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LUBRICATING GREASE COMPOSITIONS

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This invention relates to novel organo-metallic complexes or compounds with coordinated valences and to compositions containing the same. More particularly, the present invention pertains to soap-salt complexes comprising a metal salt of acetic acid, a metal salt of medium molecular weight carboxylic acid, and a metal soap of high molecular weight carboxylic acid, to methods for preparing the soap-salt complexes and to compositions containing them.

In brief compass, the invention relates to compositions consisting of or containing dehydrated and baked complexes or coordinated compounds consisting of a metal salt of acetic acid, a metal salt of a medium molecular weight carboxylic acid containing from about 3 to 10 carbon atoms, and a metal soap of a high molecular weight monocarboxylic acid containing from about 12 to 30 carbon atoms and preferably 18 to 22 carbon atoms, in which the mol ratio of acetic acid to the other acids employed exceeds 4, and in which the difference in number of carbon atoms per molecule between the average of the high molecular weight carboxylic acids and the average of the medium molecular weight carboxylic acids is at least 7. A lower mol ratio of acetic acid to the other acids may be used if the average saponification number of all the other acids exceeds 320 mgs. KOH per gm. The compositions of the invention include novel and improved lubricating greases, lubricating oils, gear oils, filter oils, etc. In particular, grease compositions containing the complexes of the invention have been found to have excellent extreme pressure and structural stability properties as well as other desirable grease characteristics.

The use of so-called soap-salt complexes as grease thickeners is well known in the art. The complex materials used heretofore consisted of combinations of metal soaps of high molecular weight carboxylic acids having from 12 to 30 carbon atoms and metal salts of low molecular weight carboxylic acids containing from 1 to 6 carbon atoms per molecule. The commonly known grease-making, high molecular weight fatty acids, saturated or unsaturated, containing from about 12 to 22 carbon atoms have been employed in conjunction with such low molecular weight carboxylic acids as acetic, propionic, alkoxy propionic, and the like to form the complex grease thickeners of the prior art. Normally about equimolar proportions of low to high molecular weight carboxylic acids have been employed by the prior art, because of the limited thickening effect of the low molecular weight carboxylic acid component. Highly desirable characteristics recently have been imparted

to compositions of that sort by drastically increasing the low molecular weight acid content, and with it the metal content of the soap-salt complexes, so that they contain at least 7 moles and up to 40 moles or more of the low molecular weight acid per mol of the high molecular weight acid.

It has now been found that novel compounds which are true complexes can be prepared by employing a metal salt of acetic acid, at least one metal salt of a medium molecular weight carboxylic acid, and at least one metal salt of a high molecular weight carboxylic acid. In accordance with the invention, the difference in average number of carbon atoms per molecule between the high and the medium molecular weight carboxylic acid should be at least 7 and the average saponification value of the carboxylic acids, other than acetic acid should be within the range of about 290 to 450 and preferably at least 320. It has also been found that when the combination of acids described above is employed with the stated carbon atom spread, a mol ratio of acetic to the other acids above 4:1 and as high as 40:1 can be effectively utilized to prepare the novel complex compounds of the invention. When lower mol ratios are desired, the average saponification number of the medium and high molecular weight acids must exceed 320.

For the purposes of this invention, carboxylic acids containing from about 3 to 10 and preferably 6 to 9 carbon atoms per molecule are designated as the medium molecular weight carboxylic acids. Those having from 6 to 9 carbon atoms are preferred. If it is desirable to use a polycarboxylic acid as the medium molecular weight acid in accordance with this invention, its saponification number must be reckoned on the basis of its molar equivalence in monocarboxylic acid. The equivalent saponification number is the quotient of milligrams equivalent weight of KOH (or 56,100) and gram equivalent of the acid. Suitable carboxylic acids coming within this definition are exemplified by the following:

Straight chain saturated aliphatic carboxylic acids:
- Pentanoic (valeric)
- Hexanoic (caproic)
- Heptanoic (enanthic)
- Octanoic (caprylic)
- Nonanoic (pelargonic)
- Decanoic (capric)

Branched chain saturated aliphatic acids:
- Isobutyric
- C_5 Oxo
- C_8 Oxo
- C_9 Oxo
- C_{10} Oxo

Hydroxy aliphatic mono- and poly-carboxylic acids:
- Glyceric
- Lactic, sap. No. 623
- Citric, sap. No. 267, equv. sap. No. 801

Aromatic mono-and poly-carboxylic acids and anhydrides:
- Benzoic
- Hydroxy benzoic
- Toluic
- o-Phthalic (sap. No. 338; equiv. sap. No. 676)
- Phthalic anhydride
- Terephthalic

Heterocyclic acids:
Furoic
Thiophene carboxylic

Mixed as well as single medium molecular weight carboxylic acids may be employed in accordance with the foregoing statements about the average carbon atom spread and average minimum saponification number of the high and medium molecular weight carboxylic acids. Similarly, commercial mixtures of medium molecular weight carboxylic acids can also be utilized to prepare the novel complexes.

The Oxo acids useful for the purposes of the present invention, e.g. the saturated branched chain C_5 to C_{10} Oxo acids, can be prepared by means of the well known Oxo synthesis. This process involves the oxonation or carbonylation of olefins with carbon monoxide and hydrogen at elevated temperatures of about 300° to 400° F. and pressures of about 2500 and 4000 p.s.i.g. in the presence of a group VIII catalyst, preferably cobalt. In U.S. Patent No. 2,632,021 the Oxo process and the nature of the reaction products, e.g. C_8 Oxo products, are disclosed in detail. The preparation of acids from the Oxo reaction products is described in U.S. Patent No. 2,537,577 and U.S. Patent No. 2,553,364. Neither the preparation of the Oxo reaction products nor the preparation of the Oxo acids therefrom are considered to be essential elements of the present invention. The C_5 Oxo acids can be derived from butylene, for example, and the C_8 Oxo acids from the C_7 olefins produced by polymerizing propylene alone or with some butylene.

High molecular weight monocarboxylic acids containing from about 12 to 30, preferably from 18 to 22, carbon atoms are useful for the purposes of this invention. These acids may be derived from saturated or unsaturated naturally occurring or synthetic fatty material. The fatty acids normally used in the manufacture of conventional greases, particularly the more saturated acids, are preferred. Examples of such acids include lauric, myristic, palmitic, stearic, mono-hydroxy stearic, di-hydroxy stearic, poly-hydroxy stearic and arachidic acids and the hydrogenated fish oil and tallow acids, which contain chiefly stearic acid. However, unsaturated acids such as oleic, ricinoleic and similar acids may also be used. The average saponification value of a mixture of the high molecular weight carboxylic acids useful for the purposes of the present invention should not be more than about 280 and is preferably not more than about 220.

The acetic acid employed in the present invention can be either glacial acetic acid or an aqueous solution of acetic acid. The concentration of acid in the solution may vary from about 60 to 99.9 wt. percent, and is preferably about 80 wt. percent. The presence of a salt of acetic acid in the complex is an essential part of the present invention, but the use of a substituted acetic acid having 2 carbon atoms per molecule is not excluded, where such modification may be desirable. For example, chloro-acetic acid, glycolic acid, thioglycolic acid, glycine, or oxalic acid may be used to modify the structure of a grease made in accordance with the invention.

The metal component of the complexes of the invention is used in a form which can combine chemically with carboxylic acids to form salts or soaps. Ordinarily the metal hydroxide is used. The choice of metal component depends to a certain extent on the use to which the multiple salt and soap complex of the invention is to be put. The alkaline earth metal hydroxides or carbonates such as those of calcium, barium and strontium are useful for many purposes of the invention. Calcium hydroxide is especially preferred. These metals afford the greatest advantages when their complexes, with mol ratios of acetic to the medium and high molecular weight acids above 5:1, are used as grease thickeners, since they result in the production of greases having outstanding load carrying characteristics and structural stability during storage and at high temperatures even without the use of conventional extreme pressure and stabilizing agents. The alkaline earth metals differ in this respect from the alkali metals, i.e. sodium, potassium and lithium. Soap-salt complexes having a high alkali metal content and which consist of the combination of acids, mol ratios and carbon atom spreads of this invention, yield greases without extreme-pressure load-carrying properties and with poor structural stability even when added to the oil dispersant in relatively high proportions. It is therefore preferred to use metals having two valences. However, when more than one metal salt or soap is used in the complex, one of them may be an alkali metal, for example, lithium.

Other metals useful for the purposes of this invention are magnesium and zinc. In some applications, wherein the metal is required to confer a catalytic effect for promoting oxidation or combustion, copper, iron, nickel or cobalt may be used. To sum up briefly, the preferred class of metals are the alkaline earth metals and zinc; and the preferred metal in that clas is calcium.

The metallic constituents of the salts and soaps may be any one or more of the metals set forth above. Though the metals may be either the same or different, in most cases the salts and soaps contain the same metal. If it is desired to incorporate a monovalent metal, e.g. lithium, into the composition along with a divalent metal, e.g. calcium, the monovalent metal should be in the salt of medium molecular weight carboxylic acid, particularly if it is a dicarboxylic acid.

In accordance with the present invention the proportion of acetic acid by weight should exceed that of the sum of medium and high molecular weight carboxylic acids; and the combination of the medium and high molecular weight acids should be selected so that the carbon atom spread, that is the difference in the average number of carbon atoms per molecule, between the high and the medium molecular weight carboxylic acids is at least about 7, preferably 7 to 15, and the average equivalent saponification value of the medium and high molecular weight carboxylic acids be within the range of about 290 to 450, and preferably above 320. When these limitations are observed, the mol ratio of acetic to the higher molecular weight carboxylic acids can be lower than 5:1 and at least 4:1; but it is particularly preferred to be higher than 5:1 and most particularly between 7:1 and 25:1, in order to get the maximum benefit of a high content of combined metal per unit weight of the composition and therefore to get maximum utility for extreme pressure application.

The constitution and chemical nature of the complexes of this invention are not fully understood. X-ray diffraction spectra of these soap-salt complexes do show, however, patterns definitely inconsistent with that of a physical mixture of the individual salt and soap constituents. The spectra also show that the temperature employed during the preparation of the complex compounds, the mol ratio of acids, etc. will influence the type of X-ray pattern obtained. Formation of the complexes or coordination compounds occurs after the salts have been heated not merely to dehydration but to higher temperatures. Consequently, these are anhydrous or dehydrated, baked complexes.

In accordance with one feature of the present invention, the soap-salt complexes containing a metal salt of acetic acid, at least one metal salt of a medium molecular weight carboxylic acid having from about 3 to 10 carbon atoms, and at least one metal soap of a high molecular weight carboxylic acid having 12 to 30 carbon atoms may be incorporated in a wide variety of liquid and semi-liquid materials of natural or synthetic origin to improve the utility of these materials. In one particular embodi-

ment, these high metal content complex compounds are incorporated in mineral and/or synthetic lubricating oils in grease-making proportions of about 5 to 40 wt. percent, preferably 10 to 30 wt. percent, to produce greases of excellent extreme pressure and structural stability characteristics. In general, the mineral or synthetic lubricating oil should have a viscosity within the range of about 50 to 2000 SUS at 100° F. and 30 to 150 SUS at 210° F., a pour point of about +20 to —75° F., a flash point of about 350° to 650° F., and a viscosity index of about 0 to 60 although 100 or higher is also desirable and can be employed. As mentioned above, synthetic as well as mineral lubricating oils can be employed as part of all of the liquid phase of the grease, and they include synthetic lubricating oils of the hydrocarbon, hydrocarbon polymer, ester, complex ester, formal, mercaptal, polyalkylene oxide, silicone or similar types. Synthetic oils such as di-2-ethylhexyl sebacate, di-C_8 Oxo, azelate and other branched chain simple esters of dicarboxylic acids can be used, as well as complex esters prepared from glycols, dicarboxylic acids, and alcohols or monocarboxylic acids.

The metal soap-salt complexes of the invention may be prepared by coneutralization of a mixture of the carboxylic acids with suitable bases, particularly the hydroxides and/or carbonates of the metals desired. The coneutralization step may be carried out in situ in the liquid menstruum to which the complex compound is to be applied in actual use. For example, the mixed acids may be coneutralized in a portion or all of a lubricating oil which then forms the dispersant of the complex and is thereby gelled to a grease. In a similar manner, the coneutralization may be carried out in other dispersants or solvent fluids, the characteristics of which are to be modified by the complex compound. This coneutralization method of preparation is particularly desirable in cases in which the salts and soap have the same metal constituent. The coneutralized material is heated to a temperature above about 400° F., preferably 450° to 550° F., in order to dehydrate it and to form the baked complex. When this heating step is carried out in a liquid dispersant, the latter should have a boiling point above 400° F. or heating should be carried out under pressure.

The coneutralization method of preparation is not necessary as long as the metal salts and soap are present when heating to the complex forming temperatures. Thus, the complex compounds of the invention may also be prepared by separately preforming at least a portion of the acetic acid salt, the medium molecular weight carboxylic acid salt, and the high molecular weight carboxylic acid soap, intimately mixing the preformed materials, and baking the resulting mixture under complex forming conditions. This method is especially useful when different metals are employed as bases for the salts and soap.

In general, the lubricating grease compositions thickened with the complexes of the invention are prepared by mixing together the desired amount of mineral and/or synthetic lubricating oil, the base and the high molecular weight carboxylic acid. The mixture is warmed while mixing to a temperature of about 90 to 100° F., but preferably just sufficient to melt the high molecular weight acid. The acetic acid and the medium molecular weight carboxylic acid employed are then added to the mixture, and allowed to react without further external heating. When temperature of reaction starts to subside, external heating is then applied and is continued until the temperature is about 400° to 550°, preferably about 450° to 550° F. At this point, heating is discontinued and the grease batch is cooled to about 250° F. Any of the conventional anti-oxidant additives, such as phenyl alpha naphthylamine, are added at this time, and the grease is further cooled to below about 200° F. The resulting grease composition may be homogenized by passing it through a Morehouse mill or Gaulin type homogenizer.

The grease compositions may also be prepared as follows:

First mix together the mineral and/or synthetic lubricating oil, the base, the high molecular weight carboxylic acid, and the medium molecular weight carboxylic acid. Warm the mixture while mixing to a temperature of about 130° to 150° F. Add acetic acid to the warmed mixture, and then heat to the complex forming temperature of about 400° to 550° F. Other than adding the medium molecular weight carboxylic acid to the initial mixture rather than in admixture with the acetic acid after the warming has taken place, this method of preparation is similar to that outlined in the preceding paragraph.

The complex compounds of the invention when prepared in a liquid dispersant or solvent may be isolated from their dispersions or solutions by solvent extraction of the dispersing medium in a solvent in which the complex is insoluble. Suitable solvents include most of the hydrocarbon solvents, acetone, etc.; the proper choice depending on the solubility characteristics of the liquid menstruum used to disperse the complex.

The invention will be more fully understood by reference to the following specific examples illustrating various modifications of the invention.

EXAMPLE I

A number of mineral oil base lubricating grease compositions having the formulations and properties given in Table I below were prepared as follows:

Grease No. A

All of the mineral lubricating oil, caprylic acid, valeric acid and hydrated lime were charged to a fire heated kettle and warmed while mixing to 150° F. The acetic acid was then added, and the heating was continued until the temperature reached 450° F. At this temperature the heating was discontinued, and the grease batch was cooled to 250° F. Phenyl alpha naphthylamine was then added, and the grease was further cooled to about 200° F. The resulting grease composition was finished by being passed through a Gaulin homogenizer at 5000 p.s.i.

Grease No. B

All of the mineral lurbicating oil, hydrated lime, stearic acid and o-phthalic acid were charged to a fire heated kettle, and the mixture was warmed to 135° F. with thorough mixing. At this temperature all of the acetic acid was added, and the heating was continued until a temperature of 510° F. was reached. Heating was then discontinued and the grease cooled to 250° F. with stirring. Phenyl alpha naphthylamine was added to the grease batch and cooling continued to 180° F. The grease was then homogenized in a Gaulin homogenizer.

Grease No. C

This grease, having the formulation listed below in Table I, was prepared by the method described above with respect to the preparation of Grease A, except that C_5 Oxo acid was employed as the medium molecular weight carboxylic acid and lauric acid was employed as the high molecular weight carboxylic acid.

Grease No. D

All of the mineral lubricating oil, hydrated lime, Hydrofol Acid 51, and lactic acid were charged to a fire heated kettle and warmed to 135° F. with stirring. The glacial acetic acid was then added to the mixture, which was then heated to 500° F. Heating was then discontinued, and the grease batch cooled to 250° F. At this temperature the phenyl alpha naphthylamine was added,

and the grease was further cooled to 200° F. The grease was then homogenized in a Gaulin type homogenizer, filtered and packaged.

Grease No. E

All of the mineral lubricating oil, stearic acid, hydrated lime, and thiophene carboxylic acid were charged to a fire heated grease kettle and mixed intimately while raising the temperature to 135° F. Glacial acetic acid was then added, and heating was continued to 500° F. The grease batch was held at this temperature for 10 minutes and then cooled to 275° F. with stirring. The phenyl alpha naphthylamine was added to the grease batch, and cooling was continued to 180°–200° F. The resulting grease composition was then pumped to a Gaulin homogenizer, homogenized at 6000 p.s.i., filtered and packaged.

Grease No. F

All of the mineral lubricating oil, hydrated lime, and stearic acid were charged to a fire heated kettle and warmed to 150° F. while mixing. The isobutyric acid and acetic acid were then added as a mixture and heating was continued until the temperature reached 430°–450° F. Heating was then discontinued and the grease batch cooled to 250° F. At this temperature the phenyl alpha naphthylamine was added, and the grease batch further cooled to below 200° F. The resulting grease composition was then finished by passing it through a Morehouse mill homogenizer at 5000 p.s.i.

Grease No. G

The mineral lubricating oil, hydrated lime, and Hydrofol Acid 51 were charged to a fire heated kettle and warmed to 135° F. with stirring. The glacial acetic acid and the C_8 Oxo acid were then added to the mixture, and heating continued to 500° F. Heating was then discontinued and the grease batch cooled to 275° F. The phenyl alpha naphthylamine was then added, and cooling was continued to 200° F. At this temperature, the grease product was passed through a Gaulin homogenizer at 3000 p.s.i.

Grease No. H

The mineral lubricating oil, hydrated lime, Hydrofol Acid 51 were charged to a fire heated kettle, and warmed to 150° F. while agitating. When the mixture started to thicken, a mixture of acetic acid and caprylic acid was added and the temperature raised to 500° F. Heating was then discontinued, and the grease batch was cooled to 250° F. with agitation. At this temperature, the phenyl alpha naphthylamine was added, and the greases further cooled to 200° F. The grease product was then Gaulin homogenized, filtered and packaged.

Grease No. I

The mineral lubricating oil, Hydrofol Acid 51, hydrated lime and benzoic acid were charged to a fire heated kettle and mixed together while heating to 135° F. Acetic acid was then added, and heating continued to 510° F. Heating was then discontinued, and the grease cooled to 250° F. while continuing to agitate. At this temperature phenyl alpha naphthylamine was added, and the grease batch further cooled to 180° F. while mixing. The grease product was Gaulin homogenized at 5000 p.s.i., filtered and packaged.

Grease No. J

This grease was prepared by the method substantially as described in the preparation of Grease No. H.

Grease No. K

This grease was also prepared by the method substantially as described in the preparation of Grease No. H, except that capric acid rather than caprylic acid was employed as the medium molecular weight carboxylic acid.

Grease No. L

This grease was also prepared by the method substantially as described in the preparation of Grease H.

Grease No. M

All of the mineral lubricating oil, the stearic acid and hydrated lime were charged to a fire heated kettle and heated to about 130° F. with stirring. The acetic acid was then added, and the grease mixture heated to a temperature of 500° F. Heating was then discontinued, and the grease cooled to 250° F. with stirring. Phenyl alpha naphthylamine was added, and the grease cooled further to 200° F. The resulting grease composition was homogenized at a high rate of shear in a Gaulin homogenizer.

The exact compositions and properties of the above compositions are tabulated in Table I below:

TABLE I

Grease No	A	B	C	D	E	F	G	H	I	J	K	L	M
Formulation (Wt. Percent):													
Glacial acetic acid	12.0	12.0	12.0	12.0	12.0	12.0	8.0	8.0	12.0	8.0	8.0	8.0	8.0
Valeric acid	3.0												
C_8 Oxo acid			3.0										
Caprylic acid	3.0							3.0		2.0			
Lauric acid			3.0									2.0	
Stearic acid		3.0			2.0	4.0							4.0
o-Phthalic		3.0											
Hydrofol Acid 51				3.5			1.0	1.0	3.0	2.0	1.0	2.0	
Thiophene Carboxylic Acid					4.0								
Iso butyric acid						2.0							
C_8 Oxo acid							3.0						
Capric acid											3.0		
Benzoic acid									3.0				
Lactic acid				2.5									
Hydrated lime	10.0	10.2	10.5	9.6	10.0	10.1	8.9	6.7	9.7	6.5	6.4	6.1	6.0
Phenyl alpha naphthylamine	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Mineral lubricating oil, 55 SUS @ 210° F	71.5	71.3	71.0	71.9	71.5	71.4	78.6	80.8	71.8	81.0	81.1	81.4	81.5
Mol ratio: Acetic acid to higher acid	4.0	7.0	4.5	5.1	5.2	5.4	5.5	5.3	5.7	6.3	6.3	9	9.5
Equivalent Sap. No. of acids (Ex acetic)	470	435	415	374	358	344	342	343	330	295	294	250	197
Carbon atom spread (Medium to higher acid)	3	10	7	15	13	14	8	10	11	10	8		
Free alkalinity (percent NaOH)		0.67						0.78	0.65	0.77		0.34	

TABLE I—Continued

Grease No.	A	B	C	D	E	F	G	H	I	J	K	L	M
Properties: Appearance	Semi-fluid	(1)	(1)	(1)	(1)	(1)	Soft uniform	(1)	(1)	(1)	(1)	(1)	(1)
Dropping Point (° F.)	500+	500+	500+	500+	500+	500+	500+	500+	500+	500+	500+	500+	500+
Penetrations (77° F.,mm./10):													
Unworked	Poor structural stability	265	342	295	275	270	300	272	186	344	262	251	242
Worked 60 strokes		288	342	320	290	285	335	328	208	370	272	272	262
Worked 100,000 strokes		320 (113° F.)	352 (110° F.)	365	335 (113° F.)	270 (114° F.)	400	362	250 (121° F.)	----------	----------	310	360
Norma-Hoffmann Oxidation Test (hrs. to 5 p.s.i. drop)	----------	400	----------	250	----------	----------	----------	----------	365	----------	----------	360	----------
Water solubility (boiling water)	----------	----------	----------	----------	----------	Nil	----------	Nil	Nil	Nil	Nil	----------	----------
Timken Test (lbs. carried)	40	50	40	40	40	40	40	----------	50	----------	----------	Failed (40)	Failed
Scar	----------	Narrow	----------	Narrow	Narrow	----------	----------	----------	Narrow	----------	----------	----------	----------
Almen Test—													
Gradual loading	----------	----------	----------	----------	----------	15	----------	----------	15	----------	----------	15	----------
Shock loading	----------	----------	----------	----------	----------	15	----------	----------	15	----------	----------	Failed (15)	----------
Wheel bearing test (660 r.p.m.)	----------	----------	----------	----------	----------	Pass	----------	Pass	----------	----------	Pass	Pass	----------
Stability in storage Crust formation	----------	----------	----------	None	----------	None	----------	None	----------	None	----------	None	----------

[1] Excellent, smooth, uniform.

It will be seen that a wide variety of medium molecular weight carboxylic acids can be employed in conjunction with acetic acid and with conventional grease-forming, high molecular weight carboxylic acids to prepare grease thickeners, which have the ability to impart outstanding structural stability and extreme pressure properties to the final grease compositions. It should also be noted that only the soap-salt complexes wherein the carbon atom spread between the medium and the high molecular weight carboxylic acids was as least 7 and wherein the average saponification value of the medium and the high molecular weight carboxylic acids was from about 290 to 450 showed the desired results. Grease Nos. A and M, for example, having either carbon atom spreads or equivalent saponification values outside the operable ranges had either poorer structural stability or extreme pressure properties than the greases of the invention.

EXAMPLE II

A number of lubricating oil compositions containing furoic acid as an acidic constituent in the thickener and having the constituents and properties listed in Table II below were prepared as follows:

Composition No. A

The mineral lubricating oil, hydrated lime, Hydrofol Acid 51 and furoic acid were charged to a fire heated grease kettle and mixed intimately while raising the temperature to 135° F. Glacial acetic acid was then added, and heating was continued to 500° F. The grease batch was held at this temperature for 10 minutes and then cooled to 275° F. with continued stirring. At this temperature phenyl alpha naphthylamine was added, and the grease batch cooled further to 180°–200° F. The grease was then homogenized in a Gaulin homogenizer at 6000 p.s.i., filtered and packaged.

Composition No. B

This composition was prepared by the method substantially as described in the preparation of Composition No. A, except that no acetic acid was employed.

Composition No. C

This composition was also prepared by the method substantially as described in the preparation of Composition No. A, except that sodium hydroxide was employed in place of the hydrated lime and no acetic acid was employed.

The exact constituents and properties of the above compositions are tabulated in Table II below:

TABLE II

Composition No.	A	B	C
Formulations (Wt. Percent):			
Glacial acetic acid	12.0	----------	----------
Hydrofol Acid 51 [1]	3.0	8.0	10.0
Furoic acid	3.0	4.0	5.0
Hydrated lime	9.8	5.0	----------
Sodium hydroxide	----------	----------	4.8
Phenyl alpha naphthylamine	0.5	0.5	0.5
Mineral lubricating oil (55 SUS/210° F.)	71.7	82.5	79.7
Mol Ratio (acetic acid to higher acids)	5.3	----------	----------
Saponification No. of acids (Ex acetic)	350	----------	----------
Carbon atom spread (Medium to higher acid)	13	13	13
Free alkalinity (Percent NaOH)	0.56	----------	----------
Properties:			
Appearance	[2]	[3]	[2]
Dropping Point (° F.)	500	----------	465
Penetrations (77° F., mm./10)—			
Unworked	265	----------	285
Worked (60 strokes)	285	----------	295
Worked (100,000 strokes)	286	----------	340
Water solubility (boiling water)	Nil	----------	Soluble
Timken Test Load—			
50 lbs.	Pass	----------	Fail
40 lbs.	----------	----------	Fail

[1] Commercial stearic acid in the form of hydrogenated fish oil acid.
[2] Excellent, stable grease.
[3] No grease structure.

At the concentrations shown in Composition No. B no satisfactory grease composition was obtained by employing the calcium salt of furoic acid in combination with the normally grease forming metal soaps of high molecular weight carboxylic acids, e.g. stearic acid, in the grease thickener.

It will be seen, however, from Composition No. A that lubricating grease compositions can be prepared from a thickener comprising the calcium salt of furoic acid, the

calcium salt of acetic acid, and the calcium soap of stearic acid. The complex thickener resulting from this combination of acids gives an excellent stable grease product having a high load carrying capacity.

Composition No. C illustrates that greases can be prepared from a thickener comprising sodium furoate and sodium stearate, but they show little load carrying capacity. This grease, for example, failed the Timken test at a 20 lb. load.

EXAMPLE III

The use of commercial mixtures of medium molecular weight acids, e.g. Neo Fat 360 which is composed of 60 wt. percent caprylic acid and 40 wt. percent of capric acid, is exemplified by this experiment. The grease was prepared by the method described in the preparation of Composition A, of Example II.

The composition and properties of the final grease composition are tabulated in Table III below:

TABLE III

Formulation	Wt. Percent
Glacial acetic acid	12.0
Neo Fat 360 [1]	4.8
Hydrofol Acid 51	1.2
Hydrated lime	9.8
Phenyl alpha naphthylamine	0.5
Mineral lubricating oil (55 SUS/210° F.)	71.8
Mol ratio (acetic to higher acids)	5.7
Saponification No. of acids (Ex acetic)	9
Carbon atom spread (medium to higher acids)	
Properties:	
Appearance	[2]
Dropping Point (° F.)	500+
Penetrations (77° F., mm./10)—	
Unworked	210
Worked (60 strokes)	220
Worked (100,000 strokes)	270
Water solubility (boiling water)	Nil
Timken Test (40 lbs. load)	[3]

[1] 60% caprylic acid; 40% capric acid; sap. value (mg. KOH/gm.)—355.6.
[2] Excellent, uniform grease.
[3] Pass (narrow scar).

EXAMPLE IV

The high metal content of the soap-salt complex grease thickeners of the invention can be achieved by employing citric acid as the medium molecular weight carboxylic acid. This tricarboxylic acid is capable of complexing with calcium acetate and calcium soap of a high molecular weight carboxylic acid, e.g. stearic, in the grease thickener, and because of its tricarboxylation allows for high calcium content with the use of a minor amount of citric acid. The high combined calcium content is necessary in order to obtain the desired extreme pressure properties.

Grease No. 1

The mineral lubricating oil, hydrated lime, stearic acid and citric acid were charged to a fire heated kettle and warmed to 135° F. while stirring. The acetic acid is then added, and the ingredients further heated to 500° F. The grease batch is cooled to 250° F. while agitating, and the phenyl alpha naphthylamine added. The grease is further cooled to below about 180° F. and then Gaulin homogenized at 6500 p.s.i.

Grease No. 2

This grease was prepared by the method substantially as described in the preparation of Grease No. 1 with the exception that 1.0 wt. percent rather than 2.0 wt. percent of citric acid was employed.

The composition and properties of these two greases are tabulated below in Table IV.

TABLE IV

Formulation (Wt. Percent)	1	2
Glacial acetic acid	12.0	10.0
Stearic acid	4.0	4.0
Citric acid	2.0	1.0
Hydrated lime	10.0	8.2
Phenyl alpha naphthylamine	0.5	0.5
Mineral lubricating oil (55 SUS/210° F.)	71.5	76.3
Mol ratio of acetic to higher acids	8.5	8.8
Saponification No. (Ex acetic acid)	397	318
Carbon atom spread (Medium to higher acid)	12	12
Properties:		
Appearance	[1]	[1]
Dropping Point (°F.)	500+	500+
Penetration (77° F. mm./10)—		
Unworked	245	255
Worked (60 strokes)	285	290
Worked (100,000 strokes)	[2] 300	[2] 270
Water solubility (boiling water)	Nil	Nil
Timken Test (40 lbs. load)	[3]	[3]
Almen Test (15 wgts. shock load)	Pass	Pass
Norma Hoffmann Oxidation Test (hrs. to 5 p.s.i. drop)	400+	400+
Wheel Bearing Tests (1,660 r.p.m.— 220° F.)	Pass	Pass

[1] Excellent, smooth, uniform.
[2] 114° F.
[3] Pass (narrow scar).

EXAMPLE V

The use of phthalic anhydride as a source of the medium molecular weight carboxylic acid constituent of the grease thickener of the invention is demonstrated by the grease prepared as follows:

The mineral lubricating oil, hydrated lime, stearic acid and phthalic anhydride were charged to a fire heated grease kettle and thoroughly mixed while warming to 135° F. At this temperature the aqueous solution of acetic acid (80 wt. percent of acetic acid) was added, and heating was continued to 510° F. The heating was then discontinued, and the grease cooled to 250° F. with stirring. Phenyl alpha naphthylamine was then added, and the grease batch was further cooled to 180° F. The grease was then Gaulin homogenized, filtered and packaged.

The formulation and properties of the final grease composition are tabulated in Table V below:

TABLE V

Formulation	Wt. Percent
Acetic acid (80—)	12.0
Stearic acid	3.0
Phthalic anhydride	3.0
Hydrated lime	10.2
Phenyl alpha naphthylamine	0.5
Mineral lubricating oil (55 SUS/210° F.)	71.3
Mol ratio of acetic to higher acids	
Saponification No. of acids (Ex acetic)	435
Carbon atom spread (Medium to higher acid)	10
Properties:	
Appearance	[1]
Dropping Point (° F.)	500
Penetrations (77° F. mm./10)—	
Unworked	275
Worked (60 strokes)	278

[1] Excellent, smooth grease.

EXAMPLE VI

A lubricating grease containing a grease thickener prepared with hydroxy benzoic acid as the medium weight carboxylic acid constituent was prepared by the method described above in preparing Grease H of Example I, except that hydroxy benzoic acid rather than benzoic

acid was employed as the medium molecular weight carboxylic acid.

The composition and properties of the grease are tabulated in Table VI below:

TABLE VI

Formulation	Wt. percent
Glacial acetic acid	12.0
Stearic acid	3.0
Hydroxy benzoic acid	3.0
Hydrated lime	9.2
Phenyl alpha naphthylamine	0.5
Mineral lubricating oil (55 SUS/210° F.)	72.3
Free alkalinity (percent NaOH)	0.33
Mol ratio (acetic to higher acids)	3
Saponification No. of acids (Ex acetic acid)	300
Carbon atom spread (Medium to higher acid)	11
Properties:	
Appearance	(1)
Dropping Point (° F.)	500+
Penetrations (77° F. mm./10)—	
Unworked	290
Worked (60 strokes)	275
Worked (100,000 strokes)	[2] 342
Water solubility (boiling water)	Nil
Timken Test (40 lbs.)	Pass

[1] Excellent, smooth, uniform.
[2] 108° F.

In brief summary, the present invention relates to soap-salt complexes comprising a metal salt of acetic acid, a metal salt of a medium molecular weight carboxylic acid containing from about 3 to 10 carbon atoms, and a metal soap of a high molecular weight carboxylic acid containing from about 12 to 22 carbon atoms. The preferred soap-salt complexes of the invention also have a carbon atom spread between the high and medium molecular weight carboxylic acid of at least 7 and an average saponification value of acids, other than acetic acid of between about 290 to 450. In addition the mol ratio of acetic acid to the medium and high molecular weight carboxylic acids is between about 4:1 to 40:1. In general, the mol ratio of medium to high molecular weight acids will be about 0.5:1 to 10:1, preferably about 1:1 to 9:1.

Lubricating grease compositions of this invention contain complex thickeners prepared from about 4 to 20 wt. percent, preferably 8 to 12 wt. percent of acetic acid, from about 0.5 to 8 wt. percent, preferably 2 to 4 wt. percent of the medium molecular weight carboxylic acid; and from about 0.5 to 10 wt. percent, preferably 1 to 5 wt. percent of the high molecular weight carboxylic acid, the above weight percentages being based on the total weight of the grease composition. Ordinarily, a major proportion of acetic acid will be employed in amounts up to or higher than twice the combined weight percentages of the other two acids. The metal hydroxide and/or carbonate employed, e.g. lime, will be employed in amounts from about 5 to 12 wt. percent, based on the total weight of the grease composition.

The invention is not limited to the specific conditions and materials of the foregoing examples. These conditions and materials may be varied within the limits indicated in the general portions of the specification. The compositions prepared in accordance with the invention may contain various conventional additives, such as oxidation inhibitors, metal deactivators, corrosion preventatives, extreme pressure agents, dyes, deodorants, etc. as will be understood by those skilled in the art.

What is claimed is:

1. A lubricating grease composition which comprises a lubricating oil thickened to grease consistency within the range of 5 to 40 wt. percent of a complex of a metal salt of acetic acid, a metal salt of a medium molecular weight carboxylic acid containing from about 3 to 10 carbon atoms, and a metal soap of a high molecular weight carboxylic acid containing from about 12 to 22 carbon atoms, wherein the mol ratio of acetic to the other carboxylic acids is at least 4:1, the mol ratio of medium to high molecular weight acids is in the range of 0:5:1 to 10:1 the average difference in number of carbon atoms per molecule between the high and the medium molecular weight carboxylic acids is at least 7, the metal constituent of said soaps and salts is selected from the group consisting of alkaline earth metals and zinc, and said complex is prepared at a temperature in the range of 400° to 550° F.

2. The lubricating grease composition of claim 1 wherein said metal constituent is calcium.

3. The lubricating grease composition of claim 1 wherein said lubricating oil base is a mineral lubricating oil.

4. The grease composition of claim 1 wherein said high molecular weight carboxylic acid contains 18 to 22 carbon atoms.

5. A lubricating grease composition which comprises a mineral lubricatnig oil thickened to grease consistency within the range of 5 to 40 wt. percent of a complex prepared at a temperature in the range of 400° to 500° F. of a calcium salt of acetic acid, a calcium salt of caprylic acid and a calcium soap of hydrogenated fish oil acid, wherein the mol ratio of said acetic acid to said caprylic acid and said hydrogenated fish oil acid is about 5:1 and the mol ratio of said caprylic acid to said hydrogenated fish oil acid is about 6:1.

6. The method of preparing a lubricating grease composition which comprises dispersing a metal base, a medium molecular weight carboxylic acid containing from about 3 to 10 carbon atoms and a high molecular weight carboxylic acid containing from 12 to 22 carbon atoms in a dispersing proportion of a mineral lubricating oil, heating the dispersion to a temperature of about 130° to 150° F., adding acetic acid to the dispersion, and heating the resulting mixture to a temperature of about 400° to 550° F., the mol ratio of acetic to the other carboxylic acids being at least 4:1, the mol ratio of the medium to the high molecular weight acids being in the range of 0.5:1 to 10:1, the metal constitutent of said metal base being selected from the group consisting of alkaline earth metals and zinc and the total amount of soaps and salts in said composition being in the range of 5 to 40 wt. percent.

7. The method of claim 6 wherein the medium molecular weight carboxylic acid is added to the dispersion with the acetic acid after heating the dispersion to a temperature of about 130° to 150° F.

8. The method of claim 6 wherein the resulting grease composition is homogenized.

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