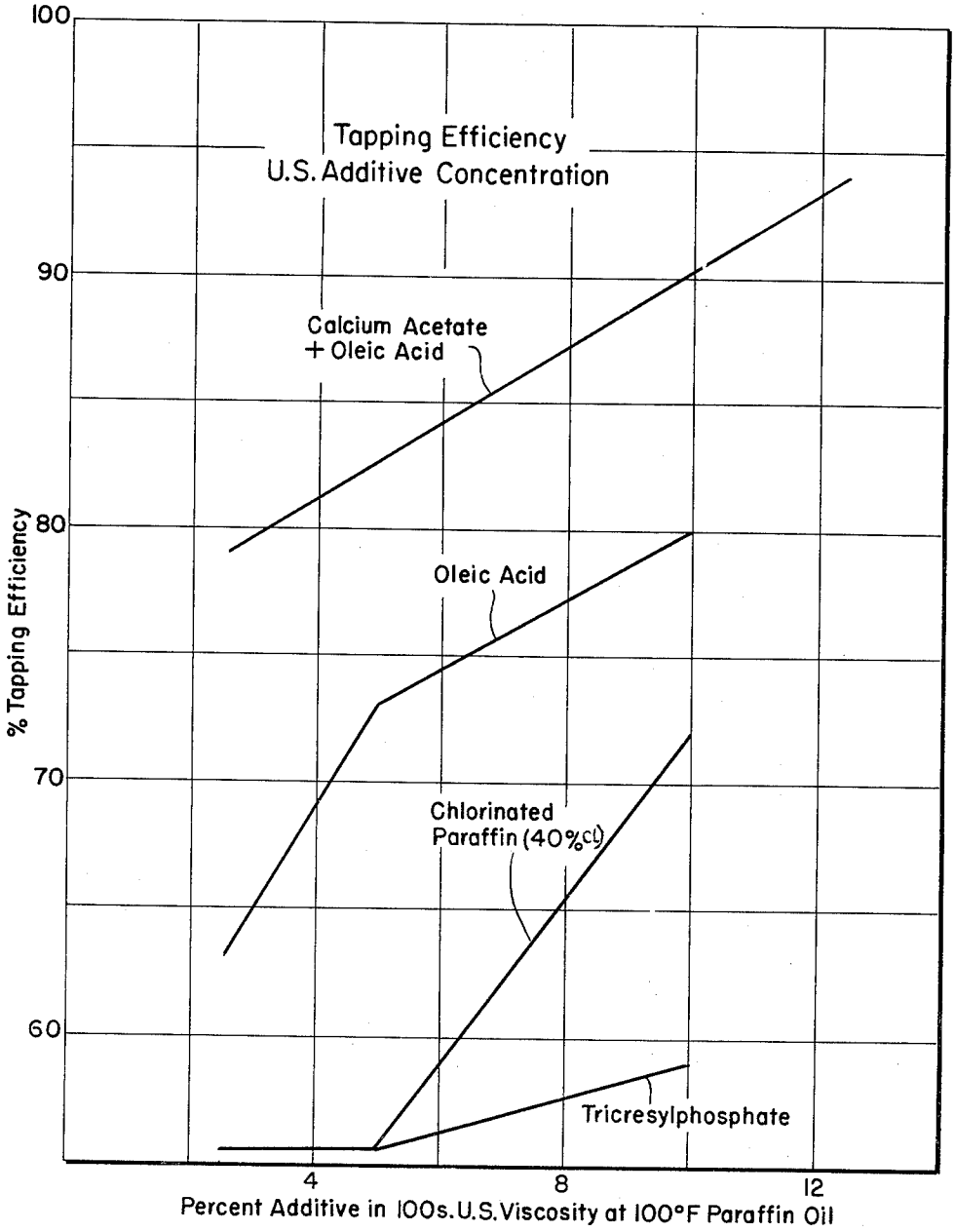
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LUBRICANT COMPOSITION CONTAINING DISPERSED CALCIUM ACETATE

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INVENTOR.
Robert H. Davis

BY Charles D. Haugett
ATTORNEY

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LUBRICANT COMPOSITION CONTAINING DISPERSED CALCIUM ACETATE

Robert H. Davis, Woodbury, N.J., assignor to Socony Mobil Oil Company, Inc., a corporation of New York

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This invention relates to lubricating oil formulations haivng the ability to carry heavy loads and operate under extreme pressure conditions without being corrosive to metals. This invention particularly relates to a lubricant formulation containing calcium acetate in the form of a stable dispersion in lubricating oil.

It is known that calcium acetate imparts load-carrying ability to lubricating oil compositions but unfortunately is not soluble in lubricating oil and hence separation occurs. The lubricant formulation, therefore, soon loses its extreme pressure properties in use as the calcium acetate separates in the system. The calcium acetate is abrasive and damages the lubricating system, particularly the circulating pump, to such an extent that the calcium acetate cannot normally be used in lubricant formulations in the form of a slurry.

Various methods have been attempted to maintain calcium acetate dispersed in a lubricating oil but these methods have been found more or less defective. For example, emulsifiers have been tried to provide the lubricant formulation as an oil-water dispersion. In many instances, of course, water is not desired in the lubricant formulation. Furthermore, the emulsion breaks under extreme operating conditions, frequently rendering the composition unable to sustain its load carrying capacity. Other suspending aids have been tried but have been found defective for one reason or another.

It was first established that gross calcium acetate suspensions were as effective on the tapping test as on the 4-ball and other extreme pressure testers. Once this was determined the calcium salts of homologous fatty acids were tested to determine if any were better than acetate. The results are reported on the basis of tapping efficiency. In the measurement of tapping efficiency of an oil, a series of holes is accurately drilled in a test metal, namely, S.A.E. 1020 hot rolled steel. These holes are subsequently tapped with a series of taps in a drill press equipped with a table, which is free to rotate about the center, being mounted on ball bearings. A torque arm is attached to this "floating" table and this arm in turn actuates a spring scale so that the actual torque during tapping with the oil being evaluated is measured directly. The same taps used in evaluating the test oil are employed in tapping with a standard reference oil, which has arbitrarily been assigned an efficiency of 100 percent. The average torque for the test oil is compared to that of the standard and a relative efficiency is calculated on a percentage basis. For example:

	Percent
Torque with standard reference oil	19.3
Torque with test oil	19.8

Relative efficiency of test oil—

$$\frac{19.3}{19.8}\times 100 = 97.4\%$$

This test is described in Lubrication Engineering, vol. 12, No. 3, May-June 1956, pages 199–203. The base reference oil selected was a heavy duty corrosive type having the following characteristics:

Visc. @ 100° F., S.U.S.	55–200.
Added sulfur, percent	0.0–1.5.
Active sulfur, percent	0.2–1.3.
Chlorine, percent	0–1.
Lubricity additive, percent	0.5–3.
Copper corrosion (3 hrs. @ 212° F.)	Blackens copper strip.

The comparative performance data of the various calcium salts tested against the reference oil is shown in Table I hereinbelow as follows:

TABLE I

Performance Data—Suspensions of Calcium Salts in 100 Sec. Paraffinic Oil

Salt	Concentration Weight	Tapping Efficiency, Percent Ref. Oil=100%
Calcium Formate	20	104
Calcium Acetate Monohydrate	20	104
Calcium Propionate	20	99
Calcium Caprylate	20	76.2

It is apparent from the Table I above that calcium acetate and calcium formate were the most effective salts on a percent weight basis. These data correlate with the 4-ball weld tests run on similar samples.

The figure shows a plot of tapping efficiency vs. additive concentration for several additives including a mixture of calcium acetate and oleic acid.

I have discovered that straight-chain carboxylic acids are useful in solubilizing calcium acetate in lubricating oil to form a stable lubricant. Of these acids the C_{18} unsaturated acids, such as oleic, linoleic and linolenic acids, are outstanding forming clear-hazy solutions with up to 40 percent calcium acetate, provided a sufficient amount of the solubilizing acid is used. The other straight-chain carboxylic acids form lubricants suitable as way lubricants, wire drawing lubricants, gear oils or other specialty lubricants wherein relatively high viscosity or excessive body are not detrimental factors. The compositions comprise between .005–40% by weight of the calcium acetate, .005–10.0% by weight of the straight-chain carboxylic acid and the balance largely lubricating oils, although very minor amounts of corrosion inhibitors, antioxidants and other specific additives may be present without detracting from the usefulness of the composition. A concentrate may first be formed for dilution with mineral oil. This concentrate may contain .005–40% by weight of the calcium acetate and .005–80% by weight of the straight chain carboxylic acid, the balance being oil.

A list of acids evaluated as dispersants is shown in Table II along with stability data. The base formula and method of preparation was as follows.

Formula:

	Percent wt.
Calcium acetate powder purified [1]	10
Organic acid	2.5
Mineral oil	87.5

[1] Obtained from Baker & Adamson Chem. Co. Their data sheet indicates a typical analysis as follows.

Assay:

	Percent
$Ca(C_2H_3O_2)_2 \cdot H_2O$	99.5
Chloride (Cl)	0.01
Sulfate (SO_4)	0.10
Heavy metals (as Pb)	0.001
Iron (Fe)	0.002

Method of preparation (100 gm. batch): A concentrate was prepared which contained the acetate, acid and approximately 20 gms. of oil; this concentrate was heated with agitation to 280° F. At this point, the remaining oil, preheated to 250° F. was added and the dispersion was stirred until cool. It should be noted, however, that the method of preparation and ratio of acid to acetate used will vary with type of acetate used; type of finished product desired and available equipment.

For example, if an extremely tacky, polymeric product is desired (as opposed to the free flowing dispersions described in "Method of Preparation" above) for use as a V.I. improver or gear oil additive, I would use a ratio of one part calcium acetate (Baker and Adamson Chemical Company purified grade—heated 5 hours at 425° F.) and two parts oleic acid stabilizer in mineral oil. This mixture would be heated to 270–350° F. with agitation.

A polymeric dispersion of hydrated calcium acetate can be prepared by first dissolving the calcium acetate in water and allowing the water to evaporate. The hydrated calcium acetate is then mixed with oleic acid and mineral oil to produce a concentrate, using only about one-half of the mineral oil of the final product, and the concentrate is allowed to stand for 10–15 hours. The concentrate is then heated to 200° F. and the balance of the mineral oil is added to produce a final formulation of 10% by weight of the hydrated calcium acetate, 2.5% by weight of oleic acid and 87.5% by weight of mineral oil.

TABLE II

Organic Acids Evaluated as Dispersants for Calcium Acetate

Acid	Percent Wt. Acid Used to Disperse 10% $Ca(Ac)_2.H_2O$	Moles Acid Used to Disperse 1 Mole $Ca(Ac)_2.H_2O$	Stability of Suspension, 2 Weeks' Storage
Stearic	2.5	0.157	Cloudy—Gel.
Oleic	2.5	0.157	Slight Haze, Fluid.
Palmitic	2.5	0.173	Cloudy.
Linoleic	2.5	0.159	Haze, Fluid—Higher Visc. Than Oleic Sample.
Myristic	2.5	0.195	Haze, Highly Thixotropic.
Caprylic	2.5	0.311	Gel.
2-Ethylhexanoic	2.5	0.311	Precipitation.
None [1]			Do.

[1] An attempt was also made to stabilize hydrated calcium acetate (prepared by dissolving B and A acetate in water and allowing water to evaporate at room temperature) in 100 sec. paraffinic oil by passing the acetate-oil slurry through a homogenizer @ 6000 p.s.i. (5 passes). Precipitation occurred after ½ hour at room temperature.

It is noted from Table II that all the straight-chain carboxylic acids were effective in solubilizing or stabilizing calcium acetate. However, the C_{18} unsaturated acids were unusual in providing a fluid product. These formulations provide a suitable lubricant formulation where fluidity is essential. Of course, the other formulations find application as a lubricant where fluidity is not essential such as in lubricating the ways for ship launching, wire drawing, gear oils, etc.

The amount of oleic acid was varied from 2.5% by weight to 10% by weight while the calcium acetate content was retained at 10% by weight. These tests indicated that the viscosity increased markedly with increasing concentration of oleic acid, the viscosity at 10% oleic acid being double that at a concentration of 2.5%. Where viscosity is a factor, therefore, such as in metal cutting oils, the oleic acid to calcium acetate ratio should not be raised above about 1 part oleic acid to 4 parts calcium acetate. It was found from these tests that the system becomes less stable when the oleic acid to calcium acetate ratio is lowered below about one part oleic acid to stabilize 4 parts of calcium acetate. Using this ratio it is possible to prepare dispersions in mineral oil which will remain stable for prolonged periods of time. This

is quite unusual since the amount of dispersant necessary is extremely low on a mole basis, i.e., 0.157 mole oleic/mole of acetate.

An extensive evaluation was made of various alcohols, amines, other types of acids, and surface active agents to determine the solubilizing effect of these agents on calcium acetate but they failed to show the favorable results exhibited by straight-chain, carboxylic acids. With the knowledge, therefore, that straight-chain, carboxylic acids disperse calcium acetate providing a stable composition, a study was made of the effect of variation of the oleic acid-calcium acetate ratio and variations in the percentage of solubilized calcium acetate on performance using the tapping test for comparative purposes. These data are reported in Table III as follows:

TABLE III

The Effect of Change in Oleic-Acetate Ratio on Performance

Percent Oleic Acid	Percent Calcium Acetate	Percent 100" Paraffinic Oil	Tapping Efficiency
1	10	89	95.0
2.5	10	87.5	93.9
5	10	85	89.3

It is seen that tapping efficiency is maximum with the minimum amount of oleic acid, although the fall off in tapping efficiency is small with increase in oleic acid concentration. The percent of each constituent in Table III is given on a percent by weight basis.

A series of tests were conducted using salts other than calcium to indicate the dispersing power of straight-chain, organic acids with respect to these salts. The results of these tests are reported in Table IV hereinbelow:

TABLE IV

Suspension of Salts by Oleic Acid Using 1:4 Ratio of Oleic Acid to Metallic Acetate

Salt	Conc. Percent Wt. 100" Paraffinic Oil	Stability
Calcium Formate	10	Precipitation.
Calcium Oxalate	10	Do.
Calcium Propionate	10	Do.
Calcium Caprylate	10	Do.
Barium Acetate	10	Do.
Magnesium Acetate	10	Do.
Sodium Acetate	10	Do.

It is seen from the above that only calcium acetate could be readily dispersed using a 1:4 ratio of oleic acid to calcium acetate.

Test work was conducted using 10% calcium acetate, 2.5% oleic acid and 87.5% mineral oil with the base mineral oil changed to provide results of all different types of base oils. It was found that best results were obtained using a paraffin base oil, which yielded a clear dispersion. On the other hand, the use of an aromatic base oil results in a dispersion that is cloudy, but still effective for many lubricating purposes.

The oleic acid-calcium acetate formulation in paraffin base oil makes an excellent non-corrosive cutting oil which contains none of the conventional extreme pressure additives which are for many reasons undesirable but tolerated only to obtain cutting efficiency. This oil formulation has a tapping efficiency of 90% or better, which previously could not be obtained without the use of compounds such as sulfur, chlorine, etc.

Retaining a ratio of 1 part acid to 4 parts acetate a series of tests was conducted using an increasing amount

of calcium acetate by weight. These data are reported in Table V as follows:

TABLE V

Percent Calcium Acetate vs. Performance

Percent Calcium Acetate	Percent Oleic Acid	Percent 100" Paraffinic Oil	Tapping Efficiency
2	0.5	97.5	78.7
5	1.25	93.75	84.7
10	2.5	87.5	93.9
20	5.0	75	96.1

Percent dispersed additive vs. tapping efficiency has been plotted in the figure. This graph also shows the tapping efficiency for several typical cutting oil additives. It is quite apparent from this data that dispersed calcium acetate is considerably superior to all of these compounds. The calcium acetate was blended with one-fourth as much oleic acid and hence the results shown on the figure are on the basis of 1 part oleic acid to 4 parts calcium acetate, the balance being mineral lubricating oil.

The invention has been amply illustrated in the detailed discussion of the invention. These examples are given only to illustrate the invention and are not intended as limitations. The only limitations are found in the attached claims.

I claim:

1. A stable lubricating composition consisting essentially of a major proportion of a mineral lubricating oil, between 0.005–40% by weight of calcium acetate and between 0.005–10% by weight of an organic, straight-chain carboxylic acid having from 8 to 18 carbon atoms therein, including the carboxyl carbon atom, sufficient to disperse the calcium acetate in the lubricating oil.

2. A stable lubricating composition consisting essentially of a major proportion of a mineral lubricating oil, between 0.005–40% by weight of calcium acetate and between 0.005–10% by weight of an unsaturated C_{18} organic, straight-chain, carboxylic acid, sufficient to solubilize the calcium acetate in the lubricating oil.

3. A stable lubricating composition consisting essentially of a major proportion of a mineral lubricating oil between 0.005–40% by weight of calcium acetate and between 0.005–10% by weight of oleic acid, sufficient to solubilize the calcium acetate in the lubricating oil.

4. Claim 2 further characterized in that the mineral lubricating oil is at least predominantly a paraffin oil.

5. A stable lubricating composition consisting essentially of about 87½% by weight of paraffin mineral lubricating oil, about 10% by weight of calcium acetate and about 2.5% by weight of oleic acid.

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