine were inspected and given demerit ratings based on their condition. An overall demerit rating was then calculated, the individual demerit ratings being weighted according to their relative importance. It should be noted that the lower the demerit rating, the better the engine test, and hence the better the oil performed in the engine. The results of these engine tests are shown in the following table:

Engine demerits

Oil	Overall	Piston Skirt	Cu-Pb Bearing Wt. Loss Grams per Bearing
Base Oil	1.09	3.38	1.26
Base Oil+0.25% zinc isopropyl xanthate	0.50	0.48	0.68

Thus, for example, the addition agent of my invention may be used in mineral lubricating oils in conjunction with one or more of the following representative materials:

Barium tert.-octyl phenol sulfide
Cobalt tert.-amyl phenol sulfide
Tin salt of wax alkylated phenol sulfide
Magnesium cetyl phenate
Nickel oleate
Barium salt of bis(2,4-diamyl phenol)-4-amyl-phenol dithioether
Zinc salt of salicylic acid sulfide octyl ester
Barium 2-stearoyl-4-amyl phenol sulfide
Aluminum-calcium mixed soap of fatty acid from oxidation of petroleum fractions
Barium octadecylate
Calcium dichlorostearate
Calcium phenyl-stearate
Nickel dibutyl dithiocarbamate
Barium dioctyl dithiophosphate
Calcium cetyl phenyl thiophosphate
Zinc methyl cyclohexyl dithiophosphate
Calcium dihexadecyl monothiophosphite
Calcium cetyl phosphate
Zinc diisopropyl salicylate
Aluminum naphthenate
Barium di-tert.-amyl phenol sulfide
Calcium phenate-barium carboxylate of octadecyl salicylic acid
Tin naphthenate
Reaction product of barium tert.-octyl phenol sulfide and phosphorus pentasulfide

The lubricating oil base stocks used in the compositions of this invention may be straight min-

eral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichloroethyl ether, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracking coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed, either alone or in admixture with mineral oils.

For the best results the base stock chosen should normally be that oil which without the new additive present gives the optimum performance in the service contemplated. However, since one advantage of the additive is that its use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. The lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubrication of certain low and medium speed Diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of Diesel service, particularly with high speed Diesel engines, and in gasoline engines, including aviation engine service, oils of higher viscosity index are often preferred, for example, up to 75 to 100, or even higher, viscosity index.

In addition to the material to be added according to the present invention, other agents may also be used, such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organometallic compounds, metallic or other soaps, sludge dispersers, anti-oxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Specific examples of such other agents include dibenzyl disulfide, 2,6-tert.-butyl-4-methyl phenol, sulfurized sperm oil, diamyl trisulfide, voltolized sperm oil, polyisobutylene, polymerized lauryl methacrylate, sulfurized wax olefins, and the product of treating a sulfur monochloride-

diisobutylene reaction product with phenol. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like, may also be employed.

Additives which are particularly desirable as plasticizers and defoaming agents are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight and branched chain aliphatic alcohols such as octyl alcohol ($C_8H_{17}OH$), lauryl alcohol ($C_{12}H_{25}OH$), cetyl alcohol

($C_{16}H_{33}OH$)

heptadecyl alcohol ($C_{17}H_{35}OH$), stearyl alcohol, sometimes referred to as octadecyl alcohol,

($C_{18}H_{37}OH$)

and the like; the corresponding olefinic alcohols such as oleyl alcohol; cyclic alcohols, such as naphthenic alcohols; and aryl substituted alkyl alcohols, for instance, phenyl octyl alcohol, or octadecyl benzyl alcohol or mixtures of these various alcohols, which may be pure or substantially pure synthetic alcohols. One may also use mixed naturally occurring alcohols such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil (which contains a high percentage of cetyl alcohol); and although it is preferable to isolate the alcohols from those materials, for some purposes, the wool fat, sperm oil or other natural products rich in alcohols may be used per se. Products prepared synthetically by chemical processes may also be used such as alcohols prepared by the oxidation of petroleum hydrocarbons, e. g., paraffin wax, petrolatum, etc. These assisting agents serve to enhance the detergent and sludge dispersive qualities and aid the solubility of the metal-containing additives and at the same time impart oiliness properties to the lubricating oil compositions.

In addition to being employed in crankcase lubricants the additive of the present invention may also be used in extreme pressure lubricants, engine flushing oils, industrial oils, process oils, general machinery oils, greases and rust preventive compositions. Also its use in motor fuels containing tetraethyl lead or other anti-knock agents is contemplated.

The present invention is not to be considered as limited by any of the examples described herein which are given by way of illustration only, but it is to be limited solely by the terms of the appended claim.

I claim:

A mineral lubricating oil containing dissolved therein an oxidation-inhibiting amount of zinc isopropyl xanthate.

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