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LUBRICATING OILS THICKENED TO A GREASE WITH HYDROUS METAL SALTS AND PROCESS FOR FORMING SAME

Arnold J. Morway, Clark, N. J., assignor to Esso Research and Engineering Company, a corporation of Delaware

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This invention relates to new and useful lubricating compositions and to the method of preparing the same. More particularly, the invention pertains to oil-dispersible compositions consisting of hydrous mixtures of metal salts of low molecular weight carboxylic acids and moderate molecular weight carboxylic acids and to sols, gels or greases containing the same.

One aspect of the present invention relates to greases or gelling agents therefor, containing no soap and consisting of or containing a hydrous mixture of metal salts comprising at least one metal salt of low molecular weight carboxylic acid having from about 1 to 3 carbon atoms per molecule and at least one metal salt of moderate molecular weight carboxylic acid having from about 7 to 10 carbon atoms per molecule in which the mol ratio of low molecular weight carboxylic acid to moderate molecular weight carboxylic acid is at least about 2 to 1. The compositions of the invention include novel and improved greases, lubricating oils, etc. In particular, greases containing the hydrous mixtures of metal salts of the invention as grease thickeners have been found to have excellent extreme pressure properties as well as other desirable grease characteristics.

The use of carboxylic acids in the preparation of grease thickeners is well known in the art. Heretofore, the mixtures of carboxylic acids employed for such purposes have consisted of mixtures of high molecular weight carboxylic acids or combinations of high molecular weight carboxylic acids and low molecular weight carboxylic acids in the form of metal soaps or metal soap-salt complexes. These complexes, for example, have been prepared from the commonly known soap-forming, grease-making, high molecular weight fatty acids, saturated or unsaturated, containing from 12 to 22 carbon atoms, and low molecular weight carboxylic acids having from 1 to 6 carbon atoms such as acetic, propionic, alkoxy propionic, furoic and the like. Normally about equimolar proportions of these low and high molecular weight carboxylic acids have been employed by the prior art in the preparation of the metal soap-salt complexes. Highly desirable characteristics recently have been imparted to these types of complex compounds 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. These complex compounds have been prepared at temperatures of about 450° to 550° F.

The present invention is based on the surprising discovery that hydrous mixtures of metal salts alone, prepared at temperatures of about 150° to 200° F. and comprising a metal salt of low molecular weight carboxylic acid, a metal salt of moderate molecular weight carboxylic acid and water, can be effectively employed as lubricating grease thickeners, which impart to the final grease compositions outstanding extreme pressure properties. It has also been found that a mol ratio of above about 2 to 1 of low to moderate molecular weight carboxylic acids can be effectively utilized to prepare the novel mixtures of hydrous metal salts of the invention. For purposes of this invention, those aliphatic monocarboxylic acids which contain from about 7 to 10 carbon atoms, and which are intermediate in chain length and in molecular weight when compared to the low molecular weight and high molecular weight carboxylic acids discussed above, are designated as intermediate molecular weight carboxylic acids.

The low molecular weight acids contemplated in this invention include saturated and unsaturated carboxylic acids having from about 1 to 3 carbon atoms, such as formic, acetic, propionic, acrylic, and lactic acid. Acetic acid is especially preferred. Mixed low molecular weight carboxylic acids wherein the acids contain from about 1 to 3 carbon atoms and have an average saponification value of above about 540 may also be employed.

The intermediate molecular weight acids are those aliphatic monocarboxylic acids containing from about 7 to 10 carbon atoms, preferably about 8 to 9 carbon atoms. Either saturated or unsaturated fatty acids may be utilized, though the saturated fatty acids are preferred. Straight chain or substantially straight chain acids are also preferred. The average saponification value of the single or mixed intermediate molecular weight acids should be about 310 to 440, preferably about 350 to 420. Some of the intermediate molecular weight monocarboxylic acids coming within the above prescriptions are exemplified by:

5-methyl-2-hexanoic
Heptanoic (enanthic)
Octanoic (caprylic)
2-ethyl hexanoic
C_8 Oxo acids
Nonanoic (pelargonic)
Decanoic (capric)
C_{10} Oxo acids

Commercial mixtures of these intermediiate molecular weight carboxylic acids having an average saponification value of from about 310 to 440 can also be employed.

The Oxo acids useful for the purposes of the present invention, e. g. the saturated branched chain C_8 and 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 temperatures of about 300° to 400° F. and pressures of about 2500 to 4000 p. s. i. g. in the presence of a group VIII metal catalyst, preferably cobalt. In U. S. Patent No. 2,632,021 the Oxo process and the nature of the reaction products, e. g. the C_8 Oxo products, are disclosed in detail. The preparation of Oxo 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 Oxo acids therefrom are considered to be directly related to the essence of the present invention. The C_8 and C_{10} Oxo acids may be derived respectively from C_7 and C_9 olefins obtained by polymerizing propylene alone or with some butylene.

The choice of the metal component depends to a certain extent on use for which the hydrous mixture of metal salts of the invention is contemplated. The alkaline earth metals, particularly calcium, are especially useful for many purposes of the invention. These metals afford greatest advantages when the hydrous mixtures of their salts are used as thickeners in the manufacture of greases, because the greases containing them have outstanding load carrying characteristics, and structural stability at high temperatures and under mechanical stress even without the use of conventional extreme pressure additives and stabilizing agents. The alkaline earth metals differ in this respect from the alkali metals, i. e. sodium, potassium and lithium. Hydrous mixtures of metal salts of high alkali metal content, formed from the acids and in the mol ratios of this invention, yield greases of less structural stability even when added to the oil dispersant in relatively high proportions.

Other metals useful for the purposes of this invention are the heavy metals of groups I, II, IV and VIII of the periodic system. In particular, metals such as copper, zinc, lead, cobalt, strontium, magnesium and cobalt can be used.

The metal components of the salts of both low and intermediate molecular weight acids may be any one or more of the metals set forth above. Though the metal of the salts may be either the same or different, in most cases the salts contain the same metal.

The hydrous mixtures of the metal salts may be prepared by co-neutralization of a mixture of the acids with suitable bases, particularly the hydroxides and/or carbonates of the metals desired. The co-neutralization step may be carried out in situ in the liquid menstruum to which the mixture of salts is to be applied in actual use. For example, the mixed acids may be co-neutralized in a portion or all of the lubricating oil forming the dispersant of a grease to be thickened by the hydrous mixture of salts. This method is particularly desirable in cases in which the salts have the same metal constituent. The temperature at which the co-neutralization is carried out will be in the range of about 150° to 200° F. When this heating step is carried out in a liquid dispersant, the latter should have a boiling point above the heating temperature or the heating should be carried out under pressure.

The hydrous mixture of metal salts may also be prepared by separately preforming at least a portion of the low molecular weight carboxylic acid salt and/or the intermediate molecular weight carboxylic acid salt. This method is especially useful when different metals are employed as bases for the salt constituents. Preformed metal salts can replace about 30 to 80% of the free acids and stoichiometric equivalent bases.

The choice of material to which the hydrous mixture of salts of high metal content are applied also depends, of course, on the use contemplated. For lubricant manufacture, the detergency and extreme pressure characteristics of the hydrous mixtures of metal salts may be utilized in combination with a wide variety of mineral as well as synthetic lubricating oils. Relatively large proportions of chemically combined yet active metal thus may be introduced into the oils without settling out. In general, the lubricating oil should have a viscosity within the range of about 60 to 2500 SUS at 100° F. and about 35 to 200 SUS at 210° F., a pour point of about +20 to −75° F., and a flash point of about 350° to 650° F. A viscosity index of 100 or higher is also usually desirable, though oils having a lower viscosity index can be employed. As previously mentioned, synthetic as well as mineral lubricating oils can be employed as part or 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 the simple diesters, di-2-ethylhexyl sebacate, di-C_8-oxo azelate, and di-isooctyl azelate or the complex esters formed from glycols, dicarboxylic acids and alcohols or monocarboxylic acids can also be used.

Hydrous metal salts mixture proportions of about 5 to 50 wt. percent, preferably about 10 to 30 wt. percent, based on the total weight of the grease, may be used in preparing the novel greases of this invention. For other compositions of this invention the proportion may be as low as one percent by weight or even 0.1% when the desired effect of metal content is simply either catalytic as for a paint dryer or anti-corrosive as for combining with a corrosive ash upon combustion.

The hydrous mixture of metal salts may also be prepared in a low viscosity mineral and/or synthetic lubricating oil and then blended with mineral and/or synthetic lubricating oils having the substantially same or higher viscosities to produce grease compositions within the scope of this invention.

The temperature at which the hydrous mixture of metal salts is prepared or treated is an important feature of the present invention, since it will determine the physical as well as the chemical characteristics of the resulting products. In accordance with this invention, temperatures of about 150° to 200° F., preferably about 175° to 200° F., are employed to prepare the hydrous mixtures of metal salts. By allowing the temperature of reaction to rise to 212° F., some of the water of reaction can be partly removed. However, this requires close control and, in general, the temperature is held below 212° F. These temperatures are below those required to dehydrate to form anhydrous mixtures or to form complexes or compounds with coordinated valences from the mixtures of metal salts. Thus, the hydrous mixtures of metal salts of the invention will contain the water of reaction or the water introduced along with the reagents, e. g. aqueous solutions of the low molecular weight carboxylic acids. The amount of water present in the hydrous mixtures of metal salts can vary widely. Usually, however, about 0.5 to 15.0 wt. percent, preferably 1 to 5 wt. percent, water based on the total weight of the hydrous mixture of metal salts will be present.

Another significant feature of the present invention is the high metal content of the hydrous mixtures of metal salts. By employing the combination of low and intermediate molecular weight acids in accordance with this invention, mol ratios of low to intermediate molecular weight acids of about 2:1 to about 40:1, preferably about 5:1 to 30:1, can be employed without encountering solubility or sedimentation problems.

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 thickened with a hydrous mixture of the metal salts of acetic acid and caprylic acid and having the formulations listed in Table I below were prepared as follows:

Product A

All of the mineral lubricating oil and hydrated lime were charged to a reaction kettle equipped with means for efficient stirring. The hydrated lime and mineral oil were mixed together to form a smooth slurry at a temperature of about 70° F. The acetic and caprylic acids were blended together and charged to the kettle. Reaction occurs immediately with the temperature rising to about 190° F. and a solid product is formed. Stirring is continued until the grease cools to 100° F. in about two hours.

Product B

This lubricant was prepared by blending 20% of grease A with 80% of a mineral lubricating oil having a viscosity of 80 SUS/210° F., i. e. the mineral oil base of grease A.

Product C

This product was prepared substantially as described in the preparation of grease A, except that the only acid employed was acetic acid.

Product D

This product was prepared by blending 20% of Product C with 80% of the mineral lubricating oil having a viscosity of 80 SUS/210° F.

Product E

This grease was prepared substantially as described in the preparation of grease A, except that an aqueous solution of acetic acid, 80% in concentration, was employed in place of the glacial acetic acid.

Product F

This lubricant was prepared by blending 20% of grease E with 80% of the same mineral lubricating oil having a viscosity of 80 SUS/210° F.

The composition of these products and their properties are tabulated below in Table I.

TABLE I

Product	A	B	C	D	E	F
Formulation:						
Glacial acetic acid	18.0	3.6	20.0	4.0		
Acetic acid (80%)					22.5	4.50.
Commercial caprylic acid (Sap. No. 327)	2.0	0.40			2.0	0.40.
Hydrated lime	12.8	2.56	13.3	2.66	12.8	2.56.
Phenyl alpha naphthylamine antioxidant	0.5	0.10			0.5	0.10.
Mineral lubricating oil (80 SUS/210° F.)	66.7	93.34	66.7	93.34	62.2	92.44.
Properties:						
Mol ratio (acetic to caprylic acids)	25.8/1	25.8/1			25.8/1	25.8/1.
Appearance	Excellent, Smooth, Uniform.	Fluid	Smooth, Uniform.	Fluid	Excellent, Smooth, Uniform.	Fluid.
Mobilometer Consistency 77° F.[1]		750		815		752.
Penetrations (77° F., mm./10)—						
Unworked	220		365		230	
Worked (60 strokes)	252		370		242	
Worked (75,000 strokes)	319		370			
Free Alkalinity (percent NaOH)	0.59					
Timken Test (lbs. carried)	50		50	Separates in 48 hrs.	50	
Corrosion	None					
Oil Separation		None	Separates oil copiously on storage.			Stable suspension after 2 weeks.

[1] Consistency is product of time in seconds and load in grams required for a perforated cone to sink through a fixed depth of semi-fluid substance. It is a relative measure of viscosity in non-Newtonian fluids.

It will be noted that greases prepared by thickening with a hydrous mixture of metal salts of low and intermediate molecular weight carboxylic acids were stable non-settling greases having outstanding extreme pressure and anti-corrosion properties. It will be further noted that substantially all of the water of reaction remains in the lubricant. Portions of the greases so prepared can also be diluted to any salt concentration by blending with additional mineral oil up to 99% or more. (See Products B and F.)

The use of acetic acid alone resulted in unsatisfactory compositions from which the salt and oil separated. (See Products C and D.)

Products E and F demonstrate that large amounts of water can be tolerated, and that in some lubricating services it can be distinctly beneficial. Aqueous solutions of acetic acid, in 80% or lower concentrations can be employed.

The lubricating compositions of the invention as described above are suitable, for example, as marine diesel engine upper cylinder lubricants. These compositions containing calcium salts are capable of reducing cylinder liner wear and minimizing acid corrosion by neutralizing the acids formed during the combustion of fuels.

EXAMPLE II

A grease was prepared from the following ingredients:

Formulation

	Weight percent
Glacial acetic acid	12.0
Commercial caprylic acid	6.0
Hydrated lime	10.0
Phenyl alpha naphthylamine	0.5
Silicone fluid 710 [1]	71.5

[1] Methyl phenyl polysiloxanes having a high ratio of phenyl to methyl groupings. Viscosity is 1060 SUS/100° F.

Preparation

All of the silicone fluid and hydrated lime were charged to a fire heated kettle and warmed with stirring to 135° F. Blended acetic and capyrylic acids were added to the mixture and the temperature rose to 212° F. briefly, while continuing stirring. An excellent, smooth uniform grease containing most of the water of reaction was obtained.

Properties

Appearance	Smooth, uniform grease
Dropping point (° F.)	500+
Penetrations (77° F., mm./10):	
Unworked	200
Worked (60 strokes)	210
Worked (100,000 strokes)	215
Water solubility (boiling water)	Nil
Almen test (weights carried)	6

This example illustrates that the hydrous mixtures of metal salts of the invention can be utilized in compositions other than mineral oils, namely in the preparation of silicone polymer greases.

In brief summary, it has now been found that a metal salt of a low molecular weight carboxylic acid can be stably dispersed in lubricating oils by a cold set method of forming a concentrated base and then blending the base to the desired salt content by diluting with additional lubricating oil. An intermediate molecular weight carboxylic acid is co-neutralized with the low molecular weight carboxylic acid and act as the stabilizing agent. By this method large amounts of hydrous metal salts of low molecular weight carboxylic acids can be suspended in the lubricating oil as a colloidal dispersion easily and inexpensively. At least some and usually all water of reaction remains in the lubricating 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, 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 base stock thickened to grease consistency with from 5 to 30 weight percent of a hydrous mixture of a metal salt of a low molecular weight monocarboxylic acid having from about 1 to 3 carbon atoms per molecule and a metal salt of an intermediate molecular weight monocarboxylic acid having from about 7 to 10 carbon atoms per molecule, in which the mol ratio of low to intermediate molecular weight carboxylic

acids is between 2:1 and 40:1, wherein said hydrous composition contains 0.5 to 15.0 weight percent water and said metal is selected from the group consisting of alkali metals, alkaline earth metals and heavy metals of groups I, II, IV and VIII of the periodic system.

2. A blended lubricating composition comprising a minor proportion of the lubricating grease composition of claim 1 and a major proportion of a mineral lubricating oil, said grease composition being present in sufficient amount to improve the lubricating properties of said blended lubricating composition.

3. The blended lubricating composition of claim 2 wherein 1 to 20 weight percent of the lubricating grease composition of claim 1 and 99 to 80 weight percent of said mineral lubricating oil is employed.

4. A lubricating grease composition which comprises a major proportion of a lubricating oil and a minor grease-making proportion of a hydrous mixture of alkaline earth metal salts of acetic acid and caprylic acid, in which the mol ratio of acetic to caprylic acid is about 5:1 to 30:1 and wherein said hydrous salt mixture contains 10.5 to 15.0 weight percent water.

5. The lubricating grease composition of claim 4 in which said lubricating oil is a mineral lubricating oil.

6. The lubricating grease composition of claim 4 in which said lubricating oil is a synthetic lubricating oil.

7. The method of preparing a hydrous oil-dispersible salt composition containing 0.5 to 15.0 weight percent water, in a lubricating oil which comprises mixing in said oil a low molecular weight monocarboxylic acid having 1 to 3 carbon atoms per molecule with an intermediate molecular weight monocarboxylic acid containing 7 to 10 carbon atoms per molecule in a mol ratio of low to intermediate molecular weight carboxylic acids of at least 2:1, reacting the mixture with a metal base sufficient in amount to form metal salts of said acids at a temperature of about 150° to 200° F. to thereby form a dispersion of said salts in said oil.

8. The method of claim 7 in which said base is an alkaline earth metal base.

9. The method according to claim 8 wherein said base is hydrated lime.

10. The method of preparing a lubricating grease composition which comprises dispersing in a lubricating oil a low molecular weight monocarboxylic acid having from about 1 to 3 carbon atoms per molecule, an intermediate molecular weight monocarboxylic acid having from about 7 to 10 carbon atoms per molecule and a metal base in grease-making proportions, heating the dispersion to a temperature of about 150° to 200° F. and then cooling to obtain said lubricating grease composition, the mol ratio of low to intermediate molecular weight acids being between 2:1 and 40:1 and said metal being selected from the group consisting of alkali metals, alkaline earth metals and heavy metals of groups I, II, IV and VIII of the periodic system.

11. The method of preparing a lubricating grease composition according to claim 10 wherein the lubricating oil is selected from the group consisting of mineral and synthetic lubricating oils.

12. The method of preparing a lubricating grease composition according to claim 11 wherein said synthetic lubricating oil is a silicone polymer oil.

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ARNOLD J. MORWAY

Application having been made by Arnold J. Morway, the inventor named in the patent above identified, Esso Research and Engineering Company, a corporation of Delaware, the assignee, Judson L. Philips of Upper Montclair, New Jersey, and John J. Kolfenbach of North Plainfield, New Jersey, for the issuance of a certificate under the provisions of Title 35, Section 256 of the United States Code, adding the names of said Judson L. Philips and John J. Kolfenbach to the patent as joint inventors, and a showing and proof of facts satisfying the requirements of the said section having been submitted, it is this 28th day of April, 1959, certified that the names of the said Judson L. Philips and John J. Kolfenbach are hereby added to the said patent as joint inventors with the said inventor named in the patent.

[SEAL]

ARTHUR W. CROCKER,
First Assistant Commissioner of Patents.