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ALKALI METAL SOAP THICKENED GREASES CONTAINING ALKALI METAL SALTS OF PHENOL-ALDEHYDE CONDENSATES

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This invention relates to lubricating compositions and more particularly to improved grease compositions.

As is well known, lubricating greases have been made by the addition of metallic soaps to petroleum oils. Such greases are commonly employed to lubricate rollers and ball bearings wherein high temperatures such as above 200° F. are frequently encountered. As would be expected, under such conditions the greases may tend to melt and run out of the bearings thereby reducing the effective performance life of the grease.

The present invention has for its object to provide greases having improved performance life when employed to lubricate at high temperatures.

The improved grease of the invention comprises a lubricating oil, sodium or lithium soap and an oil-soluble metal salt of a condensation product of a substituted phenol and an aldehyde. The metal component of the salt is the same as that employed in the soap, i.e., a sodium salt is employed with a sodium soap, and a lithium salt is employed with a lithium soap.

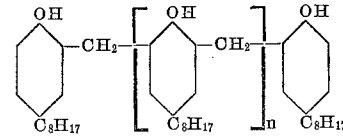
The lubricating oil ingredient in the grease compositions provided by this invention may be any of the hydrocarbon oils of lubricating grade such as those customarily used in compounding greases. While the lubricating oil in most instances is a mineral lubricating oil, synthetic lubricants such as polymerized olefins, polyalkylene oxides such as polypropylene oxide, polymerized glycols such as polyethylene glycol, esters of dicarboxylic acids such as bis-(2-ethylhexyl) sebacate and the like can be employed. The oil may be a refined or semi-refined paraffinic-, naphthenic-, or asphalt-base oil having a viscosity of about 50 to 4000 Saybolt Universal seconds at 100° F. If desired, a blend of oils of suitable viscosity may be employed instead of a single oil by means of which any viscosity within the range of 50 to 4000 Saybolt Universal seconds at 100° F. may be obtained. The oil content of the compositions prepared according to this invention comprises about 40 to about 95 percent or more by weight of the total composition. The particular oil as well as the exact amount of oil employed depends upon the characteristics desired in the final grease composition.

The sodium or lithium soap employed in the greases of this invention may be prepared from organic acids having between about 12 and 32 carbon atoms. The acid may be saturated or unsaturated and may contain substituents such as hydroxyl groups. Aliphatic acids are preferred. Examples of satisfactory acids are lauric, myristic, palmitic, stearic, arachidic, behenic, lignoceric. Mixtures of these acids or mixtures obtained by saponification of the natural fats such as cotton seed oil, lard, tallow, etc., may be used. The soaps are formed by saponifying the acid or the fat with a base such as sodium or lithium hydroxide. In general, the sodium or lithium soap content comprises about 1 to 50 percent by weight of the total composition. Amounts between about 5 and about 25 percent are preferred.

As previously indicated, an oil-soluble sodium of lithium salt of a condensation product of a substituted phenol and an aldehyde is employed in the grease compositions of this invention. Preferably the phenol selected for reaction with the aldehyde is a substituted phenol having an available ortho position in the ring. The substituent

attached to the phenol is a hydrocarbyl radical, that is, a radical selected from among alkyl, aryl, cycloalkyl, aralkyl and alkaryl groups.

When the substituent is an alkyl group, a straight or branched chain radical of from 4 to 18 carbon atoms is generally employed. Alkyl radicals having straight or branched chains of from 6 to 12 carbon atoms are preferred. In addition, mixtures of phenols containing one or more ortho- and/or para-substituted phenols may be employed such as a mixture containing a variety of alkyl, cyclo-alkyl substituted phenols. Thus, the alkyl groups or other substituents on each ring in the molecule may be different. The condensation will occur so long as there is an available ortho position on the phenol ring. Phenolic compounds used as starting materials are meta- or ortho- and/or para-substituted alkyl, aryl, cycloalkyl, aralkyl and alkaryl phenols. Included are such radicals as butyl, amyl, hexyl, octyl, nonyl, stearyl, lauryl, cyclohexyl, methylcyclohexyl, ethylcyclohexyl, benzyl, phenyl, tolyl and xylyl. For the purposes of the present invention, a preferred compound is a phenol-formaldehyde condensate having substantially the following formula wherein n is 3 on the average:



The phenol-aldehyde condensation products can be prepared by any suitable method and the method of preparation forms no part of the present invention. Usually such compounds are prepared by reacting a substituted phenol such as an octyl phenol with an aldehyde in the presence of an acid catalyst such as hydrogen chloride. The condensate so obtained is then converted to the sodium or lithium salt by any of the well known methods. For example, the condensate may be reacted directly with the metallic hydroxide or by a double decomposition reaction. A number of phenol-formaldehyde condensation products are commercially available and may be utilized to produce the sodium or lithium salt included by this invention.

The amount of the sodium or lithium salt of a phenol-aldehyde condensation products to be employed in the grease composition is relatively critical in that it has been found that when these salts are employed in the grease composition in an amount substantially below 3 percent by weight, the resultant grease does not exhibit optimum characteristics with respect to performance life. In general, the sodium or lithium salts of the class described are employed in the grease compositions of this invention in an amount between about 3 and 10 percent or more by weight of the total composition. Amounts between about 5 and about 8 are preferred.

In the greases of this invention, both the sodium and lithium soaps and the salts of the class herein described, function to thicken the lubricating oil to the consistency of a grease. In this respect, it is preferable to employ the selected sodium or lithium soap and the corresponding metal salt respectively, in a ratio ranging from about 11:1 to 1:1 by weight.

The greases in accordance with the invention may be prepared using any of the well known grease manufacturing procedures. Batch or continuous methods of manufacture may be used. In one satisfactory method a selected fatty acid or mixture of fatty acids, a phenol-aldehyde condensate and sodium or lithium hydroxide is added to a portion, as for example, one half of a lubricating oil in a pressure vessel. The fatty acids are saponified at a pressure of about 100–300 pounds per square inch at a temperature of about 320° F. Simultaneously,

the sodium or lithium hydroxide reacts with the phenol-aldehyde condensation product to produce a salt which is utilized in the grease in accordance with the invention. The reaction mass is then transferred to an open kettle for dehydration which is effected by heating. The remainder of the oil is added to this mass while heating to a temperature between 300° F. and 420° F. The mixture is then cooled to about 200° F. If desired, other additives which will be designated secondary additives, are added after which the grease composition is milled in a paint mill or colloid mill until the desired degree of dispersion is obtained. The secondary additives which may be incorporated in the grease in order to improve specific properties include antioxidants, detergents, extreme pressure agents, rust inhibitors and the like.

Instead of forming the sodium or lithium salt of the phenol-aldehyde condensate in situ as in the above procedure, a previously prepared salt can be added to the reaction mass at any stage of operation. For example, a sodium or lithium salt of a phenol-aldehyde condensate can be added along with the secondary additives, if such are employed, prior to milling the grease.

From the foregoing, it is apparent that the greases constituting my invention should contain between about 1 and 50 percent of a sodium or lithium soap, preferably about 5 and 25 percent of the specified soap, between about 3 and 10 percent and preferably between about 5 to 8 percent of a metal salt of a condensation product of a hydrocarbyl substituted phenol and an aldehyde, the metal component of the salt being the same metal as present in the soap, the balance being lubricating oil and minor amounts of other additives in case such other additives are desired.

The data given in Tables I and II provide a comparison of the greases of this invention with a conventional grease which does not contain a sodium or lithium salt of the class herein disclosed. To demonstrate the increased performance life of the greases of this invention, the greases were tested in an antifriction bearing test machine. This machine consists essentially of two flat-rimmed steel wheels, each containing two No. 6210 ball bearings, mounted on two parallel spindles, one above the other, and loaded through a system of levers and fulcrum plates by tangential contact of the wheels. The lower spindle with its wheel is connected to the loading system, and the upper assembly is brought to bear upon the lower by turning down two large screws until it counterbalances the chosen loading weight, which in these tests was 1000 pounds. To insure a fixed temperature of 250° F., the wheels are enclosed in an insulated box and heated by thermostatically controlled ring heaters surrounding the hubs. A cartridge heater in the rear of each spindle compensates for the heat loss through the heavy steel structure. Thermocouples are situated in grooves in the spindles and contact each bearing. A pulley on the upper wheel and two appropriate holes in the side of the insulated box provide for a belt driven by means of a motor mounted on the outside. A single charge of grease (10 grams) is packed into each ball bearing. The test runs continue as long as the bearings remain lubricated by the original charge, but with several interruptions for inspections, to observe developments and changing conditions. Finally, the runs are terminated and grease failure is declared when the race paths are found to be dry, a condition sometimes signalized by a sudden temperature rise in the bearing.

The lubricating oil employed in preparing these illustrative greases comprised a mineral lubricating oil having an API gravity of 22.0, a viscosity of 510, and 54.9 Saybolt Universal seconds at 100° F. and 210° F. respectively, and a flash point of 385° F. A grease was prepared by adding to a part (approximately 35 percent) of the oil in a pressure kettle, stearic acid, lithium hydroxide monohydrate in aqueous solution and the condensation

product of para-isooctyl phenol and formaldehyde. The kettle contents were heated and stirred to a temperature of 320–360° F. with a resultant internal pressure in the kettle of about 100 to 130 pounds per square inch. Under these conditions the lithium salt of the para-isooctyl phenol-formaldehyde condensation product was formed and the stearic acid was saponified to form the lithium soap. The kettle contents were maintained under these conditions for one hour and then discharged into an open kettle preheated to 350° F. Heating and stirring were continued and the temperature of the kettle contents was raised to 370–400° F. in about 3 to 4 hours. The remaining oil was slowly added at this temperature with continued stirring. The kettle contents were then cooled with stirring to about 200° F. The cooling was continued until the temperature reached 100–125° F. at which time the grease was milled by passing it through a colloid mill. Utilizing the same procedure as just described, a sodium grease was prepared employing sodium hydroxide in place of the lithium hydroxide monohydrate. For comparison, a lithium grease was also prepared which did not contain a salt of the class included by this invention. Grease compositions were thus obtained having the following approximate makeup:

Table I

Composition, percent by Weight	A	B	C
Lubricating Oil	87.02	83.90	77.13
Sodium stearate soap			15.15
Lithium stearate soap		12.07	
Lithium soap of Hyfac 410 acids	12.98		
Lithium salt of p-isooctyl phenol-formaldehyde condensation product		4.03	
Sodium salt of p-isooctyl phenol-formaldehyde condensation product			7.72
Ratio Soap/Salt		2.99:1	1.96:1
Inspection:			
Dropping Point, ° F., ASTM D 566-42	368	385	366
Penetration, ASTM D 217-52 T—			
Unworked	261	174	256
Worked 60 strokes	278	225	257
Performance Test—Anti-friction Bearing Machines, 6210 Bearing, 10 grms. grease, 750 r.p.m., 1000 lb. load, 250° F. Hours to Failure	1,573	2,925	4,348

The Hyfac 410 utilized in composition A is a commercially available mixture of acids of the approximate make-up:

	Percent by weight
Stearic acid	63
Palmitic acid	28
Oleic acid	6
Myristic acid	3

Other grease compositions in accordance with the invention were prepared as described above utilizing as the lubricating oil base a mineral lubricating oil having an API of 29.8, a viscosity of 315 Saybolt Universal seconds at 100° F. and 54.5 at 210° F., a flash point of 455° F. The greases thus obtained had the following approximate make-up:

Table II

Composition, percent by Weight	D	E
Lubricating Oil	76.39	76.38
Sodium soap of Hydrofol 150 acids	16.86	14.97
Sodium salt of p-isooctyl phenol-formaldehyde condensation product	5.74	7.64
Antioxidant (approx. 88% diphenylamine)	1.01	1.01
Ratio Soap/Salt	2.94:1	1.96:1
Inspection:		
Dropping Point °F., ASTM D 566-42	417	413
Penetration, ASTM D 217-52 T—		
Unworked	201	175
Worked 60 Strokes	245	210
Performance Test—Anti-friction Bearing Machines, 6210 Bearing, 10 grms. grease, 750 r.p.m., 1,000 lb. load, 250° F Hours to Failure	5,110	8,270

The Hydrofol 150 utilized in compositions D and E is a

commercially available mixture of acids of the approximate make-up:

	Percent by weight
Stearic acid	90
Palmitic acid	10

It is apparent from the foregoing data that the performance life of each of the compositions B, C, D and E which are compositions of this invention is eminently greater than the performance life of composition A, which is a conventional lithium grease not containing a salt of the class described herein. In addition to increased performance life, the greases of the invention exhibit improved characteristics with respect to water resistance and adhesion to metals.

It is to be noted that while the grease compositions of the invention are particularly suited for high temperature lubricating applications, their utility is not limited thereto, and the greases of the invention can be advantageously utilized to lubricate where high temperatures are not encountered.

Those modifications and equivalents which fall within the spirit of the invention and the scope of the appended claims are to be considered part of the invention.

I claim:

1. An improved grease composition comprising a lubricating oil, about 1 to about 50 percent by weight of the composition of a member of the group consisting of sodium and lithium soaps and about 3 to about 10 percent by weight of the composition of an oil-soluble metal salt of a condensation product of a hydrocarbyl substituted phenol and an aldehyde, wherein the metal constituent of the soap and the salt is the same.

2. An improved grease composition comprising a lubricating oil, about 1 to about 50 percent by weight of the composition of a member of the group consisting of sodium and lithium soaps and about 3 to about 10 percent by weight of the composition of an oil-soluble metal salt of a condensation product of a hydrocarbyl substituted phenol and an aldehyde, wherein the metal constituent of the soap and the salt is the same and the weight ratio of said soap to said salt is between about 11:1 and about 1:1.

3. An improved grease composition comprising a lubricating oil, about 1 to about 50 percent by weight of the composition of a member of the group consisting of sodium and lithium soaps and about 3 to about 10 percent by weight of the composition of an oil-soluble metal salt of the condensation product of para-isooctyl phenol and formaldehyde, said condensation product containing about 5 mols of para-isooctyl phenol per molecule of condensate, wherein the metal constituent of the soap and the salt is the same and the weight ratio of said soap to said salt is between about 11:1 and about 1:1.

4. An improved grease composition comprising a lubrication oil, about 1 to about 50 percent by weight of the composition of a metal of a C_{12} to C_{32} organic acid whose salt forming metal is selected from the group consisting of sodium and lithium, and about 3 to about 10 percent by weight of the composition of an oil-soluble metal salt of the condensation product of para-isooctyl phenol and formaldehyde, said condensation product containing about 5 mols of para-isooctyl phenol per molecule of condensate, wherein the metal constituent of the soap and the salt is the same and the weight ratio of said soap to said salt is between about 11:1 and about 1:1.

5. An improved grease composition comprising a lubricating oil, about 1 to about 50 percent by weight of the composition of a sodium soap of an organic acid containing between 12 and 32 carbon atoms, and about 3 to about 10 percent by weight of the composition of a sodium salt of the condensation product of para-isooctyl phenol and formaldehyde, said condensation product containing about 5 mols of para-isooctyl phenol per molecule of condensate.

6. An improved grease composition comprising a lubricating oil, about 1 to about 50 percent by weight of the composition of a lithium soap of an organic acid containing between 12 and 32 carbon atoms, and about 3 to about 10 percent by weight of the composition of a lithium salt of the condensation product of para-isooctyl phenol and formaldehyde, said condensation product containing about 5 mols of para-isooctyl phenol per molecule of condensate.

7. An improved grease composition comprising a lubricating oil, about 5 to about 25 percent by weight of the composition of a sodium soap of an organic acid containing between 12 and 32 carbon atoms, and about 5 to about 8 percent by weight of the composition of a sodium salt of the condensation product of para-isooctyl phenol and formaldehyde, said condensation product containing about 5 mols of para-isooctyl phenol per molecule of condensate, and the weight ratio of said soap to said salt being between about 11:1 and about 1:1.

8. An improved grease composition comprising a lubricating oil, about 5 to about 25 percent by weight of the composition of a lithium soap of an organic acid containing between 12 and 32 carbon atoms, and about 5 to about 8 percent by weight of the composition of a lithium salt of the condensation product of para-isooctyl phenol and formaldehyde, said condensation product containing about 5 mols of para-isooctyl phenol per molecule of condensate, and the weight ratio of said soap to said salt being between about 11:1 and about 1:1.

9. A method for preparing an improved lubricating grease composition which comprises adding to a portion of a mineral lubricating oil, a condensation product of a substituted phenol and an aldehyde, an organic acid containing about 12 to about 32 carbon atoms and a base selected from the group consisting of sodium hydroxide and lithium hydroxide, heating the mixture to a temperature of about 320° F. under a pressure of 100 to 300 pounds per square inch to form a soap by saponification and to form a salt by reaction of the selected base with the said condensation product, dehydrating the reaction mass by heating the reaction mass to a temperature of about 300 to 400° F., adding the remainder of the lubricating oil necessary to form a composition of desired concentration, cooling the reaction mass, milling the reaction mass to obtain a grease of desired dispersion.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,052,631 September 4, 1962

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 25, after "oil," insert -- a --; line 67, for "of" read -- or --; column 2, line 11, for "cyclo-alkyl" read -- cycloalkyl --; line 45, for "products" read -- product --; column 4, Table I, third column, line 8, for "385" read -- 375 --; column 5, line 57, after "metal" insert -- soap --.

Signed and sealed this 8th day of January 1963.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents