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LUBRICANT SUITABLE FOR MARINE DIESEL LUBRICATION COMPRISING OIL AND MIXED CALCIUM SALTS OF ACETIC ACID AND AMINOALKYL PHENOL

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This invention relates to lubricants. Particularly, the invention relates to lubricating oil compositions, having good anti-wear properties, comprising mineral oil and alkaline earth metal salts of acetic acid and aminoalkyl phenol.

While generally useful as lubricants for a variety of purposes, lubricants can be made according to the invention which are particularly effective for lubrication of marine diesel engines. Marine diesel engines have become widespread in their use. In these engines there has always been a serious wear problem with regard to the piston, the piston rings and the surface of the cylinder liner. This problem of wear has been aggravated by use of low cost residual type fuel oils which generally contain 2 to 4 wt. percent sulfur. Because of their high sulfur content, acid formed by the combustion of the sulfur, tends to corrode the steel surfaces of the engine to give very high rates of wear.

In lubricating these diesel engines, a fluid or semi-fluid lubricant is sprayed 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.

In order to be suitable for such lubrication use, it has been determined that the lubricant should have a fluid or semi-fluid consistency. This is desired in order that the lubricant may be readily pumped through the aforementioned forced lubrication systems normally associated with marine diesel engines and will spread or wet the pistons sufficiently during each stroke to achieve an overall coating on the piston surface. As indicated above, another requirement of such lubricants is that they have good antiwear properties. Because of the giant size of the pistons and cylinders used in such engines (e.g. piston and cylinder diameters of 36 to 60 inches are common), wear is a serious problem. Once the cylinder liner has worn more than about 0.6% of its diameter, it is necessary that it be replaced. In a typical marine engine of 8 to 16 cylinders such replacement cost may run in the order of several thousand dollars per cylinder. Wear of the piston and rings is also an expensive problem. Lubricants of this type should be able to minimize the wear due to corrosiveness caused by the degradation products of the oil and particularly of the sulfur. The lubricant should also be storage stable, even when subject to long periods of vibration as occurs during storage in a ship's engine room and in the presence of minor amounts of moisture.

A commercial lubricant, which found widespread acceptance for such marine diesel lubrication and which met the above requirements, is obtained by thickening mineral oil with mixed calcium salts af acetic acid and an intermediate molecular weight fatty acid, e.g. C_7 to C_{10} or C_{12}

fatty acids. Intermediate fatty acids that have been used include those available under the trade-name Wecoline AAC acid, which is a mixture of fatty acids derived from coconut oil comprising capric, caprylic and lauric acids. Using a molar ratio of about 12 moles of acetic acid (or 6 moles of acetic anhydride) per mole of the Wecoline AAC acid had proved to form a very successful lubricant. This prior lubricant within a short space of time obtained a very large share of the marine diesel lubrication market. It has now been found that marine diesel lubricants superior in several respects to those made from the Wecoline AAC and acetic acid, can be prepared by using an aminoalkyl phenol in place of part or all of the intermediate molecular weight fatty acid, i.e. the Wecoline AAC acid. By the use of the aminoalkyl phenol, marine diesel lubricants can be prepared which are superior to said intermediate fatty acid type lubricant by having a reduced tendency to gel under very hot and wet conditions. In addition, the aminoalkyl phenol results in a better dispersion of calcium acetate, excellent oxidation stability, etc.

Aminoalkyl phenols contemplated for use in the present invention are known, for example see U.S. Patents 2,353,491; 2,459,112 and 3,036,003. These materials can be prepared by reacting aldehyde, alkylene polyamine, and phenol or alkyl phenol. The reaction is preferably carried out in the presence of a mineral oil diluent. Generally, the reactants will be utilized in a ratio of about 0.5 to 2.0 moles of the aldehyde and the alkyl phenol for each nitrogen atom present in the polyamine. Whereas aldehydes in general are contemplated, preferred aldehydes will be the C_1 to C_{10} aliphatic aldehydes, such as formaldehyde, acetaldehyde, propionaldehyde, etc., with formaldehyde being especially preferred.

Alkylene polyamiens suitable in the above reaction include those characterized by the general formula:

$$H(HN—R)_nNH_2$$

wherein R is a substituted or unsubstituted C_2 to C_6 alkylene radical and n is an integer from 1 to 10. Representative amines within the above formula include diethylenetriamine, tetraethylenepentamine, ethylene diamine, propylene diamine, etc. Preferred polyamines are the alkylene diamines, with ethylene diamine being particularly preferred.

Other suitable amines include polymerized ethylene imines having a molecular weight of about 1,000 to 40,000.

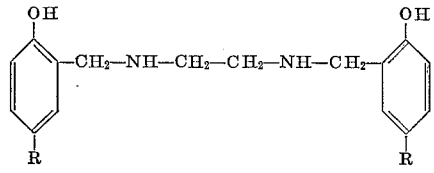
The alkylphenols are typified by at least one phenol nucleus having at least one alkyl group of 4 to 20, preferably 6 to 12, carbon atoms attached thereto. Examples of such compounds will include nonylphenol, isooctylphenol, dilaurylphenol, etc.

A typical reaction procedure involves adding the aldehyde compound to a mineral oil solution of alkyl phenol and the polyamine. The resulting mixture is heated to a temperature within the range of about 100 to 350, e.g. 160 to 200° F. and maintained at said temperature for about 1 to 4 hours. The final reaction mixture can then be further heated to a higher temperature, e.g., about 320° F., to remove any water which may be present.

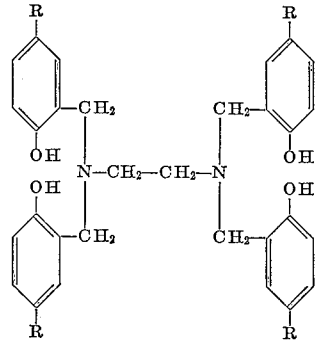
Other solvents, e.g. methanol, ethanol, isopropanol benzene, toluene, xylene, etc. can be readily utilized as the reaction diluent in place of the aforementioned min-

eral oil. Utilization of mineral oil is advantageous, however, since it eliminates the necessity of solvent stripping and final oil addition.

The reaction time, temperature, and relative mole ratios of the reactants may be readily varied to form a variety of similar compounds. For example, a preferred form of compound, believed to have the approximate general formula:



is prepared by reacting formaldehyde, an alkylphenol, and ethylene diamine in the relative mole ratios of 2 moles of both the alkylphenol and the aldehyde for each mole of the polyamine. An increase in this relative mole ratio will produce a mixture of compounds of varying degrees of hydrogen substitution on the amino groups. Thus, a utilization of the reactants in a ratio of 4 moles of both the alkylphenol and aldehyde for each mole of the polyamine will produce a reaction mixture which is believed to predominantly contain a compound having the approximate general formula:



The alkaline earth metal component of the mixed salt composition is preferably calcium since it results in the production of stable lubricants having load carrying and anti-wear characteristics even without the use of conventional extreme pressure and stabilizing agents. The other alkaline earth metals such as barium, strontium and magnesium can be used, but are not as good as calcium in these respects.

The anhydrous mixture of alkaline earth metal salts of the invention can be prepared by coneutralization of a mixture of the acetic acid and aminoalkyl phenol with suitable bases, particularly lime. The coneutralization step can be carried out in situ in the oil menstruum to which the mixture of salts is to be applied in actual use. The maximum temperature at which coneutralization is carried out, or the temperature to which the coneutralized material is heated, will generally be in the range of about 250° to about 350° F. The salt mixture is preferably heated until anhydrous, i.e. there is no free or unbound water present. It is generally desirable to use a slight excess of base, e.g. lime, in order to form a slightly alkaline final product, e.g. 0.05 to 0.2 wt. percent alkalinity as measured in terms of NaOH. This alkalinity acts to neutralize corrosive acids formed by degradation of the lubricant during use and also imparts greater stability to the lubricant.

The mixture of alkaline earth metal salts of the invention can also be prepared by separately preforming the salt of the aminoalkyl phenol, then forming the acetate salt by neutralization in the presence of the aminoalkyl phenate, then heating under substantially dehydration conditions.

The mixed salt lubricants of the invention can be prepared by using 1 to 100, preferably 5 to 40, mole

equivalents of acetic acid or acetic anhydride per mole equivalent of aminoalkyl phenol. For lubricants designed for marine diesel lubrication, good results are obtained by using a ratio of about 10 to 15, e.g. 12, mole equivalents of the acetic acid or its anhydride per mole equivalent of aminoalkyl phenol.

The finished lubricant will generally be a fluid or semi-fluid comprising a major amount of lubricating oil and about 3 to 20, preferably 5 to 12 wt. percent of the mixed salt combination. For economy purposes in heating during large scale manufacture, concentrates of 20 to 45 wt. percent of the mixed salts in oil can be made by the in situ technique, after which the concentrate is diluted with additional oil to form the finished lubricant. This dilution is readily made by adding the additional oil and mixing. Both the concentrate and finished lubricant can be homogenized in a Morehouse mill, Charlotte mill, Gaulin homogenizer etc. If enough of the mixed salt is used in the oil a soft solid grease is obtained. However, these greases do not seem to have very good structural stability. As a result, the mixed salt composition of the invention is preferably used in the form of fluid or semi-fluid lubricant.

Mineral oil is the preferred lubricating oil, although various synthetic oils such as polysilicone, silanes, esters, Ucons, etc. may be used for special uses.

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 stearin; antioxidants such as phenyl-alpha-naphthylamine; extreme pressure agents; dyes; etc.

The invention will be further understood by references to the following examples which include preferred embodiments of the invention.

EXAMPLE I

(All parts by weight)

Part A.—Preparation of aminoalkyl nonylphenol

30.3 parts of commercial nonylphenol was dissolved in a mineral lubricating oil having a viscosity of 150 SSU at 100° F. 3.6 parts of ethylene diamine (98% purity) was then rapidly added to the oil solution and the resulting mixture was heated to about 180° F. with stirring. 3.8 parts of paraformaldehyde (95% purity) was then gradually added over a period of about one hour while still maintaining a temperature within the range of about 190° to 200° F. Following this, the reaction mixture was then aged at a temperature within said temperature range for a period of about 3 hours. The reaction mixture was dehydrated by heating to a temperature of about 320° F. and sparged with dry nitrogen gas. The finished material was a 40 wt. percent solution of aminoalkyl nonylphenol in 60 wt. percent of oil of 150 SSU viscosity at 100° F.

The aminoalkyl nonylphenol used above was a commercial product consisting of about 75 wt. percent monononyl phenol and about 25 wt. percent of a mixture which was predominantly di-nonyl phenol with a small amount of phenol. The nonyl groups were derived from triisopropylene.

Part B.—Preparation of grease concentrate

10.2 parts of hydrated lime and 64.8 parts of mineral lubricating oil of 80 SSU viscosity at 210° F. were added to a steam-jacketed grease kettle and intimately mixed to a smooth slurry. While stirring, 3 parts of the oil solution of the aminoalkyl nonylphenol of Part A was added to the kettle. Next, 16 parts of glacial acetic acid was added to the kettle slowly while maintaining the temperautre of the grease composition below 200° F. After all of the acetic acid had been added, the batch was then passed through a Morehouse mill in order to obtain more thorough mixing. After passage through the Morehouse mill, the composition was returned to the grease

kettle and then 6 parts of the oil solution of aminoalkyl nonylphenol of Part A was added to the composition. The temperature of the kettle contents was raised to 205° F. and a small amount of additional lime was added to bring the free alkalinity to 0.28 wt. percent calculated as NaOH. The composition was then heated to a temperature of 320° F. which was held for 20 minutes following which the product was cooled to about 100° F. where it was again passed through the Morehouse mill. The product was an excellent, smooth grease composition having a free alkalinity of 0.15% calculated as NaOH.

Part C

A finished lubricant was obtained by mixing 25 wt. percent of the product of Part B above with 75 wt. percent of additional mineral lubricating oil of 80 SUS @ 210° F. By this dilution the final product was obtained.

The properties of the final product are summarized in Table I which follows:

TABLE I

Properties:

Appearance	Fluid, dark
Viscosity, SSU—	red, smooth.
100° F.	1360.
210° F.	86.
4-Ball Wear test, scar diameter (1800 r.p.m., 1 hour, 75° C., 10 kg. load)	0.23 mm.
Screen test, 100 mesh	No residue.
Sulfated ash, percent	5.05.
Free alkalinity as NaOH	0.08 wt. percent.

EXAMPLE II

Using the same technique as that of Example I, a second lubricant was prepared having a molar ratio of acetic acid to aminoalkyl nonylphenol of 12:1. The product of Example II was compared with a commercial marine diesel lubricant using mixed metal salts of acetic acid and coconut acids. The formulations of the compositions and their properties are summarized in Table II which follows:

TABLE II

Formulation (Wt. Percent)	Example II	Commercial Lubricant
Acetic acid (glacial)	3.75	3.84
Hydrated Lime	2.50	2.70
Aminoalkyl nonylphenol concentrate [1]	7.75	
Wecoline AAC acid		0.93
Mineral lubricating oil (80 SUS at 210° F.)	86.00	92.33
Phenol-α-naphthylamine		0.2
Properties:		
Sulfated Ash, percent	4.75	5.15
SUS Vis.—		
100° F	1,518	1,787
210° F	92.8	138.8
275° F	52.3	74.7
275° F. (after 4 hr. soaking)	52.4	73.2
300° F	46.5	68.0
300° F. (after 4 hr. soaking)	47.2	81.5
Centrifuge Solids, vol. percent (4 hrs.)	0.9	0.8
4-Ball Wear Scar Diam. (mm.)	0.22	0.3
100 Mesh Screen	Pass	Pass
Manzell Lubricator, days	100+	18
ase No. ASTM D664	[2] 37.8	[2] 29.6
Thermal Stability Test—		
150° C	[3]	[3]
190° C	[3]	[4]

[1] 40 wt. % aminoalkyl nonylphenol in 60 wt. percent oil.
[2] Mg. KOH/gm.
[3] No gel.
[4] Gel.

As seen by Table II above, the product of Example II showed very little change in viscosity upon heat soaking. For example, the product of Example II had a viscosity of 46.5 SUS at 300° F., while the same sample after being heat soaked for 4 hours at 300° F. had a viscosity of 47.2 SUS. On the other hand, the commercial lubricant increased in viscosity from 68 SUS to 81.5 SUS after 4 hours of heat soaking at 300° F. A minimum change in viscosity upon heat soaking is desired since the lubricant may be in lubrication lines near the hot engine for a considerable length of time. The product of Example II gave a wear scar diameter of 0.22 mm. in the 4-Ball Wear Test (1800 r.p.m./1 hour/75° C./10 kg. load). Both the commercial lubricant and the product of Example II completely passed through a 100 mesh screen without leaving any residue.

The Manzell lubricator test of Table II is 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 20 wt. percent of 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 product of Example II went for over a 100 day trial without fogging the sight-glass. On the other hand, the commercial lubricant went for only 14 days before the sight-glass had become sufficiently fogged so as to require disassembling and cleaning.

The base number of Table II indicates that both the product of Example II and the commercial lubricant had good reserve alkalinity for neutralizing the aforementioned sulfur corrosive compounds, e.g. sulfuric acid, which forms upon combustion of the fuel oil. Thus, the alkalinity of the product of Example II was equivalent to 37.8 mg. KOH per gram of product.

The Thermal Stability test is carried by filling an ASTM pour point jar ¾ full with the lubrciant to be tested. The test lubricant is heated for four hours and is then cooled for 45 minutes. The jar is then examined to see if the lubricant has gelled. It is seen that at the 190° C. heating level, that the commercial lubricant had gelled while the product of Example II 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. For example, a cylinder at a temperature of 190° C., when hit by the commercial lubricant of Table II would cause the lubricant to gel so as to interfere with the spreadability of the lubricant along the cylinder walls. On the other hand, the product of Example II will not form a gel at this temperature and as a result will remain fluid so that it can rapidly spread along the cylinder to more evenly wet the cylinder with the lubricant.

EXAMPLE III

Part A.—Preparation of calcium aminoalkyl nonylphenyl

30.3 parts of nonyl phenol (same as used in Example I) was dissolved in a mineral oil having a viscosity of 150 SSU at 100° F. 3.6 parts of ethylene diamine (98% purity) was added. The resulting mixture was heated to about 180° F. with stirring. 3.8 parts of paraformaldehyde (95% purity) was then gradually added over a period of about one hour while maintaining a temperature within the range of about 190° to 200° F. The reaction mixture was then aged at a temperature within said 190° to 200° F. temperature range for a period of about 3 hours. 6.1 parts of lime was added over about a one hour period while stirring and maintaining a 190–195° F. temperature. The reaction mixture was then aged for an additional hour while stirring. About 70 p.p.m. of a silicone antifoamant was added. The reaction mixture was dehydrated by heating to a temperature of about 320° F. while blowing with dry nitrogen gas. The mixture was then filtered while hot (about 300° F.), using a filter aid, to remove excess calcium hydroxide and other insoluble materials. A clear, dark, reddish-brown material was produced.

Part B.—Preparation of grease concentrate

10.77 parts of hydrated lime and 30.96 parts of mineral lubricating oil of 80 SUS viscosity at 210° F. were added to a steam-jacketed grease kettle and intimately mixed to a smooth slurry. While stirring, 39.2 parts of the oil solution of the calcium aminoalkyl nonylphenol of Part A was added to the kettle. Next, 19 parts of glacial acetic acid was added to the kettle slowly while maintaining the temperature of the grease composition below 200° F.

Part C

A finished lubricant was obtained by adding to the product of Part B above, additional mineral lubricating oil of 80 SUS @ 210° F.

The composition and properties of the finished lubricant are summarized in Table III which follows:

TABLE III

Formulation (parts by weight):	
Acetic acid (glacial)	4.3
Hydrated lime	2.46
Calcium aminoalkyl nonylphenol concentrate[1]	8.97
Mineral oil, 80 SUS at 210° F.	84.23
Properties:	
Appearance	(2)
Viscosity, SSU	(2)
100° F.	1486
210° F.	97.5
Sulfated ash, percent	5.24
Free alkalinity as NaOH	0.02

[1] Product of Example III, Part A.
[2] Fluid, dark red, smooth.

What is claimed is:

1. A lubricant suitable for lubrication of marine diesel engines comprising a major amount of mineral lubricating oil and about 5 to 12 wt. percent of anhydrous mixed calcium salts of acetic acid and aminoalkyl phenol in a ratio of 10 to 15 molar equivalent proportions of acetic acid per molar equivalent proportion of aminoalkyl phenol, said anhydrous mixed salts being prepared by dehydrating by heating a mixture of calcium salt of said aminoalkyl phenol and acetic acid neutralized with lime

in situ in said oil, said aminoalkyl phenol being the condensation reaction product of aldehyde, polyamine and a phenol reacted in a molar proportion of about 0.5 to 2.0 moles of aldehyde per nitrogen atom present in the polyamine and about equi-molar proportions of aldehyde and phenol, wherein said aldehyde is a C_1 to C_{10} aldehyde, wherein said polyamine is selected from the group consisting of polyamines of the general formula:

$$N(NH—R)_nNH_2$$

wherein R is a C_2 to C_6 divalent hydrocarbon radical and n is an integer of 1 to 10, and polymers of ethylene imine having a molecular weight of about 1,000 to 40,000 and wherein said phenol is selected from the group consisting of phenol and alkyl phenols having 4 to 20 carbon atoms in each alkyl group.

2. A lubricant according to claim 1, wherein said aldehyde is formaldehyde, said polyamine is ethylene diamine, and said phenol is nonylphenol.

3. A marine diesel lubricant consisting essentially of mineral lubricating oil and about 5 to 12 wt. percent anhydrous co-neutralized and co-dehydrated calcium salts of about 10 to 15 mole equivalent proportions of acetic acid and a mole equivalent proportion of an aminoalkyl alkylphenol prepared by the reaction of molar proportions of formaldehyde and nonyl phenol further reacted with a one-half molar proportion of ethylene diamine.

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