

1

2,999,065

LUBRICANT CONTAINING A CALCIUM SALT-CALCIUM SOAPS MIXTURE AND PROCESS FOR FORMING SAME

Clarence Liddy, Franklinville, N.J., assignor to Socony Mobil Oil Company, Inc., a corporation of New York
No Drawing. Filed Nov. 7, 1960, Ser. No. 67,499
23 Claims. (Cl. 252-39)

This invention has to do with new lubricants, particularly grease compositions characterized by a high order of effectiveness under a wide range of severe operating conditions. The novel greases contain balanced proportions of salts and soaps of low, intermediate and high molecular weight fatty acids.

This application is a continuation-in-part of applications Serial Nos. 505,063 and 849,718, filed April 29, 1955 and October 30, 1959, respectively. Each of said applications Serial Nos. 505,063 and 849,718 constitute continuations-in-part of my earlier application Serial No. 300,777, filed July 24, 1952. All of said applications have been abandoned.

It is well known that greases lose some or all of their effectiveness when subjected to severe operating conditions, and particularly when subjected to high temperature operations. In lubricating machine parts, for example, it is essential that a grease retain its structure during use; failure to do so results in a high consumption of the grease and frequent servicing. In general, available greases suffer from a marked tendency to change in character when used over a wide range of temperature, notably at high temperatures of the order of 250-350° F. and higher. Some conventional greases are characterized by excessive softening when exposed to such high temperature operation, thereby being extruded too rapidly from the area being lubricated to provide efficient lubrication.

The action of water—whether salt or fresh water—may cause the grease to thin out into a liquid which leaks out from the lubricated surfaces. This is a prime consideration inasmuch as grease-lubricated machine parts are encountered in port installations, on deck of navy and marine vessels, in steel rolling mills, in water pumps of all kinds, in mining machinery, in oil-well drilling equipment, etc. In many of such instances, relatively high operating temperatures develop, such that even lime base greases, which are highly resistant to water, become unstable. While a number of modifying agents have been incorporated into various grease types to improve their stability, such modifying agents have generally been relatively expensive and some have depreciated one or more other desirable characteristics of the grease.

It is an object of this invention, therefore, to provide greases capable of withstanding severe operating conditions. It is also an object to provide greases effective for high temperature use, such as at 250-350° F. and higher. A further object is to provide greases which retain their original character over a wide range of operating conditions. Another object is the provision of greases which are stable in the presence of water, even when in contact with water at high temperature. Still another object is to tailor-make soaps to be compatible with a variety of vehicles having comparable performance levels. Other objects will be apparent from the following description.

This invention is predicated upon the discovery that greases of outstanding stability can be prepared from a combination of calcium salts and soaps of different fatty acids in balance proportions. More specifically, it has been found that regulated proportions of calcium salts of certain low molecular weight acids having from one to six carbon atoms per molecule, calcium soaps of par-

2

ticular intermediate molecular weight acids having from seven to twelve carbon atoms per molecule and calcium soaps of certain high molecular weight acids having from thirteen to thirty-six or more carbon atoms per molecule, can be incorporated into a lubricating vehicle to form grease compositions.

Although minor amounts of low molecular weight fatty acids, having from one to six carbon atoms per molecule, have been used—in the form of their salts—in greases, it has been considered hitherto that such amounts had to be limited lest the grease structure be impaired. It has been recognized, too, that such acids could not generally be used as the sole acid component of grease. Illustrative of greases containing relatively small amounts of salts of low molecular weight acids are those described in U.S. Letters Patent 2,197,263 and 2,564,561. In contrast to such earlier grease compositions, the greases contemplated herein contain proportionally greater amounts of certain low molecular weight acids.

The outstanding stability of my superior grease composition appears to be largely due to the amount and type of salt and soaps present. I have discovered that it is necessary to control not only the fatty acid portions of the salt and soap molecules, but the cation as well. Of all the alkaline earth metals, only calcium will form a product that gives the desired performance in the compositions described.

It has been found that the calcium base greases should be formed from a combination of acids, which conform to the following relationship:

Acid	No. of C Atoms	Weight Percent of Total Acids	
		Range	Optimum
Low molecular weight.....	1-6.....	10-60	25-46
Intermediate molecular weight.....	7-12.....	10-80	25-48
High molecular weight.....	13-36 or more.....	2-75	16-80

Expressed in terms of molar ratios the balance of acids, with a C₃₆ acid representing the high molecular weight acids, is:

	Range	Optimum
Low molecular weight acid/total of intermediate and high molecular weight acids.	0.25:1 to 9:1...	0.9:1 to 4:1.
High molecular weight acid/intermediate molecular weight acid.	0.007:1 to 6:1...	0.37:1 to 3.4:1.

That this relationship is critical is revealed by the fact that when an insufficient quantity of a low molecular weight acid, such as acetic acid, is used the grease made therewith is semifluid and has an undesirably low dropping point. Correspondingly, an excessive amount of an acid such as acetic produces a structure which is difficult, if not impossible, to disperse in a stable state in the oil vehicle. A similar influence is seen in the use of too little, or of an excess, of an intermediate molecular weight acid, such as caprylic. An insufficient quantity of caprylic acid generally causes the product to harden excessively in storage; and an excess of caprylic acid causes the product to bleed oil excessively in storage. An improper balance is realized, too, when an insufficiency or excess of a high molecular weight acid, such as stearic, is used. Too little stearic acid results in oil-bleeding in storage and poor worked stability; and an excessive quantity of stearic acid is responsible for undesirable changes in storage and lowered dropping point.

Furthermore, with regard to proportions of the individual salt and soaps of the three types of acids, approximately equal parts by weight of low molecular weight

acid (e.g. acetic) and of intermediate molecular weight acid (e.g. caprylic) and a lesser amount of the high molecular weight acid (e.g. stearic) are used to form particularly advantageous greases. This is illustrated by data provided in Table I hereinafter.

Typical of the low molecular weight straight chain saturated monocarboxylic acids contemplated herein are acetic, propionic, butyric, valeric, and caproic. Of these, acetic acid is particularly desirable because it provides outstanding products.

Typical of the intermediate molecular weight saturated monocarboxylic acids which can be used herein are: heptanoic, caprylic, pelargonic, capric, lauric; and mixed unsubstituted C_8 , C_{10} and C_{12} acids having methyl side chains obtained by the Oxo Process. Preferred of such acids are those containing from seven to ten carbon atoms per molecule. Of these acids, caprylic, capric and pelargonic are particularly advantageous.

Illustrative of the high molecular weight monocarboxylic acids of the invention are: saturated aliphatic acids, such as myristic, palmitic, stearic, arachidic, benhenic, lignoceric, cerotic, unsaturated aliphatic acids having a single double bond, such as oleic; monohydroxy substituted monocarboxylic acids, such as 9-hydroxystearic, 10-hydroxystearic acid and 12-hydroxystearic; and their corresponding branched-chain isomers. Preferred again are the saturated acids, particularly stearic and palmitic acids.

It is to be understood that the high molecular weight acids can be used in their commercially available form, in the pure state and in the form of their corresponding fats and fatty oils, and particularly in their hydrogenated form. However, they are usually used in their commercially available form. It is necessary, however, to use that quantity of a material which contains a quantity of high molecular weight acid coming within the critical range recited above.

It is to be understood, of course, that more than one acid of a given type can be used, so long as the balance recited above is maintained.

The mineral oil components of the greases of this invention can vary considerably in character. In general, such oils are characterized by a viscosity (S.U.V.) of greater than about 40 seconds at 100° F., preferably from about 60 to about 6000 seconds at 100° F. It has been found, however, that the character of mineral oil used materially influences the character of the grease compositions. For example, a naphthenic oil—750 seconds at 100° F.—provides greases of more fibrous character; whereas, a paraffinic oil of the same viscosity provides greases of smoother texture. In place of all or part of the mineral oil component, other oils of lubricating viscosity can also be used. Such oils include synthetic vehicles comprising esters of aliphatic dibasic acids; silicones; silicate esters, esters of phosphorus-containing acids; fluorocarbons; etc. Typical of such synthetic oils are: di (2-ethyl hexyl) sebacate, dibutyl phthalate, di (2-ethyl hexyl) adipate. Other suitable synthetic oils are esters of poly alcohols and monocarboxylic acids, such as polyethylene glycol di(2-ethyl hexoate), trimethylolpropane tricaprylate and related esters of pentaerythritol, neopentyl glycol and the like. The synthetic vehicles are most suitable for providing greases for use in aircraft, since such greases retain their lubricating value over a wide temperature range, from about -100° F. to about 500° F.

The silicone oil components of the greases of this invention are well known. They are described, for example, by E. G. Rochow, in "Chemistry of the Silicones," chapter 4, 1st edition, 1946 and chapters 5 and 6, 2nd edition, 1951. Alkyl, aryl and alkyl-aryl silicones, described by Rochow, are advantageous in the compositions contemplated herein. The silicones are, more specifically, polysiloxanes. They are water-insoluble, substantially non-volatile liquids (at normal temperatures).

In general, polysiloxanes of high molecular weight are preferred. Typical polysiloxanes are:

Viscosity, centistokes at 100° F.

Polymethylsiloxane	100
Polymethylphenylsiloxane, medium aromaticity	59.3
Polymethylphenylsiloxane, high aromaticity	117

Particularly preferred herein is a polymethylphenyl siloxane having a viscosity of 117 centistokes at 100° F.; this is characterized by high aromaticity. This material is identified in the trade as Dow Corning Fluid 710.

The oil component, whether mineral or synthetic or a combination thereof, is generally used in amounts ranging from about 50 to about 99 percent by weight of the finished grease composition. And the calcium salt and soaps of the aforesaid acids are incorporated in such oil component in amounts ranging from about 1 to about 50 percent. Preferably, however, the quantity of calcium salt and soaps will fall within the range 5 to 30 percent by weight.

Although the greases of this invention can be prepared by conventional grease making techniques, it has been found that greases of outstanding character are realized when a novel technique or procedure is followed. This novel technique is described in said application Serial No. 505,063. This technique involves the following sequence of operations. A portion of the oil component, generally about one-third of that required for the finished grease, is charged to a conventional grease kettle and the kettle is heated such that the temperature of the oil is sufficiently high to melt all of the acids which are added; generally the temperature will be about 150–160° F. The acids, such as a mixture of acetic, caprylic and stearic acids, are added to the kettle. Then, a lime flour-oil slurry is added. While the acids and lime are being added, the temperature within the kettle is maintained between 160° F. and 180° F. In order to keep the calcium salt and soaps, which are formed, well dispersed in the oil, it is desirable to circulate the ingredients through a pump or other suitable device at this stage.

The amount of lime flour added to the kettle is insufficient to completely neutralize the free acids in the kettle. The amount of lime added at this stage can range from 0.02 percent less than that stoichiometrically required for neutrality of the acids up to 35 percent less than the total amount of lime stoichiometrically required for neutrality. The optimum amount of free acidity during this stage is equivalent to from 4 to 12 percent of the total amount of lime stoichiometrically required for exact neutrality. This marks a departure from conventional grease making procedures, inasmuch as it is customary to completely neutralize the acids and have an alkaline medium before dehydrating the mixture of oil and salt-soap.

The mixture of oil and salt-soap, which may be considered a concentrated soap-soap mixture, is heated to a temperature of about 300° F. and higher in order that it be dehydrated. After the temperature is raised from 160–180° F. to about 220° F., care must be exercised to prevent excessive foaming. Foaming can be inhibited by a silicone or similar additive. Generally, when a temperature of 280° F. is reached, the water content of the salt-soap concentrate is sufficiently low that foaming is no longer a problem. As the concentrate becomes dehydrated there is a tendency for lumps to form and it is essential, therefore, that adequate agitation be used to keep all materials well dispersed.

When a temperature of approximately 310° F. or higher is reached, the mixture begins to have greater consistency. The mixture is still acidic at this stage. The remainder of the oil component, generally about two-thirds of the total oil charge, is added. During the addition of the remaining oil, it is necessary that the mixture be sufficiently agitated or homogenized to insure substantially complete dispersion of the salt-soap phase in

5

the fluid oil vehicle. Sufficient lime flour is then added to the kettle to render the grease alkaline. Generally, an excess alkaline content of 0.3 percent as CaO is desirable for the finished grease. After the addition of the lime flour, the resulting mixture is again dehydrated. During the entire period of adding oil and lime flour, the mixture is maintained at a temperature of 300° F. or higher. After the final dehydration period, the cooling cycle is started, any additives or inhibitors are incorporated and the grease is cooled to about 180° F. for withdrawal from the kettle.

A grease typical of those contemplated herein is described in the following example:

EXAMPLE 1

Eighteen parts by weight of a naphthenic mineral oil (750 seconds S.U.V. at 100° F.) in admixture with 3.5 parts by weight of acetic acid, 3.4 parts by weight of caprylic acid and 2.0 parts by weight of stearic acid, were added to a grease kettle. The mixture was heated to 160° F. and was maintained (generally about 10 minutes) at 160° F. until all of the acids were dispersed in the oil. A lime flour slurry, containing 3.3 parts by weight of lime and 18.0 parts by weight of said mineral oil, was added to the kettle. The temperature of the kettle contents was finally raised to 310° F. and, after about ten minutes at this temperature, the mixture began increasing in consistency. Additional mineral oil—51.5 parts by weight—was then added. After the mineral oil had been thoroughly incorporated into the mixture, an additional 0.3 part by weight of lime flour was added

6

Method D 566-42. Wheel bearing grease performance properties were determined in accordance with the method of test described in the 1948 Manual of ASTM Standards on Petroleum Products and Lubricants, appendix I, pages 619-624.

The effect of water on grease stability was determined in accordance with the following technique. Ninety (90) grams of grease were charged to a rolling stability tester (described in The Institute Spokesman, 6 No. 12, page 4; March 1943). One percent of water, based upon the weight of the grease charge, was also added. The mixture of grease and water was rolled at 160 r.p.m. for two hours, following which the mixture was removed from the tester. The micro penetration of the mixture was then determined, for comparison with the original micro penetration obtained on the dry grease in its virgin state. After the micro penetration had been determined on the rolled grease, the grease was stored in an oven at 160° F. for sixteen hours. Following this storage period, the grease was cooled to room temperature (70-80° F.) and its micro penetration value was determined again. The change in micro penetration values, after the rolling period and after the storage period, as compared with the original micro penetration value of the virgin grease, is reported as "percent hardening" or "percent softening." It is desirable that a grease show no more than about twenty-five (25) percent change, either softening or hardening, after a test of this type. In making this test, one percent of water was chosen, since it has been found that this extent of water contamination is prevalent under actual operating conditions in the field.

Table 1

Example No.	1	2	3	4	5
Mol Ratio of Acetic to Other Acids.....	1.9-1	1.9-1	2-1	1-2	1 to 1.2
Hydrofol Fatty Acids, Percent.....					5.5
Cottonseed Fatty Acids, Percent.....					5.5
Refined Montan Wax, Percent.....					2.0
Acetic Acid, Percent.....	3.5	3.5	3.5	2.2	2.0
Caprylic Acid, Percent.....	3.4	3.4	3.0		
Pelargonic Acid, Percent.....				8.5	
Stearic Acid, Percent.....	2.0	1.0		5.0	
Oleic Acid, Percent.....		1.0	2.4		
Lime Flour, Percent.....	3.60	3.6	3.6	4.4	3.4
100" Paraffin Oil, Percent.....					81.6
750" 100° F. Naphthenic Oil, Percent.....	87.5	87.5	87.5	79.9	
Weight of Fatty Acids in Formulae, Percent.....	8.9	8.9	8.9	15.7	13.6
Unworked Penetration at 77° F.....	311	330	260	359	350
Worked Penetration at 77° F.....	310	322	250	316	400
Dropping Point, °F.....	600	500	500	500	285
CRG Wheel Bearing Test.....	Pass	Pass	Pass		Fail
Effect of Water on Grease Stability (1% of water added to grease is subjected to rolling stability for 2 hours, followed by storage at 160° F. for 16 hours):					
Original Micropenetration (Dry Grease).....	118	120	70		132
After 2 hours rolling—Micropenetration.....	155	154	97		135
After 16 hours at 160° F.—Micropenetration.....	100	90	60		20
Change from original—Hardening, percent.....	15	25	15		85

to the kettle contents. Heating of the mixture was continued at 310° F. until all foaming had subsided and the mixture had again thickened in consistency. At this stage, heating of the kettle was discontinued and cooling of the mixture was started. When a temperature of 180° F. was reached, the grease so formed was withdrawn from the kettle.

The character of the grease described in Example 1 above is shown below in Table I, wherein it is identified as grease 1. Also shown therein for purposes of comparison are several additional novel greases, identified as greases 2 through 4, and a grease 5 containing only a salt and soaps, respectively, of low and high molecular weight fatty acids. Greases 2 through 4 were prepared in the same manner as that described above for Example 1. Grease 5 was prepared by a conventional prior art procedure.

The data in Table I includes a showing of various physical properties of the several greases. Consistency was determined in accordance with ASTM Method D 217-48 "Cone Penetration of Lubricating Grease." The dropping point was determined in accordance with ASTM

It will be noted, from the data set forth in Table I, that greases 1 through 4 have excellent dropping points, 500° F. This is in contrast with grease 5, which has a substantially lower dropping point, 285° F. It will also be noted that greases 1 through 3 pass the wheel bearing test, whereas grease 5 fails this test. Additionally, greases 1 through 3 hardened only from 15-25%, in the test for grease stability to water, as opposed to an 85% increase for grease 5. It should be noted, too, that greases 1 through 3 contain only about 65-70% of the acids required for grease 5 and yet greases 1 through 3 are superior to grease 5 in all respects.

The effect of different mineral oil vehicles upon grease structure is illustrated by a comparison of grease 1, above, which was prepared with a naphthenic oil, with grease 6 which was prepared with a paraffinic oil. The method of preparation and quantities of materials, used were the same in each instance, only the type of oil being changed. The comparison of greases 1 and 6 is shown below in Table II.

7
Table II

	Grease 1	Grease 6
Oil, 750" @ 100° F.....	Naphthenic.	Paraffinic.
Unworked Penetration @ 77° F.....	311.....	366.
Worked Penetration @ 77° F.....	310.....	309.

As indicated above, alkaline earth metal salts and soaps other than calcium are not effective in my compositions. This fact is illustrated by Table III which presents comparative data on the barium salts and soaps (greases 7 through 15).

Table III

Example No.....	7	8	9	10	11	12	13	14	15
Stearic Acid, percent.....	5.88	6.19	10.24	9.24	13.50	5.70	5.55	8.77	5.39
Oleic Acid, percent.....						11.40			10.78
Caprylic Acid, percent.....	10.00	10.52	6.03	5.43	3.07	2.85	9.43	5.15	2.69
Acetic Acid, percent.....	2.94	1.56	3.01	5.43	3.07	2.85	2.77	5.15	2.69
Ba(OH) ₂ ·8H ₂ O, percent.....	22.38	19.80	20.47	25.58	19.00	20.20	21.15	24.24	19.15
Glycerine, percent.....							5.55	5.15	5.31
750" at 100° F. Naphthenic Oil, percent.....	58.80	61.93	60.25	54.32	61.36	57.00	55.55	51.54	53.99
Description of Final Product.....	Separated	Separated	Separated	Separated	Separated	Separated	Separated	Separated	Separated

NOTE.—Separation refers to separation of soap from the oils; in other words, the products settled down to the bottom of the grease vessel and the oil used formed a separate layer. Such compositions are not satisfactory.

The critical nature of the calcium metal salts and soaps is further illustrated by the fact that attempts to substitute alkali metal salts and soaps for the calcium salts and soaps in my compositions were unsuccessful. Greases 16, 17 and 18 having the composition shown in Table IV were found to separate on standing. These greases were made by the procedure described in Example I above, the distinction being a change of metal component.

Table IV

	16	17	18
Hydrofol Fatty Acids, percent.....			11.5
Acetic Acid, percent.....	3.9	2.6	1.9
Caprylic Acid, percent.....	7.9	7.7	5.7
Oleic Acid, percent.....	3.9	7.7	
Metal Compound, percent.....	^a 5.6	^a 5.4	^b 4.6
100" Paraffinic Oil.....			
750" @ 100° F. Naphthenic Oil.....	78.7	76.6	76.3
Wt. of Fatty Acids in Formulae, percent.....	15.7	18.0	19.1
Description of Final Product.....	Separated	Separated	Separated

^a LiOH·H₂O used.

^b NaOH used.

With regard to the calcium component of the salts and soaps of this invention, it will be apparent that calcium oxide, calcium hydroxide or calcium carbonate can be reacted with the aforesaid acids in order to provide the desired calcium salts and soaps.

It is to be noted that the type of acid used in forming my grease is quite critical. For example, the intermediate molecular weight acids of seven to twelve carbon atoms are limited to include only acids having a straight hydrocarbon chain and their methyl isomers (those acids having a single carbon atom in a side chain or chains). I have discovered that if the size of the side chain is increased to only two carbon atoms the resulting acid is no longer suitable for my composition. In this connection, a mixture of 2-ethyl hexanoic acid, stearic acid, and acetic acid has been strictly compared with a mixture of caprylic acid, stearic acid and acetic acid in forming a calcium grease composition. It has been found that the use of 2-ethyl hexanoic acid in a calcium stearate-calcium acetate grease, causes the resultant salt and soaps to disperse much less readily in mineral oil than a caprylate type grease. Following the procedure used in preparing the compositions set out above but substituting 2-ethyl hexanoic acid for caprylic acid, as a gen-

eral rule, no grease structure resulted. After dehydration, separation of the salt and soaps from the oil occurred. In other words, the salt and soaps settled down on the bottom of the grease vessel, and the oil used formed a separate upper layer. This separated salt and soaps would not disperse in the oil even when a small amount was later reheated to over 500° F. in a 750 second Coastal oil.

10 Illustrative of unusually effective high temperature greases of this invention are the following in which a silicone vehicle is used.

EXAMPLE 19

30 The following were charged to a grease kettle:

Acetic acid.....	53.3
Water	10
Caprylic acid.....	32.1
Hydrogenated tallow fatty acids.....	8.6
Dow-Corning Fluid 550.....	555

The mixture was heated to about 150° F. Dry lime flour (73% CaO), 48 parts, was then added. The resulting mixture was heated to 350° F. during a period of 1½ hours. Since the mixture was slightly alkaline, 2 parts of acetic acid were added. The mixture changed from liquid to a bodied product. After ¼ hour at 350° F., the product turned fluid. After ½ hour at 350° F., additional lime (2.5 parts) was added. The temperature was then raised to 480° F. and, after about ½ hour at the latter temperature, a bodied product was formed. This was grainy. It was milled in a 3-roll ink mill while hot and then returned to the kettle and reheated to 500° F. The resulting product had additional body. After 20 minutes at 500° F., the heating of the kettle was discontinued. The product was paddled down to room temperature (about 70° F.) during a period of 1½ hours. The product was filtered through a 300 mesh screen. The product was smooth and firm. Properties of the product, identified as grease No. 19, are given in Table V, following.

EXAMPLE 20

Charged to a grease kettle were the following materials:

Lime flour (73.3% CaO).....	45
Acetic acid.....	53.3
Water	10
Hydrogenated tallow fatty acids.....	8.6
Caprylic acid.....	32.1
Dow-Corning fluid 710.....	555

The mixture so formed was heated slowly to about 500° F. during a two-hour period. Additional lime flour (4 parts) was added. The temperature was maintained at about 500° F. for another hour. The mixture became a heavy fluid. While hot, it was passed through a 3-roll ink mill. As the product cooled, it had considerable body. The product was reheated to 480–500° F. and then paddled down to room temperature (about 70° F.). It was then passed through the ink mill. At

this stage, it had an A.S.T.M. unworked penetration of 175. The product was cut back with additional Dow Corning Fluid 710 such that the acid content of the original charge was 11.1 percent by weight. The resulting grease was passed through a 300 mesh screen. This is grease No. 20 in Table V.

With regard to the balance of acids in greases Nos. 19 and 20, the molar ratio of acetic to the sum of caprylic and other acids is about 3.5:1.

Data in Table V includes a showing of physical properties of the several greases, together with performance data therefor. High temperature performance was determined by the method outlined in CRC Method L-35; this is referred to in the table as "bearing test." Friction and wear were determined in the Precision-Shell Four Ball Wear Tester. The method used with the tester involves a 40 kilograms load, 600 r.p.m., 300° F., and a test period of one hour. Load-carrying capacity was measured by Federal Test Method Standard No. 791, Method 6503. In the latter, an extreme pressure value is given in terms of "Hertz mean load."

Included in Table V are data for other greases designed for high temperature applications. Each of such greases comprises a silicone fluid and a thickening agent. The thickening agent of grease No. 21 is an aryl urea, and of grease No. 22 is a vat dye.

Table V

Grease No.-----	19	20	21	22
Penetration:				
unworked-----		250	302	289
worked-----		255	302	285
Bearing Test:				
200 lbs. load, hrs.-----	158, 177	129, 103, 371	83, 94	105, 101, 119
6 lbs. load, hrs.-----	118	124		
Wear Test (4-Ball), mms.-----		2.57		
Hertz Mean Load-----		15.7		

The data in Table V reveal that greases Nos. 19 and 20, which typify this invention, have excellent high temperature performance and, in this respect, are superior to other greases (Nos. 21 and 22) designed for the same purpose. Greases comparable to Nos. 19 and 20 but having a mineral oil instead of a silicone vehicle, are considerably inferior at high temperatures such as are encountered in the Bearing Test.

EXAMPLE 23

Charged to a grease kettle were the following materials (all parts by weight):

Calcium acetate monohydrate-----	116
Calcium caprylate-----	80
Calcium stearate-----	37
Trimethylolpropane tricaprylate-----	767

The charge was heated slowly to 420° F. No grease body formed. The mixture was then cooled, and some body was noted at about 70-80° F. The mixture was then reheated to 510° F. and thereafter cooled to 250° F. The cooled product was passed through a 3-roll ink mill. The product was characterized by a very heavy body. It was then worked, 500 strokes, 1/16" holes. This is an excellent grease for high temperature applications, particularly for use in aviation equipment.

EXAMPLE 24

This example illustrates the preparation of the salts and soaps of this invention in a medium other than mineral oil or synthetic vehicle, and isolation of the salts and soaps.

The following materials were used (parts by weight):

Acetic acid-----	70
Caprylic acid-----	68
Stearic acid-----	40

Ca (OH) ₂ -----	72
Cetane-----	750

A grease kettle was charged with 500 parts of cetane, all of the acids and 66 parts of Ca (OH)₂. The materials were mixed well at 120-130° F. The temperature thereof was raised to 310° F. The balance of cetane was added and the resulting mixture was reheated to 310° F. Six parts of Ca (OH)₂ were added. The temperature was maintained at about 310° F. for about 15 minutes. The product was cooled, with paddling, to about 200° F. It was passed through a Tri Homo Mill, having a 0.002" setting.

Fifty parts of the product, a grease-like material, were transferred to a Soxhlet thimble and were extracted with an ASTM naphtha. A dry powder was obtained.

A mineral oil blend comprising a 500 second (S.U.V.) oil at 100° F. and 10 percent by weight of the powder was prepared. This was subjected to the Four Ball Wear Tester. The method used with the tester involves a 80 kilogram load, 1800 r.p.m., 80° F., and a test period of one minute. This test evaluates the anti-weld characteristics of the oil under test. The lower the value obtained, the better the oil in this respect. The 10% mineral oil blend reduced the wear area to about 1.17 millimeters, from a value of 2.63 millimeters for the oil alone.

EXAMPLE 25

A physical mixture of the following salts and soaps was formed (parts by weight):

Calcium acetate (a mixture of the hydrous and anhydrous forms)-----	46.1
Calcium caprylate containing 5% of water-----	38.5
Calcium stearate-----	20.0

A blend of the same mineral oil and 10 percent by weight of this mixture was also subjected to the Four Ball Wear Tester. The wear area was 1.55 millimeters, as opposed to the 2.63 millimeters for the oil alone.

These results reveal that the salt-soap products of this invention are suitable for use in preparing mild extreme pressure oils, which are useful, for example, in gears operating under low speed, high load conditions.

It is to be understood that the greases of this invention can also contain other characterizing materials and fillers. For example, the greases can contain anti-oxidants such as amines (e.g., phenyl alpha-naphthylamine), phenols (e.g., 2-6-ditertiary-butyl-4-methyl phenol), and the like; lubricity improving agents such as free fat, free fatty acids, esters of alkyl and/or aryl acids, sulfurized fats, lead soaps, etc. However, as a cautionary note, it is advisable to use small quantities of such characterizing materials to obtain the customary beneficial effects thereof.

The greases of this invention are suitable for a wide range of industrial applications. Some, for example, are suitable for multi-purpose automotive greases, serving as chassis, wheel-bearing, water-pump grease lubricants; typical of such a grease is that shown above and identified as grease 1. Others are multi-purpose industrial greases serving as plain-bearing and anti-friction greases for normally loaded and heavily loaded equipment. In general, then, greases contemplated herein range from semi-fluid types suitable as textile machinery lubricants, to solid block type greases used in lubrication of machinery in steel mills, paper mills, cement mills, etc.

I claim:

1. A grease composition comprising: an oil vehicle and a mixture therewith containing a calcium salt and calcium soaps, the mixture being present in a grease forming quantity; the calcium salt of said mixture being a salt of a low molecular weight unsubstituted straight chain saturated monocarboxylic acid (I) having from one to six carbon atoms per molecule, one of said soaps being a calcium soap of an intermediate molecular weight unsubstituted saturated monocarboxylic acid (II) having from seven to

twelve carbon atoms per molecule and having no side chain larger than a methyl group, and another of said soaps being a calcium soap of an aliphatic acid (III) having more than twelve carbon atoms per molecule and having no more than one double bond and being selected from the group consisting of an unsubstituted monocarboxylic acid and a mono-hydroxy substituted monocarboxylic acid, the percent-by-weight distribution of said acids being as follows:

- I. From about 10 to about 60
- II. From about 10 to about 80
- III. From about 2 to about 75.

2. A grease as defined by claim 1 wherein the percent-by-weight distribution of said acids is:

- I. From about 25 to about 46
- II. From about 25 to about 48
- III. From about 16 to about 50.

3. A grease as defined by claim 1 wherein the low molecular weight acid is acetic acid.

4. A grease as defined by claim 1 wherein the intermediate molecular weight acid is caprylic acid.

5. A grease as defined by claim 1 wherein the high molecular weight acid is stearic acid.

6. A grease as defined by claim 1 wherein the vehicle is a mineral oil having a Saybolt Universal Viscosity from about 60 to about 6000 seconds at 100° F.

7. A grease as defined by claim 1 wherein the oil vehicle is a naphthenic oil having a Saybolt Universal Viscosity of about 700-800 seconds at 100° F.

8. A grease as defined in claim 1 wherein the oil vehicle is a silicone oil.

9. A grease as defined by claim 1 wherein the oil vehicle is a polymethylphenyl siloxane having a viscosity of about 117 centistokes at 100° F.

10. A grease as defined by claim 1 wherein the oil vehicle is present in an amount from about 50 to about 99 percent-by-weight, and wherein the mixture of salt and soap is present in an amount from about 1 to about 50 percent by weight.

11. A grease as defined by claim 1 wherein the intermediate molecular weight acid contains from seven to ten carbon atoms per molecule.

12. A calcium grease comprising: a naphthenic oil and a mixture of calcium salt and soaps of acetic acid, caprylic acid, stearic acid and oleic acid, the percent-by-weight distribution of said acids being about:

Acetic acid.....	39.3
Caprylic acid.....	38.3
Stearic acid.....	11.2
Oleic acid.....	11.2

the salt and soap content of said grease being about 12.5 percent by weight.

13. A calcium base grease comprising: a paraffinic oil and a mixture of calcium salt and soaps of acetic acid, caprylic acid and stearic acid, the percent-by-weight distribution of said acids being about:

Acetic acid.....	39.3
Caprylic acid.....	38.3
Stearic acid.....	22.4

the soap content of said grease being about 12.5 percent by weight.

14. A calcium grease comprising: a polymethylphenyl siloxane having a viscosity of about 117 centistokes at 100° F. and a mixture of calcium salt and soaps of acetic, caprylic and stearic acids, the percent-by-weight distribution of said acids being about:

Acetic acid.....	57
Caprylic acid.....	34
Stearic acid.....	9

the salt and soap content of said grease being about 20 percent by weight and the balance being said siloxane.

15. A calcium grease comprising: a polymethylphenyl siloxane having a viscosity of about 117 centistokes at

100° F. and a mixture of calcium salt and soaps of acetic, caprylic and stearic acids, the percent-by-weight distribution of said acids being about:

Acetic acid.....	57
Caprylic acid.....	34
Stearic acid.....	9

the salt and soap content of said grease being about 15 percent by weight and the balance being said siloxane.

16. The method for preparing a calcium grease, comprising: forming a mixture of acids (I), (II) and (III), a calcium compound selected from the group consisting of an oxide, hydroxide and carbonate, and a substantial portion of the mineral oil present in the grease, the amount of calcium compound being insufficient to completely neutralize said acids and being such that the free acidity of the mixture is equivalent to from about 4 to about 12 percent of the total amount of calcium compound stoichiometrically required for complete neutrality; heating said mixture to saponify said acids; dehydrating the resulting acidic mixture; adding the remainder of the oil required for the grease; and adding an additional amount of calcium compound sufficient to react with any unreacted acid and to at least completely neutralize said acidity; said acids being:

I. A low molecular weight unsubstituted straight chain saturated monocarboxylic acid having from one to six carbon atoms per molecule,

II. An intermediate molecular weight unsubstituted saturated monocarboxylic acid having from seven to twelve carbon atoms per molecule and having no side chain larger than a methyl group,

III. An acid having more than twelve carbon atoms per molecule and having no more than one double bond and being selected from the group consisting of an unsubstituted monocarboxylic acid and a mono-hydroxy substituted mono-carboxylic acid, the percent-by-weight distribution of said acids being as follows:

- I. From about 10 to about 60
- II. From about 10 to about 80
- III. From about 2 to about 75;

and the total amount of calcium compound and acids so reacted being sufficient to provide calcium products in grease forming quantity in the oil.

17. The method of claim 16 wherein the calcium compound is calcium oxide.

18. The method of claim 16 wherein the substantial portion of mineral oil is about one-third of the total oil present in the grease.

19. The method for preparing a calcium grease, comprising: forming a mixture of acetic, caprylic and stearic acids, lime and about one-third of the oil present in the grease, the amount of lime being insufficient to completely neutralize said acids and being such that the free acidity of the mixture is equivalent to from about 4 to about 12 percent of the total amount of lime stoichiometrically required for complete neutrality; heating said mixture to saponify said acids; dehydrating the resulting acidic mixture; adding the remainder of the oil required for the grease; and adding an additional amount of lime sufficient to react with any unreacted acid and to at least completely neutralize said acidity; the weight-percent distribution of said acids being:

Acetic.....	about 39
Caprylic.....	about 39
Stearic.....	about 22

the total amount of lime and acids so reacted being sufficient to provide calcium products in grease forming quantity in the oil; and the oil being a naphthenic mineral oil having a Saybolt Universal Viscosity of about 750 seconds at 100° F.

20. A lubricant comprising an oil of lubricating viscosity and from about 1 to about 50 percent by weight of

13

a mixture containing a calcium salt and calcium soaps, the calcium salt of said mixture being a salt of a low molecular weight unsubstituted straight chain saturated monocarboxylic acid (I) having from one to six carbon atoms per molecule, one of said soaps being a calcium soap of an intermediate molecular weight unsubstituted saturated monocarboxylic acid (II) having from seven to twelve carbon atoms per molecule and having no side chain larger than a methyl group, and another of said soaps being a calcium soap of an acid (III) having more than twelve carbon atoms per molecule and having no more than one double bond and being selected from the group consisting of an unsubstituted monocarboxylic acid and a mono-hydroxy substituted monocarboxylic acid, the percent-by-weight distribution of said acids being as follows:

- I. From about 10 to about 60
- II. From about 10 to about 80
- III. From about 2 to about 75.

21. A lubricant as defined by claim 20 wherein the percent-by-weight distribution of said acids is:

- I. From about 25 to about 46
- II. From about 25 to about 48
- III. From about 16 to about 50.

22. A composition of matter consisting essentially of a mixture containing a calcium salt and calcium soaps, the calcium salt of said mixture being a salt of a low molecular weight unsubstituted straight chain saturated monocarboxylic acid (I) having from one to six carbon atoms per molecule, one of said soaps being a calcium soap of an intermediate molecular weight unsubstituted saturated monocarboxylic acid (II) having from seven to twelve carbon atoms per molecule and having no side chain larger than a methyl group, and another of said soaps being a calcium soap of an acid (III) having more than

14

twelve carbon atoms per molecule and having no more than one double bond and being selected from the group consisting of an unsubstituted monocarboxylic acid and a mono-hydroxy substituted monocarboxylic acid, the percent-by-weight distribution of said acids being as follows:

- I. From about 10 to about 60
- II. From about 10 to about 80
- III. From about 2 to about 75.

23. A composition of matter as defined by claim 22 wherein the percent-by-weight distribution of said acids is:

- I. From about 25 to about 46
- II. From about 25 to about 48
- III. From about 16 to about 50.

References Cited in the file of this patent

UNITED STATES PATENTS

2,197,263	Carmichael et al. Apr. 16, 1940
2,229,030	Adams Jan. 21, 1941
2,274,675	Earle Mar. 3, 1942
2,413,121	Swenson Dec. 24, 1946
2,413,122	Swenson Dec. 24, 1946
2,606,153	Holdstock Aug. 5, 1952
2,607,735	Sproule et al. Aug. 19, 1952
2,628,195	Allison et al. Feb. 10, 1953
2,628,202	Allison et al. Feb. 10, 1953

FOREIGN PATENTS

767,655	Germany Mar. 2, 1952
---------	----------------------------

OTHER REFERENCES

- Canadian J. Research, vol. 22, sec. B. (1944), pp. 76-89, article by Gallay et al.
- NLGI Spokesman, vol. 14, No. 12 (March 1951), pp. 7-23, by Amott et al.