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LUBRICATING OIL COMPOSITION

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No Drawing. Filed Nov. 13, 1957, Ser. No. 696,047
4 Claims. (Cl. 252-40.7)

This invention relates to lubricating oil compositions. Particularly, it relates to lubricating oil compositions suitable for use in internal combustion engines, which compositions comprise lubricating oil, alkaline earth metal mixed-salts of low and intermediate molecular weight fatty acids and a tertiary alkyl primary amine.

It had been known that alkaline earth metal mixed-salts of low and intermediate molecular weight fatty acids can be used in forming lubricants having excellent anti-wear properties. Lubricants of this type have been commercially used for lubricating the upper cylinders of marine diesel engines on a once-through application. However, such lubricants per se are not suitable for crankcase lubrication because they form very heavy deposits in the engine. This deficiency has now been overcome by incorporating an alkyl primary amine into the mixed-salt lubricant. It has been further found that the presence of the mixed-salt permits the incorporation into the oil composition of amounts of the amine greatly in excess of its oil solubility limits.

The compositions of the invention will therefore comprise, lubricating oil, about 2.5 to 8.0 e.g. 3.5 to 6.0 weight percent of an alkaline earth metal mixed-salt material and about 1 to 5, e.g. 2.0 to 4.0 weight percent of an alkyl primary amine, said weight percents being based on the total weight of the composition.

The mixed-salt material in turn will comprise, in a molar ratio, alkaline earth metal salt of about 2.5 to 20, e.g. 4 to 10 moles of a low molecular weight fatty acid per mole of the intermediate molecular weight acid. This salt mixture will generally be prepared by conneutralization of the low and intermediate molecular weight acids, in a lubricating oil menstruum, with an alkaline earth metal base.

Suitable low molecular weight acids for forming the salt include saturated and unsaturated, substituted and unsubstituted aliphatic monocarboxylic acids and their anhydrides having about 2 to 5 carbon atoms per molecule. These acids include fatty acids such as acetic, propionic, furoic, acrylic, and similar acids including their hydroxy derivatives such as lactic acid, or their anhydrides, e.g. acetic acid anhydride. Acetic acid or acetic acid anhydride is preferred.

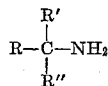
The intermediate molecular weight fatty acids operable for the mixed-salt formation include those aliphatic, saturated or unsaturated, unsubstituted monocarboxylic acids containing 7 to 12 carbon atoms per molecule, e.g., capric, caprylic, nonanoic, lauric acids, etc.

The metal base used to form the salts will generally be oxide or hydroxide of an alkaline earth metal, i.e. calcium, strontium, magnesium or barium.

The lubricating oil used in the compositions of the invention may be a mineral lubricating oil, a synthetic lubricating oil, or mixtures thereof. Synthetic lubricating oils which may be used include esters of dibasic acids (e.g. di-2-ethyl hexyl sebacate); esters of glycols (e.g. C₁₃ 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-ethyl-hexanoic acid); formals, silicones, carbonates, polyglycols and other synthetic lubricating oils known in the art.

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The amine material which is used are those tertiary alkyl primary amines of the general formula:



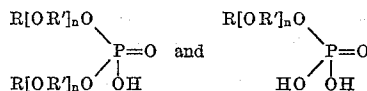
wherein R, R' and R'' are straight or branched chain alkyl radicals of 1 to 18 carbon atoms, the total number of carbon atoms in the molecule being about 16 to 36, e.g. 18 to 24. Such amines can be prepared from tertiary olefins, e.g. the various polymers of propylene and isobutene; copolymers of propylene and isobutene; copolymers of isobutene and butenes or pentenes; etc. Such polymers and copolymers are well known synthetic olefins in the petroleum industry. However, in such polymerizations, various isomerizations and migrations may occur such that a mixture of olefins are produced. Thus, when making a tertiary alkyl primary amine of 18 carbon atoms from hexa-propylene, a polymer of propylene, one may obtain a mixture of tertiary alkyl primary amines having predominantly 18 carbon atoms per molecule with minor amounts of homologous molecules with 19, 20, 21, 22, 23 and/or 24 carbon atoms. Such a mixture is conveniently designated "t-C₁₈₋₂₄H₃₇₋₄₉NH₂."

Specific examples of tertiary alkyl primary amines which may be used include the following:

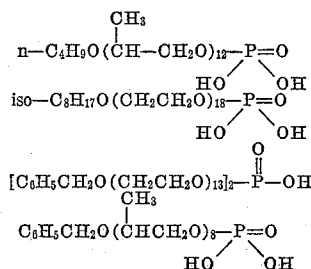
5-amino-5,13-dimethyl-hexadecane
3-amino-3,5,7,9,12-pentamethyl-tridecane
4-amino-2,4,6,8,10-pentamethyl-tridecane
2-amino-2,4,4,6,6,8,8-heptamethyl-nonane
6-amino-2,2,4,4,6,8,8-heptamethyl-nonane

Various other additives may also be added to the lubricating composition in amounts of about 0.1 to 10.0 weight percent, based on the total weight of the composition. Examples of such additives include: detergents such as calcium petroleum sulfonate; viscosity index improvers such as polyisobutylene; corrosion inhibitors such as sorbitan monooleate; pour depressants; dyes; other grease thickeners and the like.

In systems where the lubricating composition of the invention comes into contact with lead, such as copper-lead bearings, it is desirable to incorporate a minor amount e.g. 0.5 to 5% of an inhibitor to prevent lead corrosion. Particularly effective inhibitors for this purpose are the alkoxypolyalkyleneoxy mono- and diesters of phosphoric acid. These materials have the following general formulas:



wherein R represents alkyl group containing 2 to 10, e.g. 4 to 6 carbon atoms or an aryl group; R' represents an aliphatic hydrocarbon radical having 2 to 8, e.g. 2 to 4 carbon atoms and n is about 8 to 18. Also included are materials where R' may consist of different radicals in the same polymeric chain, e.g. ethylene and propylene radicals. Specific examples of such materials will include:



Materials of the above type are readily prepared by reacting P_2O_5 with an ether of a polyglycol.

Another effective lead corrosion inhibitor is zinc dialkyl dithiophosphate wherein the alkyl group contains about 3 to 6 carbon atoms.

The composition of the invention may be readily prepared by dispersing in the lubricating oil, the desired amount of the preformed fatty acid salts along with the tertiary alkyl primary amine and other inhibitors, if any. However, a preferred method is to form a concentrate of the mixed fatty acid salts in situ in lubricating oil by neutralizing the fatty acid components with a metal base, then diluting with additional lubricating oil and adding the amine and other additives to form the final lubricating product. For example, a mixed-salt concentrate containing about 30 to 50 weight percent salt can be prepared by forming a slurry of the alkaline metal base in lubricating oil, then adding to this slurry a blend of the low and intermediate molecular weight fatty acids. This mixture can then be heated to about 300 to 600° F. for about 1 to 6 hours in order to completely dehydrate the reaction mixture. If the material is heated to about 430 to 600° F. a complex mixed-salt is formed which has somewhat different characteristics from the mixed-salt prepared by heating to about 300 to 430° F. However, the present invention is applicable to both types of materials. After dehydration, the product can be cooled and milled in a homogenizing device, such as a Gaulin homogenizer, a Charlotte mill, or a Morehouse mill. This mixed-salt concentrate can then be blended with the desired amounts of lubricating oil, and the amine and other additives stirred in, followed by further homogenization, if desired.

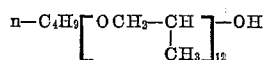
The invention will be further understood by the following examples.

Example I (all parts by weight)

20 parts of glacial acetic acid and 4.8 parts of Wecoline AAC Acids (a commercial mixture of 28 weight percent caprylic, 56 weight percent capric and 16 weight percent lauric acids) were added to a slurry of 14.8 parts of hydrated lime in 59.8 parts of a mineral lubricating oil having a viscosity of 80 SUS at 210° F. This mixture was then stirred for about 30 minutes, the temperature rising to about 220° F. External heating was then applied until the mixture had reached a temperature of 320° F. at which point substantially all the water had been removed. The mixed-salt concentrate was then cooled to 150° F. and 0.6 part of phenyl-alpha-naphthylamine were mixed into the product. The product was twice passed through a Charlotte mill and then passed to a mixing tank where the product was blended with 348 parts of additional mineral oil, Primene JM-T (mixture of C_{18-24} tertiary alkyl primary amines manufactured by Rohm & Haas) and a material consisting of about 50 wt. percent of n-butyl polypropoxy phosphate and about 50 wt. percent of ether alcohol. This product was finished by passing through the Charlotte mill again and was deaerated by passing through a Cornell homogenizer which operates under reduced pressure.

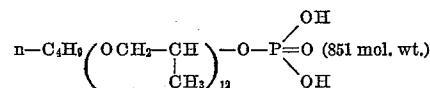
The mixture of n-butyl polypropoxy phosphate and ether alcohol referred to above was prepared as follows:

4 wt. percent of P_2O_5 was slowly added with rapid stirring to 96 wt. percent of an ether alcohol of the formula:

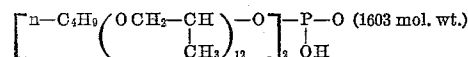


After all the P_2O_5 was added the mixture was heated to about 300° F. for about 3 hours while bubbling nitrogen through the mixture in order to agitate and prevent oxidation. The reaction mixture was cooled and analyzed and was found to contain about 50 wt. percent of the unreacted ether alcohol and about 50 wt. percent of a n-

butyl (propoxy)₁₂ phosphate having a molecular weight of 889. The molecular weight of 889 indicates that the n-butyl (propoxy)₁₂ phosphate material was predominately:



with a minor amount of the diphosphate



Although, the reaction mixture contained both phosphate and unreacted ether alcohol, only the phosphate is effective in reducing lead corrosion of the composition, the ether alcohol being inert for this purpose.

The following table summarizes the composition and properties of the finished lubricant product.

TABLE I

Formulation of finished product (weight percent):

	Percent
Glacial Acetic Acid.....	4.24
Wecoline AAC Acid.....	1.01
Hydrated Lime.....	3.10
Phenyl- α -Naphthylamine	0.14
Mineral Oil (80 SUS at 210° F.).....	86.51
C18-24 tertiary alkyl primary amines.....	2.50
50% solution of n-butyl (propoxy) ₁₂ phosphate	2.50

Properties:

Appearance—Uniform, Homogeneous, Opaque.	
Percent Ash ($CaSO_4$).....	4.3.
SUS Vis./100° F.....	1512.3.
SUS Vis./210° F.....	101.8.
Gravity API.....	19.0.
4-Ball Wear Test (1800 r.p.m., 10 kg. load, 75° C., 1 hour).	
Wear Scar dia. (mm.).....	0.20.

The above lubricant was tested in a single cylinder Caterpillar 1-A Diesel Test Engine. This test was carried out for 120 hours operating on a fuel containing 1 percent sulfur and using the Caterpillar 1-A Test Procedure CRC-L-1-545. On completion of the test, the engine was inspected and the amount of wear and deposit formation determined. The results of this test are summarized in the following table along with comparable data on a similar calcium acetate-Wecolate lubricant but which did not contain the amine and phosphate additives and also data on a mineral oil used as the base in a heavy duty premium lubricant.

TABLE II

Caterpillar engine performance (120 hours)

Composition	Demerit Ratings		Top Ring Wt. Loss (mg.)
	RZ ¹	RZ-1 ²	
A. Calcium Acetate—Wecolate Lubricant (no additives).....	1.16	1.17	-----
B. Calcium Acetate—Wecolate Lubricant+2.5% C_{18-24} tert.alkyl primary amines+2.5% Solution of 50 wt. percent n-butyl (Propoxy) ₁₂ phosphate.....	0.49	0.38	300
C. Base Oil used in commercial HD-30W crankcase lubricant ³	3.0	2.8	1,100

¹ Total ring zone area.

² Area below top ring groove.

³ Solvent extracted Mid-Continent base stock.

As seen from the above table, the composition of the invention (B) containing the amine and phosphate addi-

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tives gave a much cleaner engine than the corresponding composition without these additives (A). This improvement in reducing the deposit formation of the calcium acetate-Wecolate lubricant is due to the presence of the amine material, the phosphate additive only functioning as a lead corrosion inhibitor. Further comparison with the commercial base oil (C) illustrates the exceptional engine cleanliness and low wear of the composition of the invention (B).

Although a number of other additive materials were tested for reducing the deposit formation of the calcium acetate-Wecolate composition only the tertiary alkyl primary amines of the invention were found effective for this purpose. Thus, known detergent additives such as P_2S_5 treated polybutene, a combination of aluminum alcoholate and P_2S_5 treated polybutene, and P_2S_5 treated barium alkyl phenol sulfide were not satisfactory. Even a mixture of shorter chain C_{12} to C_{15} tertiary alkyl primary amines (predominantly C_{12} and sold under the trade-name "Primene 81-R") of the same type as the C_{16} to C_{32} alkyl amines of the invention, gave a poor performance.

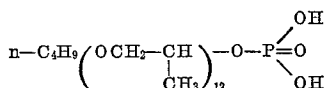
Since lubricants in most gasoline engines come into contact with copper-lead bearings, it is desirable in these instances that either the phosphate previously described or a zinc dialkyl dithiophosphate be used for inhibiting lead corrosion. The action of these two types of materials is rather specific, as other known inhibitors for oxidation and lead corrosion inhibiting such as: zinc dialkyl dithiocarbonate and P_2S_5 treated alpha pinene are not effective in these compositions.

To further illustrate the invention, other lubricating compositions can be prepared as follows:

(A) A lubricant can be prepared in the same manner as the lubricant of Example I, but without adding the 2.5 parts of the n-butyl polypropoxy phosphate-ether alcohol material.

(B) A lubricant can be prepared in the same manner as the lubricant of Example I, but using 2.5 parts of 3-amino-3,5,7,9, 12-pentamethyl-tridecane instead of the mixture of C_{18-24} tertiary alkyl primary amines, and without adding the 2.5 parts of the n-butyl polypropoxy phosphate-ether alcohol material.

(C) A lubricant can be prepared in the same manner as the lubricant of Example I, but using 2.5 parts of 6-amino-2,2,4,4,6,8,8-heptamethyl-nonane instead of the mixture of C_{18-24} tertiary alkyl primary amines and using 3.0 parts of



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instead of the 2.5 parts of the mixed n-butyl polypropoxy phosphate-ether alcohol.

What is claimed is:

1. A lubricating oil composition suitable for use in the crankcase of internal combustion engines, comprising a major proportion of mineral lubricating oil, about 2.5 to 8.0 weight percent of a dehydrated alkaline earth metal mixed salt of C_2-C_5 fatty acid and a C_7-C_{12} fatty acid in a molar ratio of about 2.5 to 20 moles of said C_2-C_5 fatty acid per mole of said C_7-C_{12} fatty acid, about 1 to 5 weight percent of a C_{16} to C_{36} tertiary alkyl primary amine, and about 0.5 to 5 wt. percent of a material selected from the group consisting of alkoxypolyalkyleneoxy mono- and diesters of phosphoric acid and mixtures thereof, wherein said alkoxy group contains 2 to 10 carbon atoms, said alkyleneoxy group contains 2 to 4 carbon atoms and the number of alkyleneoxy groups per ester group is about 8 to 18.

2. A lubricating oil composition according to claim 1, wherein said alkaline earth metal is calcium.

3. A lubricating oil composition according to claim 1, wherein said low molecular weight fatty acid is acetic acid.

4. A lubricating oil composition comprising a major proportion of mineral lubricating oil, about 2.5 to 8.0 wt. percent of a dehydrated mixed-salt material comprising 4 to 10 moles of calcium acetate per mole of calcium salt of a C_7 to C_{12} fatty acid, 1 to 5 wt. percent of a C_{18} to C_{24} tertiary alkyl primary amine and about 0.5 to 5 wt. percent of a material selected from the group consisting of alkoxypolyalkyleneoxy mono- and diesters of phosphoric acid and mixtures thereof, wherein said alkoxy group contains 2 to 10 carbon atoms, said alkyleneoxy group contains 2 to 4 carbon atoms and the number of alkyleneoxy groups per ester group is about 8 to 18.

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