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2,999,066

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

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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 low and intermediate molecular weight fatty acids, present as calcium salts and soaps.

This application is a continuation-in-part of application Serial Number 510,863, filed May 24, 1955 which, in turn, is a continuation-in-part of application Serial Number 300,775, filed July 24, 1952, both now 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 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 styles 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 in balanced proportions. More specifically, it has been found that regulated proportions of certain low molecular weight straight chain saturated monocarboxylic acids having from one to six carbon atoms per molecule and of particular intermediate molecular weight saturated monocarboxylic acids having from seven to twelve carbon atoms per molecule, can be incorporated, in the form of

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their corresponding calcium salts and soaps, 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 a 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 substantially greater amounts of low molecular weight acids.

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

It has been found that the calcium base greases should be formed from a combination of acids, in which the molar ratio of low molecular weight acid to intermediate molecular weight acid ranges from about 0.25:1 to about 10:1. However, the optimum molar ratio ranges from about 1:1 to 2.5:1.

The foregoing molar ratios are critical inasmuch as an insufficient quantity of a low molecular weight acid, such as acetic, is responsible for a semi-fluid product, and an undesirably low dropping point. Correspondingly, an excessive amount of an acid, such as acetic, produces a salt-soap structure which is difficult, if not impossible, to disperse in a stable state in an oil vehicle. A similar influence is seen in the use of too little, or an excess, of an intermediate molecular weight acid such as caprylic. An insufficiency 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.

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, undecylenic, lauric, and mixed unsubstituted C₈, C₁₀ and C₁₂ acids having methyl side chains, obtained by the oxo process. Preferred of such acids are those containing from seven to ten carbon atoms. Of these acids, caprylic, capric and pelargonic are particularly advantageous.

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. 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 tricaprilate 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 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. The calcium salts and soaps of the aforesaid acids are incorporated in such oil component in amounts ranging from about 1 percent to about 50 percent. Preferably, however, the quantity of calcium salts 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 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 and caprylic 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 metal salt and soap, 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 salt-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 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 parts by weight of acetic acid and 4.5 parts by weight of caprylic 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 2.7 parts by weight of lime and 18 parts by weight of said mineral oil, were 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, 34 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 to the kettle contents. Heating of the mixture was continued at 325° 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 Example 1. Also shown therein for purposes of comparison are the additional novel greases identified as greases 2 and 3. The barium greases 4 and 5 were prepared in the same manner described in Example 1 above. Greases 4 and 5 were not satisfactory as the barium salts and soaps separated from the oil to form a separate layer.

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 Method D 566-42.

Table I

Example.....	1	2	3	4	5
Caprylic Acid.....	5.62	13.23	13.63	8.61	12.40
Acetic Acid.....	3.71	5.93	3.08	5.68	8.20
Diethylene glycol.....			1.69		
Lime.....	3.71	7.35	5.57		
Ba(OH) ₂ ·8H ₂ O.....				24.30	35.07
Mineral Oil (Naphthenic 750" @ 100° F.).....	86.96	73.49	76.13	61.41	44.33
Tests:					
ASTM Dropping Point.....	500+	500+	470		
ASTM Penetration @ 77° F., Unworked/Worked.....	330/340	219/210	370/323		
Description of Final Product.....	(1)	(1)	(1)	(2)	(1)

¹ Satisfactory grease structure.

² Separated.

In Table II below, the grease of Example 1 is compared with grease 6 which contains only a salt and soaps of low and high molecular weight fatty acids. Grease 6 was prepared by a conventional prior art procedure.

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Table II

Example No.-----	1	6
Mol Ratio of Acetic to Other Acids.....	1.6-1	1 to 1.2
Hydrogenated Fish Oil Fatty Acids, Percent.....	5.5	5.5
Cottonseed Fatty Acids, Percent.....	5.5	5.5
Refined Montan Wax, Percent.....	2.0	2.0
Acetic Acid, Percent.....	3.7	2.0
Caprylic Acid, Percent.....	5.6	3.4
Lime Flour, Percent.....	3.8	81.6
100" Paraffin Oil, Percent.....	86.9	13.6
750" s/o 100" F. Naphthenic Oil, Percent.....	9.3	380
Wt. of Fatty Acids in Formulae, Percent.....	380	400
Unworked Pen. at 77° F.....	340	285
Worked Pen. at 77° F.....	500	
Dropping Point, °F.....		

It will be noted, from the data set forth in Table II, that grease 1 has an excellent dropping point, 500° F. This is in contrast with grease 6, which has a substantially lower dropping point, 285° F.

That mineral oils other than naphthenic oil can be used in forming greases of this invention is shown by grease 7. This grease which was prepared in the manner described above in Example 1 had a satisfactory grease structure.

Grease No.-----	7
Caprylic acid, percent by wt.....	9.3
Acetic acid, percent by wt.....	6.3
Lime, percent by wt.....	6.4
Paraffinic oil, 750" @ 100° F., percent by wt. (87 viscosity index)-----	78.0
Unworked penetration @ 77° F.....	317
Worked penetration @ 77° F.....	308

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.

EXAMPLE 8

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.....	37.1
Caprylic acid.....	56.2
Ca(OH) ₂	37.1
Cetane.....	869.6

A grease kettle was charged with 500 parts of cetane, all of the acids and 33.1 parts of Ca(OH)₂. The materials were mixed well at 160° F. The temperature thereof was raised to 310° F. The balance of the cetane was added. After the balance of the cetane had been mixed thoroughly with the mixture, the remainder of the Ca(OH)₂ was added. The resulting mixture was heated at 325° F. until it had thickened in consistency. The product was cooled, while agitated, to about 180° 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. The naphtha was evaporated. A dry powder was obtained.

A mineral oil blend comprising a 500 second (S.U.V.), solvent-refined 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 kilograms 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 1.05 millimeters, from a value of 2.63 for the oil alone.

A further test was made with a 50 kilogram load for

one hour. The value obtained with the oil alone was 2.72 and with the oil blend was 0.60.

EXAMPLE 9

A physical mixture of the following salt and soap was formed (parts by weight):

Calcium acetate (a mixture of the hydrous and anhydrous forms)-----	4.31
Calcium caprylate containing 5% of water-----	5.69

A blend of the same mineral oil and 10 percent by weight of this mixture was also subjected to the Four Ball Wear Tester (80 kilogram load, 1 minute). The wear area was 0.86, as opposed to 2.63 millimeters for the oil alone.

With a 50 kilogram load for one hour, the oil alone had a value of 2.72 and the oil blend a value of 0.53.

The results of Examples 8 and 9 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 antioxidants 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 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 and automotive greases, serving as chassis, wheel-bearing, water-pump grease lubricants; typical of such 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 of a calcium salt and a calcium soap therewith, the mixture of said salt and soap being present in a grease forming quantity, a 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, a calcium soap of said mixture being a 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 the molar ratio of said acid (I) to said acid (II) being from about 0.25:1 to about 10:1.

2. A grease as defined by claim 1 wherein the molar ratio is from about 1:1 to about 2.5:1.

3. A grease as defined by claim 1 wherein the intermediate molecular weight acid has no more than ten carbon atoms per molecule.

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

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

6. A grease as defined by claim 1 wherein the oil 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 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.

9. The method for preparing a grease composition, comprising: forming a mixture of acids (I) and (II), a calcium compound, and a substantial portion of an oil vehicle of the grease, the amount of calcium compound being insufficient to completely neutralize said acids and being such that the free acidity is equivalent to from about four to about twelve percent of the total amount of lime stoichiometrically required for complete neutrality; heating said mixture to saponify said acids; dehydrating the resulting mixture; adding the remainder of the oil required for the grease; adding an additional amount of calcium compound 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 carbons 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;

the molar ratio of said acid (I) to said acid (II) being from about 0.25:1 to about 10:1; and the total amount of calcium compound and acids so reacted being sufficient to provide calcium products in grease forming quantity in the oil.

10. The method for preparing a calcium grease composition, comprising: forming a mixture of acetic and caprylic acids, the molar ratio of said acids being about 1.6:1, lime and a substantial portion of a naphthenic mineral oil having a Saybolt Universal Viscosity of about 750 seconds at 100° F., the amount of lime being insufficient to completely neutralize said acids and being such that the free acidity is equivalent to from about four to about twelve percent of the total amount of lime stoichiometrically required for complete neutrality; heating said mixture to saponify said acids; dehydrating the resulting mixture; adding the remainder of said oil required for the grease; adding an additional amount of lime to react with any unreacted acid and to at least completely neutralize said acidity; the mixture of calcium salt-soap so formed being present in an amount from about 10 to about 15 percent by weight of said grease composition.

11. A calcium grease comprising: a naphthenic oil and a mixture of calcium acetate and calcium caprylate, the molar ratio of acetic acid to caprylic acid of said acetate and caprylate being about 1.6:1, and the calcium salt-calcium soap content of said grease being about 13 percent by weight.

12. A calcium grease comprising: a paraffinic oil and a mixture of calcium acetate and calcium caprylate, the molar ratio of acetic acid to caprylic acid of said acetate and caprylate being about 1:1.6, and the calcium salt-calcium soap content of said grease being about 22 percent by weight.

13. A grease composition comprising, an oil vehicle and a grease forming proportion of a mixture of calcium salts of acetic acid and an intermediate molecular weight, straight chain, unsubstituted, saturated carboxylic acid, having from 7-10 carbon atoms per molecule and having no side chain, the molar ratio of said acetic acid to said intermediate molecular weight acid being from about 2:1 to 10:1.

14. A lubricant comprising an oil of lubricating viscosity and from about 1 to about 50 percent by weight of a mixture of a calcium salt and a calcium soap therewith, a 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, a calcium soap of said mixture being a 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 the molar ratio of said acid (I) to said acid (II) being from about 0.25:1 to about 10:1.

15. A lubricant as defined by claim 14 wherein the molar ratio is from about 1:1 to about 2.5:1.

16. A composition of matter consisting essentially of a mixture containing a calcium salt and a calcium soap, 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, a calcium soap of said mixture being a 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 the molar ratio of said acid (I) to said acid (II) being from about 0.25:1 to about 10:1.

17. A composition of matter as defined by claim 16 wherein the molar ratio is from about 1:1 to about 2.5:1.

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