United States Patent Office 2,989,464 Patented June 20, 1961

2,989,464
STABILIZED SUSPENSIONS OF CALCIUM ACETATE IN OIL

Jerome Panzer, Roselle Park, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

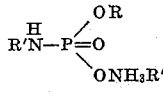
No Drawing. Filed Dec. 23, 1959, Ser. No. 861,452
7 Claims. (Cl. 252—32.5)

The present invention relates to a motor lubricant improvement in which a suspension of calcium acetate in oil is successfully stabilized, particularly in the presence of small amounts of water. The stabilization of such lubricant is effected by the incorporation therein of minor amounts of a mixture of an alkylol amide and an alkyl ammonium phosphate.

It had earlier been found that suspensions of dehydrated or anhydrous calcium acetate in oil were very effective in reducing piston ring wear in automotive engines. Lubricants containing dehydrated calcium acetate, stabilized by soap or prior surfactants, reduced wear in Caterpillar 1A engine tests much more than conventional heavy duty lubricating oil compositions. However, these calcium acetate suspensions were unsuitable for use in automotive engines because the condensation of water into the lubricant suspension caused gelling with subsequent failure of the engine. This gelling phenomenon is due to the adsorption of water by the hydrophilic anhydrous calcium acetate causing the oil to thicken to an undesirable extent. In addition to being too viscous, the water-containing gel does not have the excellent antiwear properties of the dehydrated lubricant, although it does provide some wear protection.

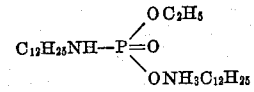
The present invention describes a lubricant which comprises a stable suspension of calcium acetate in a mineral oil, preferably a naphthenic mineral oil and which is unaffected by small amounts of water. Because of its excellent antiwear properties this product is an excellent internal combustion engine lubricant and reduces both piston ring and valve train wear. The insensitivity to water is imparted by 0.1 to 10.0 wt. percent of an additive mixture consisting of 20 to 80 wt. percent of an alkyl ammonium phosphate and 80 to 20 wt. percent of an alkylol amide, preferably 40 to 60 wt. percent of the alkylol amide and 60 to 40 wt. percent of the alkyl ammonium phosphate, neither of which is effective alone. Because the lubricant is dehydrated, its antiwear properties are excellent. The insensitivity to water allows the antiwear properties to be maintained when water enters the lubricant and, in addition, retards thickening of the lubricant. These circumstances permit the excellent boundary lubrication properties of calcium acetate to be used under a wide variety of conditions.

The alkyl ammonium phosphates which may be used have the general formula:



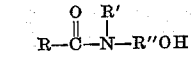
wherein R is an alkyl or substituted alkyl radical of 1 to 4 carbon atoms and R′ is an alkyl or substituted alkyl radical of 8 to 20 carbon atoms. Examples of such compounds include the stearyl amine salt of the stearyl amide of ethyl orthophosphoric acid, the lauryl amine salt of the lauryl amide of n-propyl orthophosphoric acid, the lauryl amine salt of the stearyl amide of ethyl orthophosphoric acid, etc. Surface active agents of the above type have been described in U.S. Patent 2,406,423. The preferred alkyl ammonium phosphate of this invention is

sold under the commercial trade name of Victamine C and has the formula:



wherein the alkyl groups are derived from coconut oil acids.

The alkylol amides of the invention are selected from the group consisting of mono and dialkylolamides of C_9 to C_{21} fatty acids. These materials have the general formula:



wherein R is a C_8 to C_{20} alkyl group of a saturated fatty acid, R′ is hydrogen or —R″OH, and R″ is a C_2 to C_9, e.g. C_2 to C_3, aliphatic saturated hydrocarbon radical. The hydroxyl group will generally be attached to the terminal carbon atom, although it may be attached to other carbon atoms of the R″ hydrocarbon group. Specific examples of such materials include N, N-di(2-hydroxy ethyl) lauramide; N-2-hydroxy ethyl lauramide; N-6-hydroxy hexyl stearamide and N, N-di(3-hydroxy propyl) lauramide. A commercial material consisting of about 65 wt. percent of N, N-di(2-hydroxy ethyl) lauramide as the active ingredient and available under the trade name Nopcogen 12–L, is the preferred alkylol amide of this invention, although Stepan P–616 or similar products may be used.

Various other conventional additives may also be added to the compositions of the invention. Examples of such additives include: detergents, viscosity index improvers, corrosion inhibitors, pour depressants, dyes, and the like.

The invention may be further illustrated by the following examples and the accompanying table.

COMPOSITION A

A calcium acetate lubricating oil composition was made up by combining by weight 15% of glacial acetic acid, 10% of hydrated lime, 2.5% of a lauryl diethanol amide sold commercially as Nopcogen 12–L, 2.5% of an alkyl ammonium phosphate in which the alkyl groups are derived from coconut oil acids, sold commercially as Victamine C, 2.5% of phenyl alpha-naphthylamine and 67.5% of a hydrofined naphthenic coastal oil of 55 SUS viscosity at 210° F. This mixture was heated at 320° F. until completely dehydrated, cooled and then diluted with 400 wt. percent of the said oil based on the weight of the dehydrated mixture. Then, as a final step, the composition was homogenized in a Morehouse mill.

The finished lubricating composition was then subjected to several tests. The first such test was a 23-hour low temperature Lauson test (oil temperature below 100° F.). This Lauson test consists of operating a single cylinder Lauson engine having a 6.5:1 compression ratio head with an induction motor at 1840 r.p.m. and operating at 0.5 BKW (brake kilowatt) load. This test showed that the lubricating composition gave good performance and no viscosity increase. Several samples were then run in the 4-Ball Wear Test: 1800 r.p.m., 1 hr., 10 kg., 75° C., and gave a wear scar varying from 0.25 to 0.30 mm. which is comparable to wear scars obtained from commercial calcium acetate containing lubricants.

COMPOSITIONS B AND C

Two lubricating compositions were prepared similarly to that of Composition A except that one contained only Nopcogen 12–L and the other contained only Victamine C.

COMPOSITION D

A third composition was prepared similarly to that of Composition A but containing no surfactant at all.

COMPOSITIONS E TO G

Compositions E to G were prepared by mixing 1 wt. percent water with 99 wt. percent of each of the compositions A to C described above.

All of the above compositions were tested for viscosity. In addition, they were also tested for stability by centrifuging at 1500 r.p.m. for 4 hours. This was accomplished by placing the lubricant blend in a marked graduated centrifuge test tube. The degree of separation of suspension from the oil after centrifuging could be measured by the graduations. The result is expressed in terms of percent of the original suspension occupied by the settled suspension, thus giving an indication of the stability of the suspension in the presence of different surfactants. The greater the volume percent remaining after centrifugation, the more stable the suspension.

Table I

[EFFECT OF WATER ON CALCIUM ACETATE SUSPENSION IN OIL]

Composition	Acetate, Percent	Viscosity [1]	Suspension Stability [2]
A. Dehydrated; 0.5% Nopcogen 12-L+0.5% Victamine C [3]	5	2,840	98.0
B. Dehydrated; 1% Nopcogen 12-L	5	9,000	84.0
C. Dehydrated; 1% Victamine C	5	7,640	98.0
D. Dehydrated; no surfactant	5	840	24.0
E. Composition A+1% H_2O	5	1,800	96.0
F. Composition B+1% H_2O	5	[4]	98.0
G. Composition C+1% H_2O	5	[4]	98.0

[1] Viscosity in centistokes at room temperature measured by Brookfield viscosimeter with a number 3 spindle at 6 r.p.m.
[2] Volume percent of suspension after centrifuging at 1,500 r.p.m. for 4 hours; the greater the number the more stable the suspension.
[3] Lauson test gives good performance and no viscosity increase.
[4] Semi-solid grease.

When 1 wt. percent of Nopcogen 12–L is included in a dehydrated calcium acetate lubricant, the suspension stability is fairly good at 84. When 1 wt. percent of the Victamine C is contained within the dehydrated lubricant an excellent suspension stability results of 98.0. When 0.5 wt. percent of the Nopcogen 12–L and 0.5 wt. percent of the Victamine C are in the lubricant together, then an excellent suspension stability of 98.0 ensues. When 1% water is added to a dehydrated lubricant containing the 1% Nopcogen 12–L alone or the dehydrated lubricant containing 1% Victamine C alone, the increase in viscosity becomes so marked as to result in a semi-solid or grease although the suspension stability remains very high at 98.0. When 1% water is added to the dehydrated lubricant containing equal amounts of the two additives of the invention, an excellent viscosity reading of 1800 results and a good value of 96.0 is obtained for the suspension stability. No semi-solid or grease is formed even after extensive aging.

It may be readily ascertained from the aforegoing table that when no surfactant is present in the lubricating composition, the suspension stability is poor. When either of the surfactants of the invention are present singly in the blend the suspension stability is good, but when water is added an undesirable semi-solid grease forms. It is only when both surfactants are present in the blend that both suspension stability and resistance to grease formation upon water contamination is obtained.

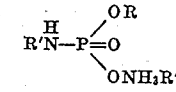
In summary then, it may be said that this invention comprises a method of obtaining a stable suspension of calcium acetate in oil, which is also resistant to grease formation upon water contamination. To achieve this result it is necessary to use an alkylol amide as one additive and an alkyl ammonium phosphate as the other, preferably together in approximately equal weight amounts.

What is claimed is:

1. A lubricating composition comprising a major proportion of mineral lubricating oil, 1 to 20 wt. percent of calcium acetate and 0.1 to 10.0 wt. percent of an additive mixture consisting of 20 to 80 wt. percent of an alkylol amide of the formula:



wherein R is a C_8 to C_{20} alkyl group of a saturated fatty acid, R′ is selected from the group consisting of hydrogen and —R″OH, and wherein R″ is a C_2 to C_9 aliphatic saturated hydrocarbon radical; and 80 to 20 wt. percent of an alkyl ammonium phosphate of the formula:



wherein R is selected from the group consisting of an alkyl radical of 1 to 4 carbon atoms and substituted alkyl radical of 1 to 4 carbon atoms and R′ is selected from the group consisting of alkyl radicals of 8 to 20 carbon atoms and substituted alkyl radicals of 8 to 20 carbon atoms.

2. A lubricating composition according to claim 1 wherein said alkylol amide is N,N-di(2-hydroxy ethyl) lauramide.

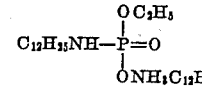
3. A lubricating composition according to claim 1 wherein the alkyl group of the said alkyl ammonium phosphate is derived from coconut oil acids.

4. A lubricating composition according to claim 1 wherein said alkylol amide is lauryl diethanolamide and the alkyl group of said alkyl ammonium phosphate is derived from coconut oil acids.

5. A lubricating composition according to claim 1 wherein said lubricating oil is a naphthenic oil.

6. A method of preparing the lubricating composition of claim 1 which comprises neutralizing with lime, in situ in at least a portion of said oil, an acid material selected from the group consisting of acetic acid and acetic anhydride, said neutralization being carried out in the presence of said alkylol amine and said alkyl ammonium phosphate, and heating said mixture to a temperature sufficient to dehydrate said mixture.

7. A process for preparing a fluid lubricating composition comprising a major proportion of a naphthenic oil, 1 to 20 wt. percent of calcium acetate, and 0.1 to 10 wt. percent of an additive mixture consisting of 20 to 80 wt. percent of lauryl diethanolamide, and 80 to 20 wt. percent of alkyl ammonium phosphate having the formula



which comprises mixing said oil, calcium acetate, and additive mixture and heating the mixture at 280 to 370° F. until completely dehydrated.

No references cited.