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LUBRICATING OIL COMPOSITIONS CONTAINING STABILIZED SALT SUSPENSION

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11 Claims. (Cl. 252—40.5)

This invention relates to lubricating oil compositions containing calcium acetate. Particularly, it relates to lubricating fluids and greases comprising lubricating oil, calcium acetate, and a surface active agent for maintaining the calcium acetate in a stable suspension.

Calcium acetate has been recently recognized as an extremely effective lubricating oil additive for reducing wear and imparting extreme pressure characteristics to the lubricant. However, simple dispersions of calcium acetate in oil are unstable as the salt settles out of the composition upon storage. In the past, in order to form stable compositions, calcium acetate has been maintained suspended in oil by means of simple metal soap, or by complexing the calcium acetate with higher molecular weight fatty acid salts or soaps, or by forming oil-water emulsions. However, for some applications, these prior methods are not wholly satisfactory. Thus, the presence of higher molecular weight salts or soaps result in high deposit formation when the lubricant is used as a crankcase lubricant; while the emulsion type materials are rather corrosive because of their water content and are also somewhat unstable tending to separate upon storage. It has also been proposed to dehydrate the emulsion type of material, but while this reduces the danger of corrosion, it still results in an unstable product and unless the dehydration is carefully controlled, a grainy unsatisfactory dispersion is obtained.

It has now been found that calcium acetate can be stably dispersed in lubricating oil in the presence of a surface active agent, preferably a non-ionic or a cationic surface active agent containing polyalkyleneoxy groups. Surface active agents of these types, which do not contain metal, have decreased tendencies to form harmful deposits when used in internal combustion engines. In this manner, excellent and stable fluid lubricating dispersions suitable for crankcase use, can be formed. By increasing the amount of calcium acetate dispersed in the oil, lubricating greases may be formed which are particularly useful for lubrication of antifriction bearings operating at elevated temperatures.

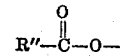
The compositions of the invention will therefore comprise lubricating oil, about 0.5 to 50, e.g., 1.0 to 30 weight percent of calcium acetate, and about 0.05 to 10, e.g., 0.2 to 5 weight percent of surface active agent. All of said weight percents being based on the final weight of the total composition. Generally, about 0.05 to 1.0 part by weight of surface active agent per part by weight of calcium acetate will be used.

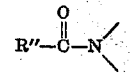
The lubricating oil portion of the composition may be either a mineral lubricating oil, a synthetic lubricating oil, or both. Operable synthetic oils include esters of dibasic acids (e.g., di-2-ethyl hexyl sebacate), esters of glycols (e.g., C_{13} oxo acid diester of tetraethylene glycol), complex esters (e.g., the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid), halocarbon oils, alkyl silicates, sulfite esters, mercaptals, formals, polyglycol type synthetic oils, etc., or mixtures of any of the above in any proportions. Although, the dispersed calcium acetate is more stable in synthetic ester oil than in mineral oil, even in ester oil the presence of the surface active agent further improves the stability of the calcium acetate dispersion and prolongs its storage stability.

The stabilizing agents which may be used include nonionic and cationic surface active agents of the general formula:

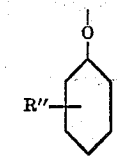
$$R—[(R'O)_x—H]_y$$

wherein R' is an aliphatic hydrocarbon radical having 2 to 4 carbon atoms, x is an integer of 5 to 200, e.g. 5 to 75, and y, which is either 1 or 2 is the valence of R; and R is a radical selected from the group consisting of: HO—, R''O—, R''—N<



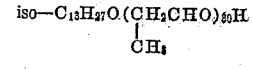


and



wherein said R'' is a straight or branched chain alkyl group containing 2 to 30, e.g. 4 to 20 carbon atoms and may be derived from a fatty acid.

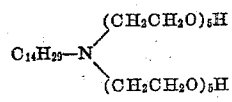
Where R represents R''O, the formula represents alkyl ethers of polyoxyalkylene glycols. Specific examples include n—$C_{13}H_{27}O$—$(CH_2CH_2O)_6H$

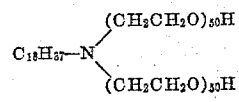


and $C_4H_9O(CH_2CH_2O)_{50}H$.

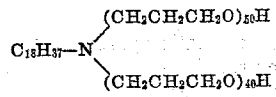
When R of the above formula is a hydroxyl group, specific examples of such materials will include polyoxyalkylene glycols such as polyethylene glycols and polypropylene glycols. A preferred type of these ether materials are the copolymers of ethylene and propylene glycols which are commercially available under the trade-name of "Pluronics." These materials have the following formula: $HO(C_2H_4O)_a(C_3H_6O)_b(C_2H_4O)_c$—H, where a and c are integers of value 2 to 150, and b is an integer of 5 to 170. The molecular weight may vary considerably but generally is between 1,000 and 20,000, e.g. 1,000 to 10,000. Thus, Pluronic L–44, Pluronic L–62, and Pluronic F–68 appear to have molecular weights of about 2800, 2300 and 8700 respectively. The ratio of the ethylene oxide groups to the propylene oxide groups in the Pluronic materials vary between about 3/1 to 1/3, e.g., in Pluronics L–62, analysis showed a ratio of about 1.15 moles of ethylene oxide per mole of propylene oxide. However, the ratio of these two alkylene oxide groups is not critical for the present invention since operable materials will include ethylene or propylene polyglycols per se.

Where R represents an R''—N< radical, the formula represents N, N polyalkyleneoxy disubstituted alkyl amines. Specific examples of such materials will include:

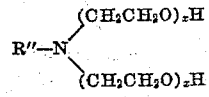




and

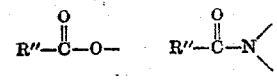


A material of this general type, commercially available under the trade-name Ethomeen T/25, was used in several of the working examples of the invention. This material has the formula:

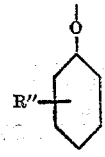


and is a tallow amine wherein the total number of ethylene oxide groups is 15.

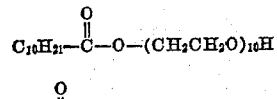
When R represents

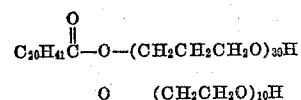


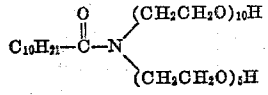
or



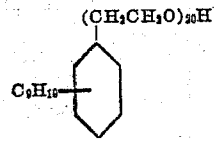
specific compounds will include







and



Surface active agents of the above general types are well known and are available under trade-names such as Ethomeens, Ethomids, Ethofats, Pluronics, etc.

Various other additive materials may also be included in the compositions of the invention in amounts of about 0.1 to 10.0 wt. percent, based on the total weight of the composition. Examples of such additives include oxidation inhibitors such as phenyl-alpha-naphthylamine, tackiness improvers such as polyisobutylene, corrosion inhibitors such as sorbitan monooleate, dyes, V.I. improvers, thickeners and the like.

The lubricants of the present invention may be prepared by simple blending of the surface active agent and preformed calcium acetate into a lubricating oil. In this case, a small amount of water is desirable in order to more thoroughly disperse the salt, the material then being dehydrated to remove the water. However, a more preferable way is by forming the calcium acetate in situ in the lubricating oil by neutralizing lime or calcium oxide with acetic acid or acetic acid anhydride. When the lubricant is to be used at high temperatures, it is preferably heated in order to achieve complete dehydration and to form the anhydrous calcium acetate. The formation of the calcium acetate in situ is preferably carried out in the presence of the stabilizing material or surface active agent, although the stabilizer can be added later. The lubricant may be homogenized in a Morehouse mill, a Gaulin homogenizer, etc. If a fluid lubricant is desired, it is generally more convenient to first form a concentrate and then to dilute it with additional oil to form the final product.

The invention will be further understood by the following examples:

EXAMPLE I

17.0 parts by weight of hydrated lime, 2.0 parts by weight of Pluronics L–62 (copolymer of ethylene and propylene glycol having a mol weight of about 2300 and a molar ratio of ethylene oxide groups to propylene oxide groups of about 1.15), and 55.0 parts by weight of a mineral lubricating oil (80 SUS at 210° F.) were charged to a steam heated grease kettle and thoroughly mixed to a smooth, uniform slurry. 25 parts by weight of glacial acetic acid were then added slowly, the heat of reaction raising the temperature of the mixture to about 220° F. After all the acetic acid was added, the material was then further stirred for 15 minutes, after which external heating was applied until the temperature rose to 320° F. to completely dehydrate the mixture and form anhydrous calcium acetate. The heat was then turned off and the product was allowed to cool to 200° F. while stirring. One port by weight of phenyl-alpha-naphthylamine was then added, after which the product was passed through a Gaulin homogenizer operating at 6000 p.s.i. shear.

EXAMPLE II

50 weight percent of the product of Example I was mixed with 50 weight percent of additional mineral oil, after which the blend was passed through a Gaulin homogenizer operating at 6000 p.s.i. shear.

EXAMPLE III

20 weight percent of the product of Example I was blended with 80 weight percent of additional mineral oil in the manner of Example II.

EXAMPLES I–A, II–A AND III–A

Examples I–A, II–A and III–A were carried out in a manner similar to that of Examples I, II and III respectively, except that 2 wt. percent of Ethomeen T/25 was used in place of Pluronics 62.

The physical properties and compositions (in terms of basic ingredients) of the products of the above examples are listed in the following table:

Table I.—Composition and properties of examples

	Example					
	I	I-A	II	II-A	III	III-A
Composition:						
Acetic Acid (Glacial)....percent..	25.0	25.0	12.5	12.5	5.00	5.0
Hydrated Lime.....do....	17.0	17.0	8.5	8.5	3.40	3.4
Pluronics L-62 [1].....do....	2.0	"	1.0	"	0.40	"
Ethomeen T/25 [2].....do....	"	2.0	"	1.0	"	0.4
Phenyl-alpha-naphthylamine do....	1.0	1.0	0.5	0.5	0.20	0.2
Mineral Oil (80 SUS at 210° F.) do....	55.0	55.0	77.5	77.5	91.00	91.0
Properties:						
Appearance.....	Excellent homogeneous smooth grease		Excellent homogeneous smooth grease		Fluid uniform smooth fluid [4]	
Dropping Point, ° F.....	500+	500+	500+	500+	"	"
Penetration 77° F. mm./10—						
Unworked.....	250	"	360	"	"	"
Worked 60 strokes.....	265	"	340	"	"	"
Worked 10,000 strokes.....	"	"	335	"	"	"
Lubrication Life in Hours [3] (250° F.—1,000 r.p.m.).....	"	"	[5] 200	"	"	"
Four-Ball Wear Test (1,800 r.p.m.—10 Kg. Load—75° C.—1 hour), Scar Spot dia. in mm....	"	"	0.25	"	0.26	"
Almen Test (Weights carried) Gradual Loading.....	"	"	15	"	13	"

[1] Copolymer of propylene and ethylene glycols.

[2] Tallow—N($(CH_2CH_2O)_xH$)($(CH_2CH_2O)_xH$) containing a total of 15 oxyethylene groups.

[3] Anti-friction Bearing Manufacturers—National Lubricating Grease Institute's test machine.
[4] 1400 SUS at 100° F. and 102 SUS at 210° F.
[5] Test still in progress.

As seen from Table I, high dropping point greases which are structurally stable and fluid lubricants can be prepared by varying the calcium acetate content. Both the grease and fluid lubricants had excellent load-carrying ability and gave low wear.

The fluid products of Example III and III-A were further tested for stability as follows: A sample bottle was filled with the lubricant and stored in an oven maintained at 210° F. for 48 hours, after which the sample was examined for salt precipitation. The products of Examples III and III-A both successfully passed the test, showing no precipitated calcium acetate. A simple dispersion of calcium acetate in oil, without the surface active agent, showed considerable salt precipitation when tested in the same manner. It is thus seen that the presence of the surface active agent stabilizes the calcium acetate dispersion.

To further illustrate the invention, Examples I, II, and III can be repeated but using in place of the Pluronics L-62, an equal weight percent of any of the following:

(a) Hexaethylene glycol

(b) $C_{18}H_{37}-C(=O)-N(-(CH_2CH_2O)_{25}H)(-(CH_2CH_2O)_{25}H)$

(c) $C_{18}H_{37}-C(=O)-O-(CH_2CH_2CH_2O)_{40}H$

(d) C_9H_{19}-(p-phenyl)-$(CH_2CH_2O)_{20}H$

In summary, the invention relates to lubricants containing calcium acetate (which includes anhydrous as well as hydrous calcium acetate) which may be the sole salt component of the composition, stabilized with a non-ionic or cationic surface active agent, which contains no metal. Either grease compositions containing about 10 to 30 wt. percent calcium acetates or fluid lubricants containing 0.5 to 10.0 wt. percent calcium acetate may be thus prepared. The use of higher molecular salts, e.g. calcium stearate or calcium petroleum sulfonate, is thereby avoided and lubricants having a lower overall metallic ash content can thus be formed.

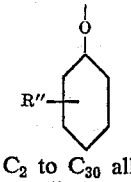
What is claimed is:

1. A lubricating composition consisting essentially of a dispersion of about 0.5 to 50 wt. percent of calcium acetate in lubricating oil, which is stabilized against calcium acetate precipitation with about 0.05 to 1.0 parts by weight per part by weight of calcium acetate of a non-metallic surface active agent selected from the group consisting of ionic and cationic surface active agents containing 5 to 200 polyalkyleneoxy groups having 2 to 4 carbon atoms per group and having at least one terminal hydroxy group in the molecule.

2. A lubricating composition according to claim 1, wherein said surface active agent has the general formula:

$$R-[(R'O)_x-H]_y$$

wherein R' is a C_2 to C_4 aliphatic hydrocarbon radical, x is 5 to 200, y is 1 to 2 and is the valence of R, and R is a radical selected from the group consisting of HO—, R''O—, R''—N<, R''COO—, R''CON< and



wherein said R'' is a C_2 to C_{30} alkyl group.

3. A composition according to claim 2, wherein said R is a HO— radical.

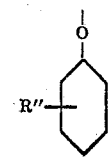
4. A composition according to claim 2, wherein said R is a R''O— radical.

5. A composition according to claim 2, wherein said R is a R''N< radical.

6. A composition according to claim 2, wherein said R is a RCOO— radical.

7. A composition according to claim 2, wherein said R is a R''CON< radical.

8. A composition according to claim 2, wherein said R is a



radical.

9. A lubricating composition consisting essentially of lubricating oil, about 4 to 30 weight percent of anhydrous calcium acetate as the sole salt component and about 0.5 to 10 wt. percent of a stabilizing material having the general formula:

$$HO(C_2H_4O)_a(C_3H_6O)_b(C_2H_4O)_c—H$$

wherein a and c are each integers of 2 to 150, b is an integer of 5 to 170 and the molecular weight is about 1,000 to 20,000.

10. A composition according to claim 9, wherein said oil is a mineral oil.

11. A method of preparing the lubricating composition of claim 1, which comprises forming said calcium acetate in situ in said lubricating oil by neutralizing calcium hydroxide with acetic acid in the presence of said surface active agent.

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