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LUBRICATING GREASES CONTAINING FINELY DIVIDED ALKALINE EARTH METAL SULFATES

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This invention relates to improvements in grease manufacture. More particularly, it relates to soap thickened greases containing alkaline earth metal sulfates and to a method of making such greases.

I have found that the combination of high extreme pressure properties with low wear required to meet various industrial specifications are obtained in soap thickened greases by employing alkaline earth metal sulfates therein in very finely divided form. In particular I have found that the combination of a minimum O.K. load of 40 pounds in the Timken test and low wear represented by a maximum scar diameter of 0.6 mm. in the Four Ball One Hour Wear Test employing a 20 kg. load, required to meet U.S. Steel Specification No. 370, is obtained in certain soap thickened greases containing substantial amounts of alkaline earth metal sulfates in this finely divided form. This result was unexpected, since it is not obtained by employing the metal sulfates in greases containing thickeners of other types, and other inorganic solids of various types having extreme pressure properties in soap thickened greases generally increase the wear obtained to an objectionable degree when they are employed in sufficient amounts to provide substantially improved extreme pressure properties.

The grease compositions of this invention comprise essentially a lubricating oil thickened to a grease consistency by a metal soap and containing a finely divided alkaline earth metal sulfate in a sufficient amount to impart improved extreme pressure properties to the composition. The alkaline earth metal sulfate may be present suitably in an amount from about 1 percent up to about 12 percent by weight, and preferably in an amount from about 2 percent to about 8 percent by weight, based on the weight of the composition. The soap thickener may be present in an amount from about 2 percent up to about 40 percent by weight of the composition. It is preferably present in an amount from about 5 to about 25 percent by weight of the composition.

The alkaline earth metal sulfate is present in the form of particles below about 3 microns diameter in their maximum dimension and preferably having a particle size in the range from about 0.1 to about 3.0 microns in diameter.

Soaps which may be employed in the above compositions are those which are suitable for use as thickening agents in lubricating greases generally, wherein the metal component may be an alkali or alkaline earth metal, aluminum, zinc, magnesium, manganese, iron, etc. A special advantage is derived in accordance with our invention in the production of aluminum soap thickened greases having extreme pressure properties, since extreme pressure agents of other types are generally ineffective or unsuitable for use in these greases because of a deleterious effect which they have upon the grease structure. Greases constituting a preferred embodiment of our invention are those comprising both an aluminum soap and an alkali metal soap in a weight ratio from about 1:3 to 3:1, respectively, and preferably about 1:2 to 2:1, respectively, and containing at least about 2 percent by weight of alkaline earth metal sulfate. I have found that a combination of superior lubricating properties are obtained in these greases, including superior extreme pressure properties, high mechanical and storage stability, excellent water-

resistance properties and other advantages. Very advantageously the grease may contain about 0.2–2.0 percent by weight of glycerol.

Saponifiable materials which may be employed in the production of these greases are higher fatty acids and hydroxy-substituted higher fatty acids containing about 10 to 32 carbon atoms, preferably from about 16 to about 22 carbon atoms, and the glycerides or other esters of such acids. Particularly suitable materials are substantially saturated hydroxy fatty acids containing 12 or more carbon atoms and 1 or more hydroxyl radicals separated from the carboxyl group by at least 1 carbon atom, and the glycerides and lower alkyl esters thereof. The saponifiable materials employed in carrying out the grease preparation by the preferred method of our invention comprise at least a substantial proportion of fatty acid glycerides, sufficient to provide an amount of glycerol in the finished grease within the range set forth hereinabove.

In addition to the higher fatty acid materials described above, it is desirable in some cases to employ a minor proportion of lower fatty acid material in the saponification mixture, such as a fatty acid containing from 1 to about 10 carbon atoms per molecule, and most suitably from 1 to about 6 carbon atoms per molecule, the glycerides and other esters of such acids. A material of this character may be employed in the saponification in an amount resulting in a lower fatty acid salt content in the finished grease from about 1 to about 10 percent by weight, preferably corresponding to a mol ratio with the higher fatty acid soap from about 5:1 to about 20:1, respectively. The lower fatty acid material may be employed with particular advantage in greases containing glycerides, as a means of increasing the dropping points where a high dropping point grease is desired. An alternative procedure which may be preferred in some cases comprises employing a preformed metal salt of a low molecular weight acid of the character described above. The preformed salt may be added to the grease mixture at any stage of the grease making process, most suitably before the grease mixture has cooled below the maximum temperature employed in the process.

The lubricating oils forming the major component of these compositions may be any oils of lubricating characteristics which are suitable for use in lubricating compositions generally. Such oils include the conventional mineral lubricating oils having Saybolt Universal viscosities in the range from about 75 seconds at 100° F. to about 225 seconds at 210° F., which may be either naphthenic or paraffinic in type or blends comprising both naphthenic and paraffinic oils. The preferred lubricating oils are those having Saybolt Universal viscosities in the range from about 300 seconds at 100° F. to about 100 seconds at 210° F., which may be blends of lighter and heavier oils in the lubricating oil viscosity range. Synthetic lubricating oils, which may be preferred in preparing greases having special properties required for special types of lubricating service, include oils prepared by cracking and polymerizing products of the Fischer-Tropsch process and the like as well as other synthetic oleaginous compounds such as polyethers, polyesters, silicone oils, etc., having viscosities within the lubricating oil viscosity range. Suitable polyethers include particularly polyalkylene glycols such as polyethylene glycol. Suitable polyesters incude the aliphatic dicarboxylic acid diesters, such as di-2-ethylhexyl sebacate, di(secondary amyl) sebacate, di-2-ethylhexyl azelate, di-iso-octyl adipate, etc. The sulfur analogs of the polyalkylene esters and polyesters are also suitable. A particularly suitable class of dicarboxylic acid ester oils are those disclosed by R. T. Sanderson in U.S. 2,628,974, obtained by reacting dibasic aliphatic acids with glycols and endblocking the reaction products with monohydric aliphatic alcohols and monocarboxylic aliphatic acids.

Silicone polymer oils may also be employed, preferably having viscosities in the range from about 70 to 900 seconds Saybolt Universal at 100° F. Suitable compounds of this type include dimethyl silicone polymer, diethyl silicone polymer, methyl cyclohexyl silicone polymer, diphenyl silicone polymer, methylethyl silicone polymer, methyltolyl silicone, etc.

Additives of the types ordinarily employed in lubricating compositions may be employed in these greases, such as oxidation inhibitors, corrosion inhibitors, tackiness agents, such as various high polymeric materials, extreme pressure agents, etc. Oxidation inhibitors which may be employed include particularly those of the amine type, such as phenylalphanaphthylamine, diphenylparaphenyldiamine, tetramethyldiaminodiphenyl methane, and bis (2-hydroxy-3-t-butyl-5-methylphenyl) methane. With particular advantage, a surface active agent of the type which imparts water resistant properties to the composition may be employed, such as quaternary ammonium salts of fatty acids, polyglycol ethers, metal alkyl sulfates or sulfonates, imidazolines of the type of 1-betahydroxyethyl-2-tallowimidazoline, etc. Additives of each of the above types are ordinarily employed in the composition in amounts from about 0.1 to about 5.0 percent, and most suitably in amounts from about 0.2 to about 2.0 percent by weight.

The preparation of these greases may be carried out by any convenient method with addition of the alkaline earth metal sulfate at any stage of the grease making process or by formation of the alkaline earth metal sulfate in situ during the process. A very advantageous method of forming these greases comprises forming the alkaline earth metal sulfate in situ by reaction between a water soluble metal sulfate and an alkaline earth metal base and carrying out the saponification reaction employing this reaction product as the saponifying agent. We have found that greases are obtained in this manner containing the alkaline earth metal sulfate in very finely divided nonabrasive form, as required for obtaining the desired combination of high extreme pressure and low wear properties.

Mixed base greases are very advantageously prepared employing mixtures of metal hydroxides obtained by reaction of an alkaline earth metal hydroxide in aqueous solution with water soluble metal sulfates. Metal hydroxide mixtures comprising trivalent metal hydroxides formed in this manner react readily with saponifiable fatty acid materials, differently from the trivalent metal hydroxides obtained by other methods.

A particularly suitable class of water soluble metal sulfates for use as starting materials in the production of greases in accordance with our invention comprises the alums, having the formula:

$$M_2SO_4 \cdot M'_2(SO_4)_3 \cdot 24H_2O$$

wherein M is an alkali metal and M' is a trivalent metal. Examples of suitable compounds of this class include potassium aluminum sulfate, sodium aluminum sulfate, potassium ferric sulfate and potassium chromiun sulfate. Reaction of these compounds with alkaline earth metal hydroxides produces a mixture of metal hydroxides in a form which react readily with saponifiable fatty acid materials to form mixed base soaps and containing finely divided alkaline earth metal sulfate in suitable proportions and in a form imparting high extreme pressure properties to the grease composition. The preferred procedure for forming this reaction mixture comprises carrying out the reaction in the presence of a portion of the lubricating oil employed in the grease employing a lubricating oil which is substantially unreactive under the reaction conditions. This procedure further insures the production of the metal sulfate in very finely divided form by preventing agglomeration of the crystals as they are formed.

The following examples describe representative grease preparations carried out in accordance with this invention.

EXAMPLE I

A grease was prepared having the following calculated composition in percent by weight:

Lithium 12-hydroxystearate	7.0
Calcium sulfate	5.0
Glycerine	0.7
Diphenylamine	0.5
Excess LiOH	0.1

Lubricating oil, remainder.

The lubricating oil contained in the above composition was a blend in about a 4:1 ratio by weight, respectively, of a refined paraffinic residual oil having a Saybolt Universal viscosity at 210° F. of about 103 seconds and a refined paraffinic distillate oil having a Saybolt Universal viscosity at 100° F. of about 176 seconds.

The grease preparation was carried out in the following manner: A fire-heated laboratory kettle was charged with 7.16 pounds of hydrogenated castor oil, and 27.3 pounds of the lubricating oil blend. The mixture was heated with stirring to 160° F., 6.79 pounds of 10 percent lithium hydroxide in aqueous solution added, and the mixture heated at 190–200° F. for 1 hour. The heat was then increased and the temperature of the mixture brought up to 390° F. while 38.4 pounds of the residual oil were added during the heating from 310° F. to 350° F. When the mixture was heated to 390° F., the heat was cut and the mixture cooled from 390° F. to 290° F. in 48 minutes with recirculation from the bottom to the top of the kettle through an external line containing a shear valve set to give a 40 pounds per square inch pressure drop across the valve. The grease mixture was then further cooled to 200° F. in 27 minutes while 200 pounds of the residual oil were added gradually with continued recirculation. When the grease mixture had cooled to 220° F., 5.0 pounds of finely divided calcium sulfate having a particle size in the range from about 0.1 micron to about 3.0 microns in their maximum diameter and 0.5 pound of diphenylamine (dissolved in 2.0 pounds of residual oil) were added and recirculation of the grease mixture continued for 15 minutes thereafter.

The grease obtained as described above was a smooth brown grease having very superior extreme pressure properties and low wear properties in addition to other desirable lubricating properties as shown by the following test results.

Penetration, ASTM, 77° F.:	
Unworked	302
Worked, 60 strokes	294
Worked, 10,000 strokes	298
Dropping point, ASTM, ° F.	400
ASTM bomb oxidation test:	
(100 hrs., 210° F.) lb. drop	4
Dynamic water resistance, percent loss	0
Water absorption, percent	110
Worked penetration before	279
Worked penetration after	317
ASTM wheel bearing test:	
(6 hrs., 235° F.) Leakage, g. (rating, good)	4
Timken O.K. load, lb.	65
Mean hertz load, kg.	34
4 ball wear test (20 kg.):	
Scar diameter, mm.	0.368

In contrast to the result obtained by employing calcium sulfate in the above soap thickened grease, no appreciable increase in extreme pressure properties was obtained by employing this material in greases thickened with carbon black or Bentone 34.

EXAMPLE II

A grease was prepared having the following calculated composition in percent by weight:

Calcium 12-hydroxystearate	5.0
Calcium sulfate	5.1
Glycerine	0.9
Lubricating oil, remainder.	

The lubricating oil contained in the above composition was a blend in about a 55:45 ratio by weight, respectively, of a residual fraction from a naphthene base crude having a Saybolt Universal viscosity at 210° F. of about 207 seconds and a refined distillate fraction from a naphthene base crude having a Saybolt Universal viscosity at 100° F. of about 139 seconds.

The grease preparation was carried out in the following manner: A jacketed steam-heated laboratory kettle was charged with 7.0 pounds of Hydrofol Acids, 1.26 pounds of lime, 10.5 pounds of water, and 37.0 pounds of the distillate oil. The kettle contents were heated to 290° F. and an additional 16.9 pounds of the distillate oil preheated to 290° F. added. The mixture was then held at 290° F. for ½ hour to complete the saponification. Heating was then discontinued and 66.4 pounds of residual oil added while cooling to 220° F. in 183 minutes and while recycling the grease mixture from the bottom to the top of the kettle through an external recycle line containing a shear valve set to give a pressure drop of 90–100 pounds per square inch across the valve. The recirculation was carried out at a rate such as to give about 30 pounds of grease mixture per minute recirculated. After the oil addition had been completed at 220° F., 6.78 pounds of the calcium sulfate and 1.3 pounds of glycerine were added with continuous recirculation. The calcium sulfate employed was that described in Example I. The recirculation was continued while the mixture was cooled down to the drawing temperature of 200° F.

The grease obtained as described above had the desired combination of high extreme pressure properties and low wear properties in adidtion to other desirable lubricating properties as shown by the following test results.

Penetration, ASTM, 77° F.:	
Unworked	295
Worked, 60 strokes	281
Worked, 10,000 strokes	292
Dropping point, ASTM, ° F.	265
Dynamic water resistance test, percent loss	0
ASTM bomb oxidation test:	
(100 hrs., 210° F.) lb. drop	15
Timken O.K. load, lb.	55
Mean hertz load, kg.	41
4 ball wear test (20 kg.):	
Scar diameter, mm.	0.470

EXAMPLE III

A grease was prepared having the following calculated composition in percent by weight:

Aluminum mono-12-hydroxystearate	6.5
Sodium 12-hydroxystearate	5.8
Calcium sulfate	5.1
Diphenylamine	0.4
Lubricating oil	Remainder

The lubricating oil contained in the above grease was a blend of the type described in Example II.

The grease preparation was carried out in the following manner: A metal base solution was prepared by introducing 227 grams of sodium aluminum sulfate, 440.0 grams of the lubricating oil blend, 79.4 grams of lime and 700.0 grams of water into a pestle stirred laboratory kettle and the mixture heated for 1 hour at 184–189° F. To the reaction product thus obtained, 296 grams of Hydrofol Acids and 250 grams of the lubricating oil blend

were added and the mixture heated at 294–297° F. for 3 hours, sufficient to complete the saponification and to dehydrate the grease mixture. The grease mixture was then cooled down to about 209° F. in about 80 minutes with the gradual addition of 1240 grams of the lubricating oil blend followed by 11.3 grams of diphenylamine. The grease was drawn at 203° F. and finished with one pass through a Premier Colloid Mill set at 0.002-inch clearance.

The grease obtained as described above was a brown slightly grainy product wherein a combination of desirable lubricating properties was obtained as shown by the following test results.

Penetration, ASTM 77° F.:	
Unworked	230
Worked, 60 strokes	288
Worked, 100,000 strokes	305
Dropping point, ASTM, ° F.	270
Dynamic water resistance, percent loss	5.0; 2.5
Water absorption, percent	25
Penetration, worked, before	268
Penetration, worked, after	277
ASTM bomb oxidation test:	
(210° F., 100 hrs.) lb. drop	16
Mean hertz load, kg.	36

The extreme pressure properties and other lubricating properties of the above grease with the exception of the lower dropping point were substantially equivalent to those of a commercially successful mill grease of the same grade comprising calcium 12-hydroxystearate as the thickening agent in a mineral lubricating oil of the same type and containing 12 percent by weight of a commercial Pb–S–Cl containing extreme pressure additive. By the addition of an extreme pressure additive of this type to our grease compositions, still higher extreme pressure properties were obtained in combination with the desired low wear properties, substantially superior to those of the calcium 12-hydroxystearate thickened grease containing no inorganic solid. The following table shows the extreme pressure properties of a grease of substantially the same composition as that of Example III but containing 5 percent by weight of the Pb–S–Cl additive in comparison with those of the calcium 12-hydroxystearate thickened grease containing 12 percent of this additive.

Table I

Grease Composition	Ca 12-hydroxystearate thickened containing 12% Pb-S-Cl additive	Example III containing 5% Pb-S-Cl additive
Timken OK Load, lbs.	35-40	45
Mean Hertz Load, kb.	35	46
Four Ball 1 hr. Wear Test (5 kg., 1,800 r.p.m., 130° F.), Scar diameter, mm.	0.3	0.376

EXAMPLE IV

A grease was prepared having the following calculated composition in percent by weight:

Aluminum monococonate	4.8
Sodium coconate	4.1
Calcium sulfate	4.6
Calcium acetate	9.0
Phenylalphanaphthylamine	0.3
Lubricating oil	Remainder

The lubricating oil contained in the above grease was a blend in a 60:40 ratio by weight, respectively, of a dewaxed paraffinic residual fraction having a Saybolt Universal viscosity at 210° F. of 157 seconds and a refined paraffinic distillate oil having a Saybolt Universal viscosity at 100° F. of 175 seconds.

The grease preparation was carried out in the following manner: A reaction mixture was prepared by intro-

ducing 700.0 grams of the lubricating oil blend, 700.0 grams of water, 227.0 grams of sodium aluminum sulfate and 79.4 grams of lime into a pestle stirred laboratory grease kettle and heating the mixture for 1 hour at 180–190° F. To the reaction mixture thus obtained, 219.5 grams of coconut fatty acids were added and the saponification carried out by heating the mixture for two hours at 180–190° F. The coconut fatty acids employed was a commercial product having a neutralization number of 254.3, a saponification number of 253 and an iodine number of 12.2. Following the saponification, 262 grams of calcium acetate were added and the grease mixture dehydrated by heating for 3 hours at 281–286° F. An additional 773 grams of the oil blend were then added while cooling to 204° F., followed by 8.9 grams of phenylalphanaphthylamine and the mixture heated for 30 minutes at 400° F. The grease mixture was then cooled with stirring to the drawing temperature of 200° F. in 125 minutes.

The product obtained as described above was a slightly fibrous grease, having very superior lubricating properties as shown by the following test results.

Penetration, ASTM, 77° F.:	
Unworked	245
Worked, 60 strokes	242
Worked, 10,000 strokes	217
Unworked, after 1 month	257
Dropping point, ASTM, ° F.	500+
ASTM bomb oxidation test:	
(210 ° F., 100 hrs.) lb. drop	0
Dynamic water resistance, percent loss	2.5
Water absorption, percent	55
Penetration, worked, before	242
Penetration, worked, after	275
Mean hertz load, kg.	45

As shown by the above test results, the grease representative of a preferred embodiment of our invention had a very exceptional combination of desirable properties including high dropping point, excellent mechanical stability, oxidation and water resistance and superior extreme pressure properties as shown by the Mean Hertz Load test.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A lubricating grease comprising a lubricating oil thickened to a grease consistency by a metal soap and containing about 1–12 percent by weight, sufficient to impart substantially improved extreme pressure properties to the said grease, of calcium sulfate in finely divided form.

2. The composition of claim **1** containing about 2–8 percent of the said calcium sulfate.

3. The composition of claim **1** wherein the said soap is a hydroxy fatty acid soap.

4. The composition of claim **1** wherein the said soap is a calcium soap.

5. The composition of claim **1** wherein the said soap is a lithium soap.

6. The composition of claim **1** wherein the said soap comprises a mixture of an alkali metal soap and an aluminum soap in a 1:1 mol ratio.

7. The composition of claim **1** containing about 1–10 percent by weight of a metal salt of a low molecular weight fatty acid.

8. The composition of claim **1** containing about 0.2–2.0 percent by weight of glycerol.

9. A method of grease manufacture which comprises saponifying a saponifiable material with a basic reacting mixture comprising an alkali metal hydroxide and an aluminum hydroxide and containing calcium sulfate in finely divided form in the presence of at least a portion of the lubricating oil contained in the grease, heating at a higher temperature to dehydrate the mixture and to condition the soap, cooling and adding any additional lubricating oil contained in the said grease, said basic reacting mixture being obtained by reacting an alum with a calcium base in approximately stoichiometric proportions in aqueous solution.

10. The method of claim **9** wherein the said alum is sodium aluminum sulfate.

11. The method of claim **9** wherein the said reaction between alum and a calcium base is carried out in a portion of the lubricating oil contained in the said grease.

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