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3,116,247

CLAY GREASE COMPOSITIONS

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This invention relates to improved lubricating grease compositions. More particularly, the invention relates to greases gelled with oleophilic clays and containing certain extreme pressure additives.

Lubricating grease compositions suitable for general use throughout the mechanical arts should possess good lubricating properties and, for heavy duty use, also should inherently possess extreme pressure characteristics when operated in either a dry or wet environment.

It has been possible in the past to formulate oleophilic clay grease compositions having good resistance to leaching by water as well as having desirable mechanical characteristics. The ability to operate under extreme loading, however, has not been satisfactorily obtained by the use of many well known extreme pressure agents such as are commonly employed in oils and soap-base grease compositions. In general, the extreme pressure additives normally used in the past have proved to have a deleterious effect on oleophilic clay greases or have not exhibited sufficient extreme pressure properties to warrant their use.

It is an object of the present invention to provide improved grease compositions. It is a particular object of the invention to provide oleophilic clay grease compositions having improved extreme pressure properties. Other objects will become apparent during the following detailed description of the invention.

Now, in accordance with the present invention, greases gelled with oleophilic clays can be improved with respect to their extreme pressure properties by the addition thereof of 3–25% by weight of an alkaline earth metal salt of an aliphatic carboxylic acid. Preferably, in accordance with this invention, the alkaline earth metal salt is calcium and is present in between about 5 and 15% based on the total weight of the grease.

Suitable classes of acids from which the salts may be prepared, either prior to incorporation into the grease or in situ, include particularly fatty acids (preferably saturated fatty acids), aliphatic dicarboxylic acids and hydroxy carboxylic acids. Suitable fatty acids are formic, acetic, propionic, butyric and capronic acids. Unsaturated acids may be utilized such as acrylic, crotonic, maleic and fumaric. Preferred dicarboxylic acids are oxalic, malonic, succinic, glutaric and adipic acids. Hydroxy carboxylic acids include those having one or more hydroxy radicals and one or more carboxylic acid radicals. Typical species of these varieties include lactic, citric and tartaric acids. The alkaline earth metals include particularly calcium, magnesium, cadmium and strontium.

Specific salts utilized for the purpose of increasing the

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extreme pressure properties of the subject class of greases include the following: calcium formate, calcium acetate, magnesium propionate, magnesium butyrate, cadmium caproate, strontium acrylate, strontium crotonate, calcium oxalate, calcium valonate, calcium lactate, magnesium citrate and magnesium tartrate. Of course, mixtures of these various alkaline earth metal salts may be utilized as well.

The proportions in which the salts are present in the grease compositions may vary according to requirements. Generally, no more than 30% by weight is required to achieve the desired properties, although higher proportions may be utilized. Satisfactory extreme pressure greases may be made containing 3–25% by weight of the finely divided salts, based on the total composition, and greases containing from 5–15% by weight of the salts have been shown to possess very satisfactory extreme pressure properties.

The alkaline earth metal salts are incorporated into the grease compositions in finely divided form, that is to say, having a particle size of the order of 125μ or less. Generally it is preferred that the salts should have a particle size of less than 15μ , and more preferably less than 5μ . The finely divided salts may be incorporated into the grease compositions in any one of a number of ways, and at any stage in the grease manufacture. For example, the finely divided salt may be incorporated into the lubricating oil before the addition of the gelling agent. Alternatively, the finely divided salts may be milled into a preformed base grease, or they may be mixed with a lubricating oil which may be the same or different to the lubricating oil used in forming the base grease and subsequently stirred into the base grease.

If the salt is water-soluble, a convenient method of incorporating it into a grease gelled with certain bentonitic clays comprises dissolving the water-soluble material in water and emulsifying the resultant solution with an oil in the presence of an emulsifying agent capable of forming water-in-oil emulsions of the two phases. The emulsified mixture is dehydrated by heating to evaporate the water and the resultant suspension of finely divided material in oil is added to the base grease. In this method, an average particle size of the salt of less than 2μ may be readily obtained. The preferred method is to mix the alkaline earth metal salt, which has been air milled with a lubricating oil of the same type as has been used in making the base grease and subsequently to incorporate the mixture into the base grease using a conventional stirring equipment, e.g. a Hobart mixer.

Alternatively to air milling a preformed salt and mixing it with a lubricating oil, the salt may be formed in situ in a lubricating oil. For example, a very suitable calcium acetate-in-oil mixture may be prepared by slurring lime in a lubricating oil, adding to the slurry an amount of glacial acetic acid equivalent to the lime, and passing the thickened oil through a triple roll paint mill to break up aggregates. In this way, a mixture in oil of calcium acetate having a particle size of 1 to 2 can be obtained.

The lubricating oil in the compositions of the present

invention may be any of the oils of lubricating grade such as are commonly used in greases. The oil may be refined, unrefined or semi-refined, paraffinic-, naphthenic- or asphaltic-base mineral lubricating oil or a synthetic lubricating oil, having a viscosity from about 50 to 4000 SUS at 100° F. If desired, a blend of oils of suitable viscosity may be employed instead of a single oil, by means of which a desirable viscosity within the recited range may be secured. The particular oil as well as the exact proportion of the oil component employed depends upon the characteristics desired in the final composition. Refined mineral lubricating oils are very suitable as components of greases to be used at high temperatures.

Synthetic lubricants may be employed in place of, or in addition to the mineral oils. The various classes of synthetic lubricants are well known in the art and do not require detailed description here. Typical classes of such lubricants include phosphates, such as tris(2-ethylhexyl) phosphate, dicarboxylates, such as bis(2-ethylhexyl)sebacate and corresponding silicates and borates.

The substantially anhydrous grease compositions with which the alkaline earth metal salts are commingled are those wherein an oleophilic clay, preferably an oleophilic montmorillonitic clay such as bentonite or hectorite may be used. The oleophilic character of the clay grease gelling agent is imparted thereto by reacting with or absorbing on the clay surface a cationic oleophilic surface active agent, particularly high molecular weight amines, amino amides or quaternary ammonium compounds, all of which are known in the art.

The clays which are useful as starting materials for making the modified oleophilic clay in accordance with these known principles are those exhibiting substantially base exchange properties, and particularly those exhibiting comparatively high base exchange properties and containing cations capable of more or less easy replacement. These clays particularly contemplated herein include the montmorillonites, such as sodium, potassium, lithium and other bentonites, particularly of the Wyoming type; magnesium bentonite (sometimes called hectorite) and saponite. These clays are characterized by an unbalanced crystal lattice and are believed to have negative charges which are normally neutralized by inorganic cations. They may be modified in order to create the oleophilic nature thereof by adsorption of one or more of the oleophilic cationic surface active agents referred to above or by reaction of a quaternary ammonium compound such as those referred to in U.S. Patent 2,531,427, issued to E. A. Hauser. Suitable cationic materials for adsorption on clays are described in numerous patents including U.S. 2,831,809 and 2,875,152. The clays are normally converted to a satisfactory oleophilic form by the use of 0.25-1.5 parts by weight of the cationic material for each part by weight of the degangued clay.

For reaction with the clays it is customary to employ salts of amines and particularly of quaternary ammonium compounds such as salts of dimethyl-dicetyl ammonium hydroxide. For absorption of a water proofant on the surfaces of the clay it is preferred to utilize long chain amines having more than 18 carbon atoms per molecule and preferably amino amides wherein at least about one-third of the amino groups are in amide form with higher fatty acids.

The surface active agents are generally used in a proportion between 30 and 100% by weight, preferably 70-95% by weight based on the inorganic gelling agent.

In preparing the compositions of the present invention it is a preferred procedure to add the gelling agent, which has been pretreated to render it compatible with oil, to a portion of the desired lubricating oil and mix thoroughly. A dispersing agent, e.g. propylene carbonate, may be added and the mixture thoroughly stirred to disperse the gelling agent. The remainder of the oil, which is preferably preheated, is then added and a small pro-

portion of water is added when the mixture has cooled below 100° C. The whole mixture is then homogenized to form the grease. To this grease, the finely divided salts are added in the manner stated above.

It will be understood that the compositions of the invention may contain other extreme pressure agents or other additives such as are commonly used. Thus the compositions may contain minor proportions of anti-oxidants and/or corrosion inhibitors. Examples of suitable anti-oxidants are arylamines, particularly phenyl amines and more particularly the phenyl naphthylamines such as phenyl alpha-naphthylamine. Suitable corrosion inhibitors are alkali metal nitrites, e.g. sodium nitrite or alkali metal chromates, e.g. potassium chromates.

The invention will now be illustrated by the following examples:

EXAMPLE I

120 lbs. of a high viscosity index mineral oil having a viscosity of 66 seconds Redwood I at 210° F. was charged to an open steam heated kettle fitted with a stirrer. 30 lbs. of "Bentone 34" (a bentonite clay which has been treated with a water-proofing proportion of dimethyl dioctadecyl ammonium chloride) was added and the mixture stirred for about ½ hour. 2.25 lbs. of propylene carbonate was then added as a dispersant for the Bentone 34 and the mixture stirred for a further ½ hour. A further 150 lbs. of the oil, preheated to 160° C., was then added and stirred into the slurry. When the mixture had cooled to below 100° C. 0.3 lb. of water was then added, stirred in and the charge then filled-off via a Manton-Gaulin homogenizer operating at 300 p.s.i. During manufacture, the charge was circulated from the bottom of the kettle via a pipe on to the top of the charge. This base grease contained no E.P. additive.

600 g. of pure dried calcium acetate having a particle size up to 125 microns was stirred into 750 g. of the same oil. This mixture was fed through a laboratory triple roll paint mill three times to give a smooth paste which was then stirred into 4,650 g. of the above base grease in a Hobart mixer at room temperature.

The resulting grease was tested for E.P. properties on the Timken machine using the method disclosed in the SAE Journal 28, 53, (1931) and also its I.P. penetration was determined. The results are summarized in Table I.

EXAMPLE II

Pure dried calcium acetate having a particle size less than 5 microns was added to a H.V.I. oil having a viscosity of 66 seconds Redwood I at 210° F. to give a calcium acetate content of 24% w. in the mixture. 2,288 gms. of this mixture was blended into 3,212 gms. of the base grease, as prepared in Example I by stirring in a Hobart mixer at room temperature.

The resulting grease was tested on the Timken machine as a useful measure of its E.P. properties, and its penetration was also determined. The results are summarized in Table I.

Examples III to XIV illustrate the effect on the properties of the grease when produced by using various additives, by varying the concentrations of additive present and by varying the particle size. The penetrations and Timken O.K. values of the greases were determined and the results are tabulated in Table I. In each of the examples the base grease to which the finely divided salts were added was prepared by the same general method as described in Example I, and the additives incorporated into the base grease as a suspension in oil in the manner of Example II.

All the greases exemplified in Examples III-XIII as well as those of Examples I and II were found to possess enhanced E.P. properties, and had a drop point in excess of 300° C. A sample of the base grease was also tested by way of comparison.

Table I

Example	Base grease	I	II	III	IV	V	VI
Bentone 34, percent w.	10.0	7.7	5.8	6.0	7.1	5.2	5.9
Propylene carbonate, percent w.	0.7	0.6	0.4	0.4	0.5	0.4	0.4
Water, percent w.	0.1	0.08	0.06	0.06	0.09	0.05	0.06
H.V.I. oil, percent w.	89.2	81.6	83.7	83.5	87.3	74.3	83.6
Additive		Calcium acetate.	Calcium acetate.	Calcium acetate.	Calcium acetate.	Calcium acetate.	Strontium acetate.
Additive concentration, percent w.		10	10	10	5	20	10
Additive particle size		up to 125 μ .	<5 μ	5 μ or less + few up to 15 μ .	mainly <5 μ .	5 μ or less + few up to 10 μ .	mainly 5 μ
I. P. Penetration:							
Unworked	273			301	316	300	303.
Worked	310	293	309	293	315	287	311.
Timken OK value, lbs.	10	35-45	50-55	50-60	45	75	30.

Example	VII	VIII	IX	X	XI	XII	XIII
Bentone 34, percent w.	6.2	6.4	6.6	6.4	6.7	6.4	6.5
Propylene carbonate, percent w.	0.4	0.5	0.5	0.5	0.5	0.5	0.5
Water, percent w.	0.06	0.06	0.06	0.06	0.06	0.06	0.06
H.V.I. oil, percent w.	83.3	83.0	82.8	83.0	82.7	83.0	82.9
Additive	Calcium benzoate.	Calcium formate.	Calcium propionate.	Calcium tartrate.	Calcium succinate.	Calcium lactate.	Calcium oxalate.
Additive concentration, percent w.	10	10	10	10	10	10	10
Additive particle size	mainly <10 μ .	mainly 10 μ .	<10 μ	<15 μ	<15 μ	mainly <5 μ .	<5 μ .
I.P. Penetration:							
Unworked	290	287	297	297	283	333	287.
Worked	287	283	291	292	279	332	280.
Timken OK value, lbs.	30	25	43	65	45	65	40.

EXAMPLE XIV

A lubricating grease was made by dispersing hectorite clay in water and treating it with the amino amide formed between tall oil acids and a condensation product of epichlorohydrin and ammonia. The treated clay was added to a H.V.I. oil. Phenyl alpha naphthylamine and sodium nitrite were also incorporated so that the resulting grease "A" had the following composition:

	Percent
Hectorite clay	5.4
Amino amide	4.0
H.V.I. oil	89.4
Phenyl alpha naphthylamine	0.5
Sodium nitrite	0.5
Water	0.2

Calcium acetate having a particle size of less than 10 μ was stirred into the above grease as a suspension in H.V.I. oil in such an amount that the total composition contained 10% by weight of calcium acetate. The Timken O.K. values and I.P. penetrations of the grease "A" with and without the additive were determined and the results are given in Table II.

Table II

	Grease "A"	Grease + additive
I.P. penetration:		
Unworked	268	245
Worked	271	273
Timken O.K. value, lbs.	10	55

A test was carried out to determine the effect on the gelling power of inorganic gelling agents in the presence of extreme pressure additives such as are conventionally used in soap gelled greases. It will be understood that the three greases illustrated below are outside the scope of the present invention and are included for comparative purposes only. In Table III, the loss of gelling power resulting from the addition of lead naphthenate and an additive containing sulfur, chlorine and lead based on a vegetable oil, known under the trade name Elco SCL, to a bentonitic clay gelled grease is illustrated by the penetration values. It will be seen that the penetration values are substantially increased by the presence of the above additives, whereas from Table I it can be seen that the

presence of the finely divided salts of the present invention has no adverse effect on the penetration values of the greases.

Table III

Bentone 34% wt.	8.6	8.6	9.0
Propylene Carbonate	0.7	0.7	0.7
Water	0.1	0.1	0.1
Lead naphthenate (as 50% concentrate in spindle oil)	5.0		
Elco SCL		5.0	
H.V.I. oil (66 secs. Red. I at 210° F.)	85.6	85.6	90.2
I.P. Penetration:			
Unworked	371	372	277
Worked	387	406	277

We claim as our invention:

1. A grease composition comprising a major proportion of a lubricating oil, a sufficient amount of an organophilic high base-exchange clay to thicken said oil to a grease consistency and 3-25% by weight of finely divided particles of an alkaline earth metal salt of an aliphatic carboxylic acid having 1-6 carbon atoms per molecule.
2. A grease composition comprising a major proportion of a mineral lubricating oil, a grease-forming proportion of a compound of an organic nitrogen base and a bentonite and 5-15% by weight of finely divided particles of an alkaline earth metal salt of a saturated fatty acid having 1-6 carbon atoms per molecule.
3. A grease composition comprising a major proportion of a mineral lubricating oil, a grease-forming proportion of a compound of an organic nitrogen base and a bentonite and 5-15% by weight of finely divided particles of an alkaline earth metal salt of a saturated aliphatic dicarboxylic acid having 2-6 carbon atoms per molecule.
4. A grease composition comprising a major proportion of a mineral lubricating oil, a grease-forming proportion of a compound of an organic nitrogen base and a bentonite and 5-15% by weight of finely divided particles of an alkaline earth metal salt of a saturated aliphatic hydroxycarboxylic acid having 2-6 carbon atoms per molecule.
5. A grease composition comprising a major proportion of a mineral lubricating oil, a grease-forming proportion of a compound of an organic nitrogen base and a bentonite and 5-15% by weight of calcium acetate.
6. A grease composition comprising a major propor-

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tion of a mineral lubricating oil, a grease-forming proportion of a compound of an organic nitrogen base and a bentonite and 5-15% by weight of strontium acetate.

7. A grease composition comprising a major proportion of a mineral lubricating oil, a grease-forming proportion of a compound of an organic nitrogen base and a bentonite and 5-15% by weight of calcium tartrate.

8. A grease composition comprising a major proportion of a mineral lubricating oil, a grease-forming pro-

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portion of a compound of an organic nitrogen base and a bentonite and 5-15% by weight of calcium formate.

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