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CALCIUM ACETATE LUBRICANT

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This invention relates to calcium acetate lubricants having good antiwear properties, which are clear and filterable, and which are particularly useful for cylinder lubrication of marine diesel engines. These lubricants comprise lubricating oil, calcium acetate as the antiwear agent, and certain surfactants for maintaining the calcium acetate suitably dispersed in the oil.

In lubricating marine diesel engine cylinders, the lubricant should have good antiwear properties and be of fluid, or semi-fluid, consistency for pumping through the centralized forced-feed lubrication system and to evenly spread and wet the piston and cylinder. The lubricant should be storage stable, and heat stable so that it does not unduly gel or thicken when moving through hot feed lines or when it contacts the surface of the hot cylinder which it is to lubricate.

Lubricants for such marine diesel lubrication, which substantially met the preceding requirements, have been made by dispersing calcium acetate as an antiwear agent in mineral lubricating oil, with calcium salt of C_7 to C_{30} fatty acid as suspending agent for the oil-insoluble calcium acetate. Usually, these lubricants are made by coneutralizing with lime, the acetic and C_7 to C_{30} fatty acid in situ in the oil. Recently, having phosphosulfurized (usually P_2S_5 treated) polyisobutylene and/or polyisobutylene succinic anhydride present during the coneutralization has been found to be very effective in further improving the stability, i.e. preventing separation or gelling. However, these prior calcium acetate lubricants frequently are hazy and often contain sediment resulting from manufacture. For example, sediment can result from calcium carbonate, or incompletely reacted lime, or from contaminants in the raw materials, or agglomerated or undispersed particles of calcium acetate, etc. In general, these prior lubricants cannot be readily filtered and are somewhat unstable, i.e. the sediment tends to settle out, particularly if the level of calcium acetate is increased to a total base number (TBN) according to ASTM D–664 much above 40.

It has now been found that by having alkyl phenol and alkanolamine present during the aforesaid coneutralization, as additional suspending and stabilizing agents, haziness can be eliminated and filtering can be made easy thereby removing sediment. Also, these additional stabilizing agents allow making very highly concentrated calcium acetate dispersions of 200 to 300 TBN, i.e., containing about 40–50 wt. percent calcium acetate, which are clear, filterable and stable.

The calcium acetate lubricants of the invention will therefore comprise lubricating oil, and the coneutralized mixture of acetic acid, C_7 to C_{30} fatty acid, phosphosulfurized polyisobutylene and/or polyisobutylene succinic anhydride, alkyl phenol and alkanolamine. The amount of lime is such as to form a substantially neutral product.

The oil component of the lubricant is preferably mineral lubricating oil, alhough synthetic lubricating oils such as Ucon oils, ester oil, polycarbonate oils, polysilicone oil, etc. can be used.

The C_7 to C_{30} fatty acids can be considered as of two types, namely the intermediate molecular weight fatty acids, i.e. C_7 to C_{12} acids, and high molecular weight fatty acids, namely C_{13} to C_{30} fatty acids. Examples of C_7 to C_{12} fatty acids mentioned above include capric, caproic, lauric, etc., which acids are usually commercially available as mixtures, e.g. coconut oil acid. Examples of C_{13} to C_{30} fatty acids include tallow fatty acids, oleic, palmitoleic, gadoleic, erucic, stearic, etc.

Phosphosulfurized polyisobutylene is well known and can be prepared by reacting phosphorus pentasulfide with polyisobutylene of 600 to 4,000, preferably 700 to 1400, Staudinger molecular weight for about 0.5 to 15 hours at 150° to 600° F.

While polyisobutenyl succinic acid can be used, polyisobutenyl succinic anhydride is preferred as it is more readily obtainable since it can be simply prepared by heating together equal molar proportions of maleic anhydride and polyisobutylene of about 700 to 3,000, preferably 800 to 1300, molecular weight, as described, for example, in U.S. Patent No. 3,018,250, col. 3, lines 57 to 71, Example 1.

The alkyl phenols which can be used include phenol alkylated with one or two, C_5 to C_{20} branched or straight chain alkyl groups, such as tripropylene, tetrapropylene, isooctyl, n-nonyl, etc.

Operable alkanolamines include mono-, di- and trialkanolamines wherein the alkanol group contains 2 to 3 carbon atoms such as ethanol, n-propanol and isopropanol groups. Specific examples of these alkanolamines include diethanolamine, triethanolamine, tripropanolamine, etc.

The alkanolamine aids in eliminating haziness and improves filterability of the final lubricating oil product. However, if too much alkanolamine is added, there is an increased tendency to thicken the lubricant which would result in either a soft grease or a more viscous fluid than is desired. It is, therefore, desirable to supplement the alkanolamine with the alkyl phenol, which also reduces haze and improves filterability but does not unduly thicken the lubricant.

Various additives can be added to the finished lubricant in amounts of 0.1 to 10.0 wt. percent, based on the weight of the finished lubricant. Among additives that can be added are: corrosion inhibitors such as sodium nitrate, lanolin, wool grease stearine, antioxidants such as phenyl α-naphthylamine; dyes; etc.

Based upon 100 parts by weight of the finished fluid lubricant, the finished lubricant of the invention will generally comprise a major amount of mineral oil and a coneutralized mixture of 1.0 to 7.0, preferably 2 to 6, parts of acetic acid; 0.2 to 5.0, preferably 0.3 to 1.0, parts of higher fatty acid, either all intermediate molecular weight fatty acid, or all high molecular weight fatty acid, or a mixture of intermediate and high molecular weight fatty acids in any proportion; 0.5 to 5.0 parts of polyisobutenyl succinic anhydride and/or 0.5 to 5.0 parts of P_2S_5 treated polyisobutylene; 0.2 to 5.0, preferably 0.5 to 3.0, parts of alkyl phenol; and 0.2 to 5.0, preferably .3 to 2.0, parts of alkanolamine.

The lubricant is preferably first made as a concentrate by dispersing lime and all the above-mentioned ingredients, except the acetic acid, in about ½ to 1⁄16 of the oil, then adding the acetic acid very slowly, e.g. over a 5 hour period in large batches, so as to keep the temperature of the mass below about 210° F. and while stirring. This prevents agglomeration of the calcium acetate and results in a finer particle size for the calcium acetate. The mixture is then dehydrated at about 300° to 350° F. until about 60 wt. percent to about 80 wt. percent, preferably 65 to 75 wt. percent of the water of hydration is removed, which ranges represent the optimum water removal for fastest filtration. The mixture is preferably filtered while hot so as to keep the viscosity low, and while using diatomaceous earth filter aid. Removing more or less than the 60 to 80 wt. percent of the water of reaction gives poorer filtration results. The reasons for this are not altogether understood at present. However, ti is believed that the water present controls the aggregate sizes of the dispersed calcium acetate and the best sizes for filtration are achieved at the prescribed water levels. At lower than prescribed water levels, viscosity and filter plugging control the filtration rate. At levels greater than those given above, the concentrate gels and becomes non-filterable. The concentrate, after filtration, is cooled to about 200–250° F. where any additional additives can be added, and is then diluted with the remainder of the oil to form the final lubricant. Of course, various modifications in the preceding procedure can be made, although the specified procedure is preferred.

The invention will be further understood by reference to the following examples, which include a preferred embodiment of the invention, and wherein all parts are by weight.

Example I

A base or concentrate was prepared by mixing together 8 parts of polyisobutenyl succinic anhydride, 2.1 parts of diethanolamine, 1.7 parts of Wecoline AAC acid, 4 parts of commercial nonyl phenol, 10.65 parts of hydrated lime and 56.75 parts of mineral lubricating oil of 80 SUS viscosity at 100° F. 16 parts of glacial acetic acid were slowly added to the mixture while maintaining the temperature between 150° and 200° F. When all the acetic acid was added, the mixture was heated to 320° F. until about 75 wt. percent of the water of reaction was removed. The mass was then filtered at 300° F. through filter with cloth using diatomaceous earth filter aid (3 wt. percent) admixed with the concentrate, and cooled to about 200° F. where 0.8 part of phenyl α-naphthylamine was added as an oxidation inhibitor. One part of this concentrate, which was clear, i.e. free of haze and transparent, was then diluted with 3 parts of additional mineral lubricating oil of 80 SUS viscosity at 100° F.

The polyisobutenyl succinic anhydride used above was the reaction product of polyisobutylene having a molecular weight of about 800 and maleic anhydride.

The Wecoline AAC acid was a coconut oil fatty acid consisting of about 46 wt. percent capric acid, about 28 wt. percent caprylic acid and about 26 wt. percent lauric acid.

The nonyl phenol was a commercial material consisting of phenol alkylated with tripropylene and comprised about 60 wt. percent mono-nonyl phenol, about 30 wt. percent dinonyl phenol, and small amounts of trinonyl phenol, unreacted phenol, etc.

Example II

A base concentrate was prepared as follows: 8 parts of an oil solution consisting of 70 wt. percent P_2S_5 treated polyisobutylene in about 30 wt. percent mineral lubricating oil, 2.1 parts of diethanolamine, 1.7 parts of tallow fatty acid, 4 parts of nonyl phenol (same as in Example I), 10.65 parts of hydrated lime and 56.75 parts of mineral lubricating oil were mixed together in a reactor. 16 parts of glacial acetic acid were slowly added while stirring and maintaining the temperature below about 150° F. The mixture was then heated to 320° F. until about 75 wt. percent of the water of reaction was removed, then filtered through filter using diatomaceous earth (3 wt. percent) admixed with the concentrate and cooled to 200° F. where 0.8 part of phenyl α-naphthylamine was added. One part of the concentrate, which was clear and transparent, was then diluted with 3 parts of additional mineral lubricating oil to form the finished lubricant.

The P_2S_5 treated polyisobutylene was prepared by reacting polyisobutylene of about 800 Staudinger molecular weight with about 15% P_2S_5, based on the weight of the polyisobutylene, at about 425° F. for about 8 hours under a nitrogen atmosphere.

The tallow fatty acid used above had a saponification number of about 195 and a Wijs iodine number of about 55.

Example III

Another finished lubricant was prepared according to the method of Example I except that different proportions were utilized, tallow fatty acid was used in place of the Wecoline AAC acid and a different oil was used.

The compositions and properties of finished lubricants of Examples I to III are summarized in the following table:

TABLE I

	Example I		Example II		Example III	
	Base	Finished	Base	Finished	Base	Finished
Formulation (parts by weight):						
Hydrated lime	10.65	2.66	10.65	2.66	16.0	4.8
Glacial acetic acid	16.00	4.00	16.00	4.00	24.0	7.2
Wecoline AAC acid	1.70	.42				
Polyisobutenyl succinic anhydride	8.0	2.00			8.0	2.4
Nonyl phenol	4.00	1.00	4.0	1.00	4.0	1.2
Diethanolamine	2.1	.55	2.1	.55	2.1	.63
Phenyl α-naphthylamine	0.80	.20	0.80	.20		
Mineral lubricating oil, 80 SUS at 210° F	44.2	89.17				
Tallow fatty acids			1.7	.42	1.7	.51
P_2S_5 polyisobutylene (70 wt. percent in 30 wt. percent oil)			8.0	2.00		
Mineral lubricating oil, 150 SUS at 100° F			56.75	89.17	44.2	83.26
Properties:						
Filterability and clarity	Good		Good		Good	
Centrifuge solids, vol. percent		Trace		.25		Trace
4-hour gel test at 374° F		Pass		Pass		Pass
4-ball wear test (10 kg., 1,800 r.p.m., 1 hr.) mm. scar		0.235		.280		0.25
Visc. at 210° F., SUS		108		88	261	103
Visc. at 100° F., SUS		1,961		1,270	3,184	1,198
Base No. (ASTM D-664)		45.3		34.8	270	83
Sulfated ash		4.75		5.0	30.9	9.5
Free acidity, claculated as percent oleic acid					2.0	

The Centrifuge Solids Test was the volume percent of separated sediment material obtained after centrifuging in an ASTM centrifuge having a diameter of 12 inches, for 4 hours at 1500 r.p.m. The products of the invention showed little sediment, thus indicating good stability.

The 4-Hour Gel Test was carried out by filling an ASTM pour point jar up to mark, which is about ½ full, with the lubricant to be tested. The test lubricant was heated for four hours at 374° F. and then allowed to cool for 45 minutes. The jar was then examined to see if the lubricant had gelled. The lubricants of Examples I to III all passed this test, i.e. they did not gel. This lack of gelling is used as an indication of the spreading ability of the lubricant when it hits the hot cylinder it is being used to lubricate. This Gel Test is also an indication of the lubricant's tendency to remain fluid in long feed lines in hot locations.

As seen by the preceding data, each of the concentrates of the examples was filterable and resulted in clear, transparent finished lubricants which were stable to sedimentation, as indicated by the very low centrifuge solids, and were also heat stable as indicated by their passing of the 4-Hour Gel Test.

Attempts to make similar lubricants, but without the phenol and alkanolamine resulted in hazy, sediment containing lubricants which were of a murky appearance.

What is claimed is:

1. A clear and filterable, substantially neutral, fluid lubricant comprising a major amount of mineral lubricating oil and the reaction product of lime, 1 to 7 wt. percent acetic acid, .2 to 5 wt. percent of C_7 to C_{30} fatty acid, 0.5 to 5.0 wt. percent of a material selected from the group consisting of polyisobutenyl succinic anhydride having a polyisobutenyl group of 600 to 4000 mol. wt., P_2S_5 treated polyisobutylene of 700 to 3000 mol. wt., and mixtures thereof; about .2 to 5 wt. percent of phenol alkylated with one to two C_5 to C_{20} alkyl groups, and about .2 to 5.0 wt. percent of an alkanolamine containing 2 to 3 carbon atoms in the alkanol group.

2. A clear and filterable, substantially neutral, fluid lubricant comprising a major amount of mineral lubricating oil, and the reaction product of a neutralizing amount of lime, 2 to 6 wt. percent of acetic acid, .3 to 1 wt. percent of C_7 to C_{30} fatty acid, 0.5 to 5.0 wt. percent of a material selected from the group consisting of polyisobutenyl succinic anhydride having a polyisobutenyl group of 700 to 1400 mol. wt., P_2S_5 treated polyisobutylene of 800 to 1300 mol. wt., and mixtures thereof, about 0.5 to 3 wt. percent of phenol alkylated with one to two C_5 to C_{20} alkyl groups, and about .3 to 2 wt. percent of an alkanolamine containing 2 to 3 carbon atoms in the alkanol group.

3. A lubricant according to claim **2**, wherein said fatty acid contains 7 to 12 carbon atoms, said material is polyisobutenyl succinic anhydride, said phenol is nonyl phenol and said alkanolamine is diethanolamine.

4. A lubricant according to claim **2**, wherein said fatty acid is tallow fatty acid, said material is P_2S_5 treated polyisobutylene, said phenol is nonyl phenol and said alkanolamine is diethanolamine.

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