United States Patent Office 2,976,243 Patented Mar. 21, 1961

2,976,243

STABLE CALCIUM ACETATE-MINERAL OIL DISPERSION

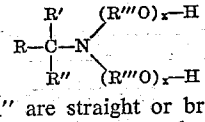
Arnold J. Morway, Clark, N.J., and John O. Smith, Jr., Swampscott, Mass., assignors to Esso Research and Engineering Company, a corporation of Delaware

No Drawing. Filed Nov. 1, 1957, Ser. No. 693,820
7 Claims. (Cl. 252—40.7)

This invention relates to lubricating oil compositions containing stabilized dispersions of calcium acetate. Particularly, it relates to lubricating oil compositions containing calcium acetate and a tertiary alkyl amine as a stabilizing agent.

Simple dispersion of calcium acetate, in lubricating oil, imparts load-carrying ability and anti-wear properties to the oil. But, simple dispersions of this type are unstable and upon storage the metal salt settles out of the composition. One proposed method of forming more stable lubricants is by emulsifying a water solution of calcium acetate into lubricating oil. However, such emulsions are not completely satisfactory since they are rather corrosive because of their water content and are still somewhat unstable, tending to separate upon storage over long periods. It had also been proposed to dehydrate the emulsion type of material. While this reduces the danger of corrosion, it still results in an unstable product and unless the dehydration is carefully controlled, a grainy unsatisfactory dispersion results. It has now been found that dispersions of calcium acetate in lubricating oil may be stabilized with a small quantity of certain amines. Such dispersions are relatively inexpensive, and yet because of their calcium acetate content, they have extremely good load-carrying and anti-wear properties. Furthermore, not only does the amine material function as a stabilizing agent, but it also acts as an antioxidant to inhibit degradation of the oil. In this manner, either grease compositions or fluid lubricants can be formed. Such greases can be used for general purpose lubrication, such as, ball and roller bearings, automotive chassis lubrication and other industrial applications. The fluid type lubricants can be used in the crankcase of internal combustion engines, and for lubricating the upper cylinders of marine diesel engines. Because of their high content of metal salt and corresponding acid-neutralizing ability, they are particularly useful when the engine is operating on an acid forming fuel, such as the high sulfur-content diesel fuels currently coming into favor for marine diesel use.

The amines used as stabilizers include tertiary alkyl primary amines and tertiary alkyl polyalkyleneoxy amines. These materials may be represented by the general formula:



wherein R, R′, R″ are straight or branched-chain alkyl radicals of 1 to 18 carbon atoms, the sum of R, R′ and R″ being about 16 to 36, e.g. 17 to 23 carbon atoms; R‴ is a C_2 to C_4 aliphatic hydrocarbon radical and x is 0 to 10.

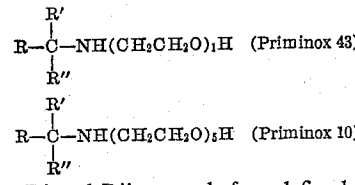
When x of the above formula is 0, then the formula represents tertiary alkyl primary amines. Such amines can be prepared from tertiary olefins, e.g. the various polymers of propylene and isobutene; copolymers of propylene and isobutene; copolymers of isobutene and butenes or pentenes; etc. Such polymers 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. A commercial amine material of this general type is manufactured by Rohm and Haas and is a mixture of C_{18-24} tertiary alkyl primary amines. This commercial material is available under the trade-name Primene JM–T and was used in several examples of the invention.

Specific examples of other 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

When at least one x of the above formula is one or greater, the formula represents tertiary alkyl polyalkyleneoxy amines. These materials are prepared by reacting an alkylene oxide (e.g. ethylene oxide, propylene oxide or butylene oxide) with any of the tertiary alkyl primary amines described above. Products of this type are also commercially available. Examples of such commercial materials include:



wherein R, R′ and R″ are as before defined.

The lubricating oil used in the compositions of the invention may be either a mineral lubricating oil or a synthetic lubricating oil. If synthetic oils are used, they are preferably used with a major amount of mineral oil. Synthetic oils which may be used include esters of monobasic acids (e.g. C_8 oxo alcohol ester of C_8 oxo acid), esters of dibasic acids (e.g. di-2-ethyl hexyl sebacate), esters of glycols (e.g. C_{13} oxo acid diester of tetraethylene glycol), complex esters, esters of phosphoric acid, halocarbon oils, silicones, polyglycol type synthetic oils; etc. or mixtures of any of the above in any proportions.

The lubricating compositions of this invention will therefore comprise a major proportion of lubricating oil, about 2.5 to 30, e.g. 3.0 to 8.0 weight percent of calcium acetate and about 0.1 to 10.0, e.g. 0.5 to 5.0 weight percent of tertiary alkyl primary amine. Where a grease is desired, then about 20 to 30 weight percent of the metal salt and about 1.0 to 5.0 weight percent of the amine is used, while the fluid lubricants will generally contain about 2.5 to 8.0 weight percent salt and 0.5 to 5.0 weight percent amine. All of said weight percents being based on the weight of the total composition.

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 oxidation inhibitors such as phenyl alpha naphthylamine; viscosity index improvers such as polyisobutylene; corrosion inhibitors such as sorbitan monooleate; pour depressants; dyes; detergents and the like.

Generally, the compositions of the invention will be prepared by neutralizing lime or calcium oxide with acetic acid or acetic anhydride in the presence of lubricating oil or other inert liquid dispersant. The mixture may then be heated to about 250 to 500° F. sufficient to at least evaporate any free water. The amine may also be present during this neutralization step or it may be added later. A preferred method consists of dispersing

lime and the amine in the lubricating oil followed by addition of acetic acid or its anhydride. The mixture is then heated to a temperature of about 300 to 500° F. until complete dehydration occurs, i.e. anhydrous calcium acetate is formed. The product may then be cooled while stirring and any conventional additives can be added. The mixture may then be homogenized by passing it through a Gaulin homogenizer, a Charlotte mill, a Morehouse mill, etc. The mixture may be cut back with additional lubricating oil to form the final lubricant product which is further homogenized. The lubricating compositions may also be formed by simple mixing of calcium acetate and the amine into lubricating oil. However, this latter method is not preferred because of the difficulty of obtaining a fine dispersion of the calcium acetate.

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

EXAMPLE I

A grease composition was prepared from the following ingredients:

Formulation	Percent Weight
Glacial acetic acid	25.0
Hydrated lime	17.0
Primene JM-T(C_{18-24} tert. alkyl primary amines)	2.0
Mineral lubricating oil of 80 SUS. viscosity at 210° F.	56.0

The lime, Primene JM–T, and lubricating oil were intimately mixed in a steam kettle. The acetic acid was then slowly added while mixing, the temperature during this time rising to about 220° F. with the formation of a heavy solid lubricant. Mixing was continued for an additional ½ hour and then heating was initiated to raise the temperature to about 320° F. This temperature was maintained for about 30 minutes in order to insure complete dehydration of the mixture and formation of anhydrous calcium acetate. The mixture was then cooled, while stirring, to about 100° F. after which it was passed through a Gaulin homogenizer operating at about 6000 p.s.i. shear.

EXAMPLE II

20 weight percent of the final product of Example I was blended with an additional 80 weight percent of the mineral lubricating oil used in Example I. This blend was twice passed through a Gaulin homogenizer operating at 6000 p.s.i.

The properties of the products of Examples I and II are summarized in the following table:

Table I

	Example I	Example II
Properties: Appearance	Thixotropic smooth uniform product. Sets to a soft solid on standing at rest but fluidizes on exertion of shearing stress.	Excellent fluid, homogeneous lubricant.
Stability		No sign of separation on 15 day storage.
Viscosities (Ubbe), Saybolt Seconds— Vis./100° F.		1,247.2
Vis./210° F.		128.7 (V.I. 122).
4-Ball Wear Test (1800 r.p.m.—10 kg. Load—75° C.—1 Hour) Scar dia. in mm	0.26	0.23.
Almen Test		15 wts. gradual loading, Pin condition—excellent.

As seen from the above table, either greases or fluids having excellent anti-wear properties may be prepared, which contain anhydrous calcium acetate as the sole salt component. By using the amine materials of the invention as stabilizing agents, the use of salts of higher monocarboxylic acid, e.g. calcium stearate, in order to maintain the calcium acetate suspended, is avoided.

EXAMPLE III

A product containing 6.0 weight percent of calcium acetate, 1.0 weight percent of the C_{18-24} tertiary alkyl primary amine mixture (Primene JM–T) and 93.0 weight percent of a mineral lubricating oil having a viscosity of 65 SUS at 210° F. was prepared in the manner of Example II, i.e. by first forming a concentrate of the calcium acetate in situ and then blending it with additional oil. This product 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 one 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 was summarized in the following table along with comparable data on a solvent extracted Mid-Continent base stock used in a commercial heavy duty premium oil.

Table II

CATERPILLAR ENGINE PERFORMANCE (120 HOURS)

Lubricant	Demerit Ratings RZ [1]	Demerit Ratings RZ–1 [2]	Percent C, TRG [3]	Top Ring Weight Loss, mg.
Base Oil used in commercial HD–30W crankcase oil	3.0	2.8	-------	1,100
6.0% calcium acetate, 1.0% C_{18-24} t.alkyl primary amines, 93.0% Mineral oil	0.6	0.6	0.5	300

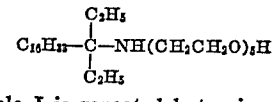
[1] Total ring zone area.
[2] Area below top ring groove.
[3] Top ring groove.

The results summarized in Table II illustrate that the compositions of the invention can serve as crankcase lubricants, having low deposit forming tendencies and yet at the same time substantially reducing wear.

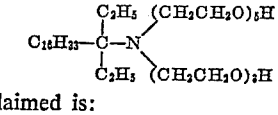
To further illustrate the invention, other compositions can be prepared as follows:

(A) Example I is repeated but using 2.0 weight percent of 5-amino-5,13-dimethyl-hexadecane in place of the 2.0 wt. percent of Primene JM–T.

(B) Example I is repeated but using 5.0 weight percent of an amine of the formula:

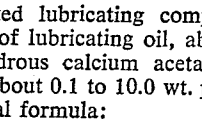


(C) Example I is repeated but using 5.0 weight percent of an amine of the formula:



What is claimed is:

1. A dehydrated lubricating composition comprising a major portion of lubricating oil, about 2.5 to 30.0 wt. percent of anhydrous calcium acetate as the sole salt component and about 0.1 to 10.0 wt. percent of an amine having the general formula:



wherein R, R′ and R″ are C_1 to C_{18} alkyl radicals, and R, R′ and R″ combined contains a total of 16 to 36

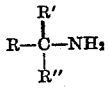
carbon atoms, R''' is a C_2 to C_4 aliphatic hydrocarbon radical and x is 0 to 10.

2. A dehydrated lubricant according to claim 1, wherein said lubricating oil is a mineral oil.

3. A dehydrated lubricant according to claim 1, wherein said amine is a tertiary alkyl primary amine.

4. A dehydrated lubricant according to claim 1, wherein said amine is a tertiary alkyl polyalkyleneoxy amine.

5. A fluid dehydrated lubricating oil composition comprising a major portion of lubricating oil, about 2.5 to 8.0 wt. percent of anhydrous calcium acetate and about 0.5 to 5.0 wt. percent of an amine having the general formula:

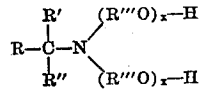


wherein R, R' and R'' are C_1 to C_{18} alkyl radicals, and R, R' and R'' combined contain a total of 16 to 36 carbon atoms.

6. A dehydrated lubricating oil composition according to claim 5, wherein R, R' and R'' combined contains a total of 17 to 23 carbon atoms.

7. A method of preparing a stable dehydrated lubricating composition comprising a major portion of lubricating oil and containing calcium acetate as the sole salt

component, which comprises neutralizing lime in said lubricating oil with a material selected from the group consisting of acetic acid and acetic acid anhydride, in the presence of a stabilizing amount of an amine having the general formula:



wherein R, R' and R'' are C_1 to C_{18} alkyl radicals, and R, R' and R'' combined contains a total of 16 to 36 carbon atoms, R''' is a C_2 to C_4 aliphatic hydrocarbon radical and x is 0 to 10.

References Cited in the file of this patent

UNITED STATES PATENTS

2,079,051	Sullivan et al.	May 4, 1937
2,744,870	Stillebroer et al.	May 8, 1956
2,854,410	Bidault	Sept. 30, 1958

OTHER REFERENCES

Georgi: Motor Oils and Engine Lubrication, Reinhold Pub. Corp., New York, N.Y., 1950, page 170.

"Tertiary-Alkyl Primary Amines," pub. by Rohm and Haas Co., September 1954, page 16.