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LUBRICANT CONTAINING CALCIUM SALTS OF ACETIC ACID, C_{14} TO C_{30} FATTY ACID, AND PHOSPHOSULFURIZED POLYOLEFIN

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This invention relates to lubricants. Particularly, the invention relates to lubricating oil compositions having good antiwear properties, comprising oil and alkaline earth metal salts of: low molecular weight fatty acid, a higher fatty acid, and a phosphosulfurized polyolefin.

Lubricants can be made according to the invention which are useful for a variety of purposes, including automotive lubrication and lubrication of the cylinders of marine diesel engines.

In lubricating marine diesel engines, a fluid or semi-fluid lubricant is sprayed or forced directly onto the cylinder upon each stroke of the piston by means of a centralized force-feed lubrication system. The lubricant is to a large extent consumed during each stroke of the piston, thereby requiring continuous application of the lubricant. The lubricant should have a fluid, or semi-fluid, consistency to permit the lubricant to be readily pumped through the centralized forced-feed lubrication system and to evenly spread or wet the piston and cylinder. Another requirement of marine diesel cylinder lubricants is that they have good antiwear properties. Thus, prevention of wear is very important due to the giant size of the pistons and cylinders used in such engines (e.g. piston and cylinder diameters of about 36 inches are common) since replacement of liners and other worn parts is very expensive. The lubricant should also be storage stable, even when subject to long periods of storage under hot (e.g. 120° to 140° F.) and vibrating conditions such as frequently occurs during storage in a ship's engine room. The lubricant should also be heat stable so that it does not unduly gel or thicken when moving through hot feed lines or when it hits the surface of the hot cylinder.

Lubricants for such marine diesel lubrication, which met the preceding requirements, have been made by thickening mineral lubricating oil with mixed calcium salts of acetic acid and an intermediate molecular weight fatty acid, e.g. C_7 to C_{12} fatty acids. In these prior lubricants, the calcium acetate salt primarily provided the anti-wear properties, while the intermediate molecular weight fatty acid salts served primarily as stabilizing agents for maintaining the calcium acetate suitably suspended in the oil. Due to the short chain length of the intermediate fatty acid salts, their suspending power for the calcium acetate was not as great as desired, with the occasional result that some separation of oil and salt occurred in storage and in use. This separation led to plugged lines and valves, and loss of anti-wear properties due to loss of active ingredient. Furthermore, the particle size of the calcium acetate was frequently larger than desired for maximum stability. Attempts to improve the stability of the prior calcium acetate type marine diesel lubricants with soaps of high molecular weight fatty acids, e.g. C_{16}–C_{18} acids, resulted in much better stability but tended to give undesirably viscous semi-solid to solid lubricants.

It has now been found that improved marine diesel lubricants, superior in several respects to those made from the intermediate molecular weight fatty acids and acetic acid, can be prepared by using a combination of high molecular weight fatty acid and phosphosulfurized polyolefin in place of part or all of the intermediate molecular weight fatty acid. This use of high molecular weight fatty acid in combination with the surfactant effect of the P_2S_5

treated polymer can result in a calcium acetate type lubricant of exceptional stability and wherein the particle size of the calcium acetate is very small, e.g. about 2.0 microns. This small particle size allows easy filtration of the fluid lubricant to remove unreactive contaminants (e.g. silica and aluminum oxide, from commercial lime). The filtered products are clear, bright and show no haze. It has been further found that if the bulk of the dehydration of the lubricant is carried out in the presence of free acidity, the phosphosulfurized polyolefin surfactant tends to remain more active, a more fluid lubricant results and formation of less desirable carbonates is minimized. On the other hand, prior attempts to manufacture calcium acetate type cylinder lubricants using the intermediate fatty acids, while dehydrating the lubricant on the acid side, (e.g. heating at 225° to 350° F.) resulted in undesirably viscous and solid products. Another finding of the present invention is that the combination of ingredients of this invention permits forming lubricants superior to said prior intermediate fatty acid type lubricants in having a reduced tendency to gel under hot conditions. This is important in engines which operate at very high temperatures, where gelling of the lubricant will interfere with the spreading of the lubricant onto the piston and cylinder, and will also interfere with pumping the lubricant through hot, narrow diameter, feed lines.

In brief, the compositions of the invention result in a better dispersion of calcium acetate, greater fluidity, and improved spreadability than is obtained by use of the aforesaid prior compositions.

The higher molecular weight fatty acid used in the present invention includes C_{14} to C_{30}, preferably C_{14} to C_{20} fatty acids. While saturated fatty acids can be used, the unsaturated acids are preferred. Such preferred fatty acids will include tallow fatty acids, oleic, palmitoleic, gadoleic, erucic, arachidonic, myristoleic acid, etc. These fatty acids are usually derived from either animal or vegetable sources. In some cases, commercial fatty acid derived from naturally occurring materials will contain both saturated and unsaturated acid. For example, some commercial fatty acids will contain about 40 or even 60 wt. percent of saturated fatty acids, with the remainder being principally mono-unsaturated fatty acid along with minor amounts of poly-unsaturated fatty acid. Trace amounts of lower fatty acid may also be present. These mixed saturated and unsaturated fatty acid materials will usually have Wijs iodine numbers of about 35 to 110, preferably 40 to 80, and saponification numbers of 250 to 150, preferably 225 to 175 mg. KOH/gm.

A commercial stabilized fatty acid, available from Emery Industries, under the tradename of Emery 636 Fatty Acid, was used in several of the working examples of the invention. This acid is a coproduct from the dimerization of mono and polyunsaturated soya fatty acids. Due to its previous subjection to polymerization, the Emery 636 Fatty Acid is so reformed as to be stabilized and potentially unpolymerizable. Analysis of this Emery 636 Acid shows the following:

WT. PERCENT ANALYSIS OF EMERY 636 FATTY ACID

	Percent
Saturated acid:	
$C_{14}H_{28}O_2$	2.2
$C_{16}H_{32}O_2$	15.1
$C_{18}H_{36}O_2$	13.9
C_8 to C_{12} acids	4.2
Unsaturated acid:	
$C_{14}H_{26}O_2$	2.2
$C_{16}H_{26}O_2$	8.6
$C_{18}H_{34}O_2$	33.4
$C_{18}H_{32}O_2$	20.3

The Emery 636 Fatty Acid has the following physical characteristics:

Titer, °C.	34–38
Iodine value (Wijs)	55–75
Saponification value ——mg.KOH/gm.—	182–205

The phosphosulfurized olefins are well known and are prepared by reacting an olefin or an olefin polymer with P_2S_5 to form a material believed to be a dithiophosphoric acid. More specifically, the phosphosulfurized olefins are generally prepared by reacting phosphorus pentasulfide with a polymer of a monoolefin, e.g. an alpha olefin, having 2 to 6 carbon atoms, said polymer having a molecular weight in the range of 600 to 4,000 Staudinger, preferably 700 to 1400 Staudinger, for about 0.5 to 15 hours at 150° to 600° F. P_2S_5 treated polybutene is particularly preferred. Preparation of these phosphosulfurized polyolefins is more fully described in U.S. Patent 2,875,188. The phosphosulfurized polyolefin can be used per se, or it can be first hydrolyzed. Hydrolyzation is readily carried out by treating the phosphosulfurized polyolefin with steam to thereby increase the acidity of the phosphosulfurized polyolefin by converting =S groups to —SH groups. This hydrolyzation technique and product is also well known in the art.

The low molecular weight fatty acid used in the invention will include those of 2 to 4 carbon atoms such as acetic, propionic, etc. Acetic acid or its anhydride is preferred.

The alkaline earth metal component of the mixed salt composition of the invention includes calcium, barium, strontium and magnesium, although calcium is preferred. Usually, the acids are neutralized in the presence of the phosphosulfurized polyolefin with alkaline earth metal base, e.g. a hydroxide, oxide or carbonate. Lime (calcium hydroxide) is preferred.

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

In general, the lubricants of the invention will comprise a major proportion of lubricating oil and a minor wear-reducing or thickening amount of the coneutralized acid mixture of the invention. The final lubricants will generally contain salt of about 1.0 to 10.0 wt. percent, based on the total weight of the lubricating composition, of the mixed fatty acid. Final liquid lubricants for automotive crankcase lubrication or lubrication of marine diesel engine cylinders will generally contain salt of about 3.0 to 10.0 wt. percent of the mixed fatty acid, and salt of about 0.2 to 5.0 wt. percent of phosphosulfurized polyolefin. Preferred final lubricants will contain salt of about 3.0 to 8.0 wt. percent of fatty acid and salt of about 0.2 to 2.0 wt. percent of the phosphosulfurized polyolefin. However, for purposes of economy, concentrates containing salt of 10 to 40 wt. percent, usually 25 to 35 wt. percent of the fatty mixture (and salt of a corresponding proportion of phosphosulfurized polyolefin, e.g. about 1.5 to 10 wt. percent will be first prepared and then later diluted with additional oil to form the final lubricant of the invention. These concentrates can also be used as soft greases for general use.

The salt of the fatty acid mixture is preferably formed by coneutralizing, in at least a portion of the oil, about 5.0 to 50, preferably 10 to 35 mole equivalent proportions of the lower fatty acid, e.g. acetic acid or acetic anhydride, per mole equivalent of the higher fatty acid material. Thus, the composition or concentrate can be prepared by coneutralizing the acids (including the acidic phosphosulfurized polyolefin) in the presence of oil with the alkaline earth metal base, followed by dehydration at a temperature of about 250° to 350° F. This dehydration is preferably carried out in two steps—the first dehydration step being on the acid side. This is done by initially utilizing an amount of base insufficient to react with all the acid present, e.g. 80 to 99 wt. percent of the base required for complete neutralization is used in this initial stage. After dehydrating on the acid side, the lubricant can be made neutral or slightly alkaline by a second stage reaction involving the addition of a small additional amount of metal base, followed by further dehydration to evaporate the water of reaction of this resulting second neutralization. By this two stage process, a more fluid stable final product is obtained. In the case of marine diesel lubricants, it is frequently desirable that the final product have a slight alkalinity in order to better neutralize corrosive acids formed by the combustion of the fuel oil used in the engine, for example, sulfuric acid formed by the burning of sulfur present in the low cost residual fuel oils commonly used to power marine diesel engines.

Good results have been obtained by carrying out the first stage of the neutralization such that the free acidity during the dehydrating step is equivalent to about 0.5 to 3.0 wt. percent as oleic acid, based on the total weight of the concentrate. The second stage dehydration is preferably carried out while the product is neutral or has a slight alkalinity, e.g. 0.05 to 0.3 wt. percent as free sodium hydroxide, based upon the weight of the concentrate.

High kettle skin temperatures should be avoided during teh aforesaid dehydration steps, since this will tend to cause the finished lubricant to later gel and solidify at elevated temperatures. Thus, when the lubricant base of the invention was prepared in steam jacketed grease kettles at steam pressures of 110–120 p.s.i., giving kettle bulk temperatures of 300–320° F., excellent products were obtained showing no tendency to gel in subsequent oven tests (4 hours at 374° F.). However, when Dowtherm was employed in the kettle jacket, to obtain comparable bulk temperatures (300–320° F.) the Dowtherm had to be maintained at 450° F. This resulted in finished products which gelled (solidified) when heated in an oven for 4 hours at 374° F. Lowering the Dowtherm temperature to 350° F. gave excellent non-gelling products, but only a maximum bulk temperature in the grease kettle of 260° F.

Generally, if the alkalinity of the final lubricating composition is increased too much, the storage stability of the composition, as measured by centrifuge solids, decreases. However, for some applications, final lubricants having base numbers of about 60 or more, according to ASTM D–66 can be obtained, which are very stable, by a pre-centrifuging of the lubricant concentrate during its manufacture. Thus, by making an alkaline concentrate, then centrifuging the concentrate before it is further blended with additional oil to form the finished lubricant, the less stably suspended salts are removed from the concentrate. At the same time, by centrifuging the concentrate, the total volume of material requiring centrifuging is much less than if it was attempted to centrifuge the more dilute finished lubricant.

It will be understood that various minor modifications of the preceding procedure can be utilized without departing from the inventive scope of the invention. For example, preformed alkaline earth metal salt of C_2 to C_4 fatty acid, and/or preformed alkaline earth metal salt of the aforesaid higher fatty acid component can be added to the oil and heated together with the phosphosulfurized polyolefin, or the alkaline earth metal salt of the phosphosulfurized polyolefin. Or the phosphosulfurized polyolefin or its salt can be added to the composition after the in situ neutralization of the C_2 to C_4 fatty acid and the higher fatty acid. However, this latter procedure is not preferred, since it appears to result in a more viscous product than when the metal salts of the acetic and higher fatty acid are formed in oil in the presence of the phosphosulfurized polyolefin.

Alkaline earth metal salts and soaps of other acids can also be incorporated in the final product, including

salts of inorganic acids such as phosphoric acid, nitric acid, hydrochloric acid, etc. These salts and soaps can be formed during the neutralization steps previously noted, by neutralizing the corresponding acid with the alkaline earth metal base.

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 nitrite, lanolin, wool grease stearine; antioxidants such as phenyl-α-naphthylamine; auxiliary extreme pressure agents; auxiliary antiwear agents; dyes; etc.

To further improve stability to water contamination as well as further minimizing gelling tendencies at high temperatures, small amounts of various surface active agents, including those of the type normally used as lubricating oil detergent additives, can be added to the final composition, usually in amounts of about .1 to 5.0 wt. percent. For example, the previously described unneutralized phosphosulfurized polyolefin can be used. Thus, the unneutralized or acidic phosphosulfurized polyolefin appears to be effective in preventing gelling, while its alkaline earth metal salt appears to be effective as a suspending agent for the C_2 to C_4 fatty acid salt, e.g. calcium acetate. Other useful additives are amino alkyl phenols such as those described in U.S. Patents 2,353,491; 2,459,112 and 3,036,003. A particularly preferred material of this type is prepared by reacting nonyl phenol with ethylene diamine and para formaldehyde. Another recently developed surface active agent is polyisobutylene succinic anhydride wherein the isobutylene group has a molecular weight of about 700 to 1200, as well as polyamine derivatives thereof, namely amic acids and imides obtained by reacting polyamines, for example tetraethylene pentamine, with said aforesaid polyisobutylene succinic anhydride. Another preferred material is alkaline earth metal petroleum or synthetic alkyl aryl sulfonates of about 300 to 700 molecular weight.

The invention will be further understood by reference to the following examples which include a preferred embodiment of the invention.

Example I.—Preparation of concentrate

A mixed salt concentrate was prepared having the following formulation wherein all percents are weight percents:

	Percent
Glacial acetic acid	16.0
Emery 636 Fatty Acid	2.5
Oil solution of 70 wt. percent phosphosulfurized polyisobutylene in 30 wt. percent mineral lubricating oil	3.0
Hydrated lime	10.2
Phenyl-α-naphthylamine	0.2
Mineral lubricating oil of 80 SUS viscosity at 210° F.	68.1

The oil and the bulk of the hydrated lime were mixed together in a steam jacketed grease kettle to form a slurry. One-half of the Emery acid and ⅓ of the phosphosulfurized polyisobutylene was added to the kettle. The kettle contents were mixed and homogenized by passage through a Charlotte colloidal mill. Then the acetic acid was slowly added while mixing and homogenizing while keeping the temperature below 210° F. to prevent boiling. After all the acetic acid had been added, the balance of the Emery Fatty Acid and the phosphosulfurized polyisobutylene was added while mixing and homogenizing. Free acidity determination at this point showed 2½ wt. percent, based on the kettle contents, as free acidity calculated as oleic acid. The grease mixture was then externally heated while continuing mixing to 300° F., which temperature was held for 15 minutes. At the end of this time, the free acidity had dropped to 1.2% as oleic acid. A small amount of additional lime as a 40 wt. percent lime slurry in mineral lubricating oil was added to neutralize the free acidity and to give a free alkalinity as 0.05 wt. percent NaOH. The product was then cooled to 250° F. where the phenyl-alpha-naphthylamine was added. The product was then further cooled to 100° F. Mixing by homogenizing was continued during the entire process including cooling. An excellent smooth semi-fluid (at room temperature) product resulted.

The phosphosulfurized polyisobutylene in said oil solution was prepared by reacting polyisobutylene of about 800 Staudinger molecular weight with 15 wt. percent P_2S_5, based on the weight of the polyisobutylene at about 425° F. for about 8 hours under a nitrogen atmosphere.

PREPARATION OF FINISHED LUBRICANT

25 parts of the concentrate was mixed with 75 parts of additional mineral oil. The resulting mixture was homogenized to give a semi-fluid composition having a 40 base number.

Comparison product A.—Example I was repeated using exactly the same amount of total reactants in the same manner except that all the lime was added at one time to the acids, followed by dehydrating at 320° F., so that the entire neutralization was carried out on the alkaline side.

Comparison products B, C and D.—These products were prepared in the manner of comparison product A but using different formulations.

The compositions and properties of the preceding compositions are summarized in the following table:

TABLE I

Composition (wt. percent)	Example I		Product A		Product B		Product C		Product D	
	Base	Finished	Base	Finished	Base	Finished	Base	Finished	Base	Finished
Glacial acetic acid	16.0	4.0	16.0	4.0	16.0	4.00	16.00	4.00	16.00	4.00
Wecoline AAC acid					3.8	0.95				
Emery 636 fatty acid	2.5	0.60	2.5	0.6			3.80	0.95		
P_2S_5 polyisobutylene solution	3.0	.75	3.0	0.75					4.00	1.00
Hydrated lime	10.2	2.55	10.2	2.55	10.2	2.55	10.20	2.55	10.20	0.55
Phenyl-α-naphthylamine	0.2	0.05	0.2	0.05	0.4	0.10	0.40	0.10	0.20	0.05
Mineral lubricating oil 80 SUS. at 210° F.	68.1	92.05	68.1	92.05	69.9	92.40	69.60	92.40	69.60	92.40
Manufacturing technique	Acid		Alkaline		Alkaline		Alkaline		Alkaline.	
Properties:										
Appearance	Excellent		Excellent		Excellent		Excellent		Excellent.	
4-hr. gel test at 374° F	Fluid		Fluid		Gels		Gels		Fluid.	
Centrifuge test, percent sediment 4-hr. @ 1500 r.p.m.	0.2%		1.9%		0.8%		10.0%		7.0%.	
Visc. at 100° F., SSU	1500		1687		1798		2088		1504.	
Visc. at 210° F., SSU	92.5		96.8		138		Gels		94.6.	
Ash (SO_4) wt. percent	4.8		4.8		4.9		4.9		4.9.	
4-ball wear scar, mm. dia. (1 kg.-1 hr.-1800 r.p.m.).	0.216		0.31		0.27				0.32.	
Stability in storage	Good		Good		Poor		Good		Separates.	
Lubricator life	100 days +				4 days					
Muffle furnace (450° F.) hrs	16+				2				2.	

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 is heated for four hours at 374° F. and is cooled for 45 minutes. The jar is then examined to see if the lubricant has gelled. It is seen that the comparison finished lubricant product B, which represents the prior art, had gelled while the finished product of Example I had not. This gelling or 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.

The centrifuge test was carried out in an ASTM centrifuge and the volume percent of separated material was reported.

The lubricator life test of Table I was carried out by passing the lubricant under test through a Manzell lubricator at the rate of 2 quarts of lubricant a day. The Manzell lubricator includes a sight-glass filled with an aqueous solution containing 50 wt. percent of a calcium nitrate tetrahydrate as the sight-glass fluid. These lubricators are widely used in conjunction with marine diesel engines. The lubricator permits visual observation of the rate of flow of the lubricant which is forced into the bottom of the sight-glass and then floats up through the higher density sight-glass fluid to an upper line from where it is then forced to the cylinder being lubricated. The finished product of Example I went for 100 days without fogging the sight-glass or displacing the sight-glass fluid. The test was stopped after 100 days. On the other hand, the comparison finished lubricant, product B, went for only 4 days before 75% of the sight-glass fluid had become displaced and the sight-glass had become sufficiently fogged so as to require disassembling and cleaning.

The Muffle Furnace test was carried out by passing the lubricant at the rate of 1 quart a day through a ⅛ inch, i.d. steel line equipped with a M.A.N. check valve of the type used on marine disel engine lubricator feed lines. The check valve and the surrounding portion of the feed line were maintained at 450° F. inside a muffle furnace. The test ended when the valve or line, had become sufficiently plugged to rupture a blow-out patch in the line set for 300 p.s.i. This test simulates passage of the lubricant through hot diesel engine lubricating feed lines.

In sum, the data of the table shows that the product of the invention (Example I finished) resulted in a lubricant which was very fluid, as indicated by its 1500 SSU viscosity at 100° F., very stable against sedimentation as measured by the centrifuge test, gave very low wear, was slow to foul the Manzell lubricator, and had good thermal and storage stability. The data also shows the advantage of the "acid" technique as opposed to the alkaline technique (compare Example I and product A); the improvement over the prior art as represented by product B; and the inability of either the fatty acid alone (product C) or the P_2S_5 treated polyisobutylene alone (product D) to form such excellent lubricants as that of Example I.

Example II

In order to further demonstrate the desirablity of utilizing the unsaturated high molecular fatty acid as compared to shorter chain saturated fatty acid, representative compositions were prepared according to the technique used in preparing the inventive composition of Example I. The exact formulations of these compositions and their properties are summarized in Table II which follows:

TABLE II

Formulation, percent wgt:		
Glacial acetic acid	4.00	4.00
Tallow fatty acid [1]	0.63	
Wecoline AAC acids [2]		0.63
P_2S_5 polyisobutylene solution [3]	0.75	0.75
Hydrated lime	2.55	2.55
Phenyl-α-naphthylamine	0.05	0.05
Mineral lubricating oil, 80 SUS. at 210° F.	92.02	92.02
Properties:		
Ash ($CaSO_4$) percent	4.80	4.76
Visc. at 100° F. SUS	1,616	1,718
Visc. at 210° F. SUS	94.4	101.4
Centrifuge test, percent sediment 4-hr. at 1500 r.p.m	0.05	0.35
4-hr. gel test at 374° F	Fluid	Solid gel

[1] Sap. No. of 205, Iodine No. 50.
[2] Coconut fatty acds consisting of about 46 wt. percent capric acid, about 28 wt. percent caprylic acid and about 26 wt. percent lauric acid.
[3] Same as in Example I.

As seen by Table II, the lubricant of the invention prepared from the unsaturated tallow fatty acid did not gel in the 4-hr. gel test, while the comparison lubricant prepared from intermediate molecular weight fatty acids did gel. Also, the greater suspending power of the higher molecular weight tallow fatty acid is noticeable in the relatively lower centrifuge solids (0.05% vs. 0.35%).

Example III

To demonstrate the desirability of utilizing the acid technique of the invention, wherein the bulk of the dehydration of the product is carried out on the acid side, against the more conventional technique of the prior art wherein the dehydration is carried out on the alkaline side, the following compositions were prepared:

Lubricant A—Preparation of concentrate.—A mixed salt concentrate was prepared having the following formulation wherein all percents are weight percents:

	Percent
Glacial acetic acid	16.0
Emery 636 Fatty Acid	2.5
Oil solution of 70 wt. percent phosphosulfurized polyisobutylene in 30 wt. percent mineral lubricating oil (same as in Example I)	3.0
Hydrated lime	10.2
Phenyl-α-naphthylamine	0.2
Mineral lubricating oil of 80 SUS viscosity at 210° F.	68.1

The oil and the bulk of the hydrated lime were mixed together in a steam jacketed grease kettle to form a slurry. One-half of the Emery 636 Fatty Acid and ⅓ of the phosphosulfurized polyisobutylene solution was added to the kettle. The kettle contents were mixed and homogenized by passage through a Charlotte colloidal mill having an 0.003" opening. Then the acetic acid was slowly added while homogenizing and while keeping the temperature below about 210° F. to prevent boiling. After all the acetic acid had been added, the balance of the Emery Fatty Acid and the phosphosulfurized polyisobutylene solution was added while homogenizing. A free acidity determination at this point showed 3.19 wt. percent based on the kettle contents, as free acidity calculated as oleic acid. The grease mixture was then externally heated while continuing mixing to 300° F., which temperature was held for about 15 minutes. At the end of this time, the free acidity had dropped to 2.34 wt. percent as oleic acid. A small amount of additional lime in the form of a 40 wt. percent lime slurry in mineral lubricating oil was added to neutralize the free acidity and to give a free alkalinity of about 0.28 wt. percent NaOH. The product was then cooled to 250° F. where the phenyl-alpha-naphthylamine was added. The product was then further cooled to 100° F. Mixing by homogenizing through said Charlotte mill was continued during the entire process including cooling. 25 parts of the resulting concentrate was then mixed with 75 parts of additional mineral oil

to form the final product which was homogenized again through the Charlotte mill.

Lubricant B.—A concentrate was prepared from the same components as lubricant A, but in a more conventional manner by simply adding the lime to the oil, followed by the addition of the acetic, tallow acid and the phosphosulfurized polyisobutylene, which gave a material having a free alkalinity of 0.34 wt. percent as NaOH. The material was then dehydrated at a temperature of 320° F. and the free alkalinity at the finish of the dehydration was 0.29 wt. percent NaOH. The concentrate was then diluted with additional oil to form a finished lubricant.

The exact concentrate compositions, the diluted final products and the properties of said final products are summarized in Table III which follows:

TABLE III

	Lubricant A	Lubricant B
Concentrate formulation (% weight):		
Glacial acetic acid	16.00	16.0
Tallow fatty acid [1]	2.5	2.5
Oil sol. of P_2S_5 polyisobutylene	3.0	3.0
Hydrated lime	10.2	10.2
Phenyl-α-naphthylamine	0.2	0.2
Mineral Lubricating Oil, 80 SUS at 210° F	68.1	68.1
Free acidity at start as oleic	3.10	
Free acidity at finish as oleic	2.34	
Free alkalinity at start as NaOH		0.34
Free alkalinity at finish as NaOH		0.29
Finished product:		
Glacial acetic acid	4.00	4.00
Tallow fatty acid	0.63	0.63
Oil sol. of P_2S_5 polyisobutylene	0.75	0.75
Hydrated lime	2.55	2.55
Phenyl-α-naphthylamine	0.05	0.05
Mineral lubricating oil, 80 SUS at 210° F	92.02	92.02
Properties:		
Ash (SO_4) percent	4.80	4.85
Vis./100° F. SUS	1,616	1,687
Vis./210° F. SUS	94.4	96.7
Centrifuge test, percent sediment, 4-hr. @ 1500 r.p.m.	0.05	1.9
Alkalinity (Wt. percent NaOH)	0.07	0.07

[1] Sap. No. of 205, Iodine No. 50.

The data of Table III indicates preparation of the concentrate in the presence of free alkalinity (lubricant B) will give higher centrifuge solids indicative of poor storage stability (separation of solid material in barrels, day tanks etc.) than when the concentrate is prepared on the acid side (lubricant A).

Example IV

To demonstrate how precentrifuging can be used to form high alkalinity stable final products, the following compositions were prepared:

Composition 1.—This composition had the following ingredients:

	Percent
Glacial acetic acid	16.0
Animal fatty acid (tallow fatty acid)	2.5
Oil sol. of P_2S_5 polyisobutylene (same as in Ex. I)	3.0
Hydrated lime	10.2
Phenyl-alpha-naphthylamine	0.2
Mineral oil of 80 SUS at 210° F.	68.1

The bulk of the mineral oil and lime, the animal fatty acid and the oil solution of phosphosulfurized polyisobutylene was added to a steam jacketed grease kettle and mixed intimately, followed by the slow addition of acetic acid so as to maintain the temperature of the reaction mixture below about 210° F. After all the acetic acid had been added, the composition was then mixed for an additional ½ hour and then homogenized in a Charlotte mill having an 0.003" opening. At this point the free acidity of the composition was about 2 wt. percent calculated as oleic acid and based upon the total weight of the kettle contents. Heating was then initiated and the temperature of the mixture was raised to 320° F. which was held for 30 minutes. Next, the free acid was neutralized by the addition of a small amount of lime, dispersed in oil, to thereby give a final composition having a free alkalinity of 0.05% calculated as NaOH. Cooling was then initiated and the product was cooled to 250° F., where the phenyl-alpha-naphthylamine was added as an oxidation inhibitor. The base grease was then further cooled to 100° F., where it was milled by circulating from the kettle through a Charlotte mill and back to the kettle until a smooth homogeneous mass was obtained.

Composition 2.—A portion of composition 1 was diluted by mixing with three times its weight of additional mineral oil to form Composition 2.

Composition 3.—A portion of composition 1 was centrifuged at 1500 r.p.m. for four hours which resulted in about 1.5 wt. percent solid separation. The remaining liquid portion of the lubricant was then employed to form composition 3 by mixing with three times its weight of additional mineral oil.

Composition 4.—A lubricant concentrate was prepared in the same manner as composition 1, except that different proportions of ingredients were used.

Composition 5.—A portion of composition 4 was first centrifuged at 1500 r.p.m. for four hours which resulted in 6 percent solid separation and 94 percent liquid portion. The liquid portion was decanted and diluted with additional mineral lubricating oil to form composition 5.

Compostion 6.—Composition 6 was prepared by diluting 4 parts of composition 4 with 6 parts of oil.

Composition 7.—This composition was prepared by centrifuging a portion of composition 1 which separated 1.5 percent sediment, then decanting the liquid portion and diluting 4 parts of the decanted liquid portion with 6 parts of additional oil.

Composition 8.—This composition was prepared by diluting 4 parts of composition 1 with 6 parts of oil.

The formulations of compositions 1 to 8 and their physical properties are summarized in Table IV which follows:

TABLE IV.—EFFECT OF PRECENTRIFUGING

	Composition							
	1	2	3 [1]	4	5 [1]	6	7 [1]	8
Composition (wt. percent):								
Glacial acetic acid	16.0	4.0	4.0	25.00	6.25	6.25	6.40	6.40
Tallow fatty acid [2]	2.5	.63	.63	2.50	.625	.625	1.00	1.00
Oil sol. P_2S_5 polyisobutylene	3.0	.75	.75	3.00	.5	.5	1.20	1.20
Hydrated lime	10.2	2.55	2.55	16.00	2.67	2.67	4.08	4.08
Phenyl α-naphthylamine	0.2	.05	.05	0.20	.03	.03	.08	.08
Mineral lubricating oil of 80 SUS at 210° F	68.1	92.02	92.02	53.30			87.24	87.24
Precentrifuged	No	No	Yes	No	Yes	No	Yes	No
Properties:								
Visc. at 100° F., SUS		1,616	1,640			1,618	1,600	1,620
Visc. at 210° F., SUS		94.4	95		94	93		
Centrifuge test, percent sediment 4-hr. at 1500 r.p.m.	1.5	0.45	0.04	6.0	0.40	1.5	0.20	1.6
Base No. ASTM-D-664		40	40		60	60	60	60
Other tests:								
4-hr. gel test at 374° F		Fluid	Fluid		Fluid	Fluid	Fluid	Fluid
Muffle furnace at 450° F., hours		18+	18+		18+	18+	18+	18+

[1] Approximate composition because of small loss of solids in precentrifuging.
[2] Sap. No. of 205, Iodine No. of 50.

As seen by Table IV, composition 1 gave 1.5 percent sediment in the centrifuge test. Composition 2, which was formed by simply diluting composition 1 with additional oil, gave 0.45 percent sediment. Composition 3, which was prepared by first centrifuging a portion of composition 1 and then diluting, gave only 0.04 percent sediment. Thus, by percentrifuging the concentrate and preparig the final lubricant only from the decanted portion of the centrifuged material, a more stable final product is obtained. By centrifuging the concentrate, the total mass to be centrifuged is, of course, much less than if the final product were to be centrifuged. Composition 4 shows a concentrate prepared with a much greater amount of salt which gave 6 percent sediment. Upon percentrifuging a portion of composition 4, and then diluting it back to form composition 5, the resulting composition 5 gave only 0.4 percent sediment which is acceptable, and yet a much higher base number of about 60 was obtained. On the other hand, composition 6 illustrates that if a base number as high as 60 is obtained without percentrifuging the concentrate, the sediment then becomes 1.5 percent which is unacceptable. Compositions 7 and 8 demonstrate another way of making a higher base numbered product. In this case, by a lesser dilution of composition 1 with percentrifuging, only 0.2 percent sediment was obtained (composition 7). Without precentrifuging, 1.6 percent sediment was obtained (composition 8).

These compositions with base numbers of about 60 have become desirable in some types of engines to provide excess alkalinity for neutralizing corrosive acids which form upon the combustion of the residual fuel, particularly, fuels containing relatively large amounts of sulfur which tend to form sulfuric acid upon combustion. Previously, it had been exceedingly difficult to obtain calcium mixed salt fluid lubricants having high base numbers, i.e. about 60, and yet at the same time were sufficiently stable to sediment formation. As demonstrated by the data of Table IV, the compositions of the invention permit formation of high base number materials by precentrifuging the grease concentrate before it is diluted back to form a final lubricating composition. Also, in all cases, compositions were formed which successfully passed the 4-hr. gel test, and which were able to withstand in excess of 18 hours in the Muffle Furnace Test, which results indicate stable high quality lubricants.

Example V

A grease concentrate was prepared having the following composition:

	Percent
Glacial acetic acid	16.0
Tallow fatty acid	2.5
Oil sol. of P_2S_5 polyisobutylene (same as in Example I)	3.0
Hydrated lime	10.2
Phenyl-α-naphthylamine	0.2
Mineral oil	68.1

This grease was prepared by adding the mineral oil, the hydrated lime, 60% of the tallow fatty acid, and about ⅓ of the oil solution of the phosphosulfurized polyisobutylene to a steam jacketed grease kettle and mixing. To this mixture was added, without external heating, the acetic acid. After mixing for an additional ½ hour, the remainder of the fatty acid and the oil solution of the phosphosulfurized polyisobutylene was added. All during the preceding operation, the material in the kettle was being constantly stirred by being pumped and recycled through a Charlotte mill having an opening of 0.003" clearance. The product at this stage had a free acidity of 2.26 wt. percent as oleic acid. The material was heated to 320° F. and held for ½ hour. At this point, the free acidity had decreased to 2.12 wt. percent as oleic acid. Additional lime was then added to neutralize the free acidity and to give 0.13 wt. percent free alkalinity in terms of NaOH. The composition was then cooled to 250° F. where the phenyl-alpha naphthylamine was added followed by cooling to 100° F. The kettle contents were then passed to storage through the Charlotte mill.

Lubricants a, b, c, and d.—The preceding grease concentrate was then diluted with varying amounts of oil to form different concentrations of mixed-salt in the final lubricant and consequently to obtain different base numbers. In addition, varying amounts of an over-based calcium sulfonate oil solution available under the tradename of Bryton C–300 from the Bryton Chemical Company was added to the diluted concentrate. Bryton C–300 consists of about 30% calcium sulfonate having an average molecular weight of about 440, about 43.5% mineral lubricating oil and the remainder is essentially calcium carbonate with a small amount of calcium hydroxide. Bryton C–300 has a base number of 300 mg. KOH/gm. The calcium sulfonate is prepared from detergent alkylate bottoms, i.e. the bottom fraction obtained after distillation of benzene alkylated with tetrapropylene.

The compositions prepared and their properties are summarized in Table V which follows:

TABLE V

	Lubricant			
	a	*b*	*c*	*d*
Formulation (Percent wt.):				
Glacial acetic acid	4.00	6.40	3.78	3.66
Tallow fatty acid [1]	0.63	1.00	.59	.57
Oil sol. of P_2S_5 polyisobutylene	0.75	1.20	.70	.68
Hydrated lime	2.55	4.10	2.39	2.34
Phenyl-α-naphthylamine	0.05	0.08	.05	.05
Mineral lubricating oil, 80 SUS at 210° F.	92.02	82.22	86.83	84.45
Bryton C–300			5.66	8.25
Properties:				
Visc. at 100° F., SSU	1,616	1,947	1,775	1,746
Visc. at 210° F., SSU	94.4	111.4	98.4	99.3
4-hr. gel test at 374° F	Fluid	[2]	Fluid	Fluid
4-ball wear scar, mm. dia. (1 kg.–1 hr.–1800 r.p.m.)	0.28	0.28	0.25	0.23
Base No. (ASTM D–664)	43.2	57.0	52.1	62.2
Centrifuge solids, percent sediment 4-hr. @ 1500 r.p.m.	0.45	1.0	0.40	0.40

[1] Sap. No. of 205, Iodine No. of 50.
[2] Viscous fluid.

As demonstrated by the data of Table V, Lubricant *a* shows that a relative low viscosity fluid which does not unduly gel in the gel test can be obtained with a base number of 43.2. However, without precentrifuging, if the concentration of the mixed salts is increased to form Lubricant *b* so as to obtain a higher base number, then a higher viscosity material is obtained wihch tends to gel to form a viscous fluid in the gel test. However, Lubricants *c* and *d* demonstrate that high base numbers can be obtained, the viscosity of the lubricant can be kept relatively low, and in addition the resulting lubricant will not gel in the gel test, when using a surfactant such as calcium sulfonate as an additive.

What is claimed is:

1. A fluid lubricating oil composition suitable for marine diesel cylinder lubrication comprising a major amount of mineral lubricating oil and calcium salts of: (A) about 3 to 10 wt. percent of acetic acid and C_{14} to C_{30} fatty acid in a relative mole ratio of about 5 to 50 mole equivalent proportions of acetic acid per mole equivalent of C_{14} to C_{30} fatty acid, and (B) about 0.2 to 5.0 wt. percent of a phosphosulfurized polymer of a C_2 to C_6 monoolefin, said polymer having a molecular weight of about 600 to 4,000 Staudinger.

2. A lubricant according to claim **1**, which contains about 0.1 to 5.0 wt. percent of calcium alkylaryl sulfonate of about 300 to 700 molecular weight.

3. A lubricating oil composition according to claim **1**, wherein said C_{14} to C_{30} fatty acid is a mixed fatty acid having a Wijs iodine number of about 35 to 110 and a saponification number of about 150 to 250 mg. KOH/gm.,

said mole ratio is about 10 to 35 mole equivalent of acetic acid per mole equivalent of said C_{14} to C_{30} fatty acid, and said monoolefin is polyisobutylene.

4. A lubricating oil composition according to claim 3, wherein said mixed fatty acid is tallow fatty acid.

5. A fluid lubricating oil composition suitable for marine diesel cylinder lubrication comprising a major amount of mineral lubricating oil and coneutralized calcium salts of: (A) about 3 to 8 wt. percent of acetic acid and C_{14} to C_{30} fatty acid having Wijs iodine numbers of about 40 to 80 and saponification numbers of about 175 to 225 mg. KOH/gm. in a relative mole ratio of about 10 to 35 mole equivalent proportions of acetic acid per mole equivalent of C_{14} to C_{20} fatty acid, and (B) about 0.2 to 2.0 wt. percent of a P_2S_5 treated polyisobutylene of about 700 to 1400 Staudinger molecular weight.

6. A method of preparing a lubricant concentrate comprising coneutralizing with lime in mineral lubricating oil, about 10 to 40 wt. percent of acetic acid and C_{14} to C_{30} fatty acid, in a relative molar ratio of about 5 to 50 molar equivalents of said acetic acid per molar equivalent of said C_{14} to C_{30} fatty acid, and about 1.5 to 10.0 wt. percent phosphosulfurized polymer of a C_2 to C_6 monoolefin, said polymer having a molecular weight in the range of 600 to 4,000 Staudinger, with about 80 to 99 wt. percent of the total amount of lime required for complete coneutralization, heating the resulting mixture to dehydrate said mixture, then further neutralizing the resulting mixture by the addition of a small amount of additional lime followed by again heating to dehydration to form a lubricant concentrate ranging from neutral to slightly alkaline.

7. A method of preparing a lubricant concentrate which comprsies centrifuging the lubricant concentrate of claim 5 to remove prospective sediment therefrom, removing the liquid residue, and diluting the liquid residue with additional mineral oil to form a fluid lubricant containing calcium salt of about 3 to 10 wt. percent of said acetic and C_{14} to C_{30} fatty acids.

8. A method according to claim 7, wherein said C_{14} to C_{30} fatty acid material contains at least 40 wt. percent of mono-unsaturated fatty acid.

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DANIEL E. WYMAN, *Primary Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,202,606 August 24, 1965

Arnold J. Morway et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 14, line 8, for "comprsies" read -- comprises --; line 9, for the claim reference numeral "5" read -- 6 --.

Signed and sealed this 28th day of June 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents