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ALUMINUM COMPLEX SOAP GREASE

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ABSTRACT OF THE DISCLOSURE

A grease composition for lubricating bearings operating at temperatures up to about 350° F. comprises a mineral lubricating oil base having an aniline point below about 230° F. and a grease-forming amount of an aluminum complex soap of benzoic acid and (1) a saturated fatty acid having from 20 to 22 carbon atoms per molecule or (2) a saturated fatty acid mixture which contains at least 50 percent by weight of C_{20} and/or C_{22} fatty acids. The molar ratio of benzoic acid to C_{20}–C_{22} fatty acids is about 1.25:1 to about 2:1, benzoic acid to C_{20}–C_{22} fatty acids, respectively. If a saturated C_{14} to C_{22} fatty acid mixture which contains about 50 to about 60 percent by weight of C_{20} and/or C_{22} fatty acids is used, the molar ratio of benzoic acid to saturated C_{14} to C_{22} fatty acid mixture is about 0.7:1 to about 1:1, benzoic acid to saturated fatty acid mixture, respectively, The grease composition of the invention is distinguished over grease compositions prepared from an aluminum complex soap of benzoic acid and hydroxystearic acid or fatty acid mixtures which predominate in C_{16} and C_{18} acids.

This invention relates to a lubricating composition and more particularly to an aluminum complex soap grease composition having improved physical characteristics.

Increased production rates have placed increased loads on existing machinery and particularly on the bearings of such machinery. With increased loads on machinery, bearings are subjected to greater frictional forces with the evolution of heat causing the bearings to operate at temperatures above those which would normally be encountered. Also, many of today's cars are equipped with disc brakes. It is generally recognized that wheel bearings of cars equipped with disc brakes operate at higher temperatures than those equipped with drum brakes.

One of the problems encountered in lubricating bearings opearting at high temperatures is the provision of a grease composition which will remain semisolid when subjected to high temperatures. A semisolid structure is desirable to prevent loss of grease by leakage from bearings thereby causing excessive wear and scoring of bearings due to inadequate lubrication. Inasmuch as many bearings operate at temperatures in the order of 200° to 325° F. and higher, a grease composition for such bearings should have a low penetration and a high dropping point, i.e., a dropping point of at least about 500° F.

In the past, grease compositions having high dropping points have been obtained by thickening lubricating oils to a grease consistency with various sodium soaps. Unfortunately, the sodium soap greases are not resistant to emulsification in water. Since many grease compositions come in contact with water either during use or during storage, it is desirable for a grease composition to have a high resistance to the effects of water. Highly water resistant greases have been obtained by using various calcium soaps as oil thickening agents, but the calcium soap greases in general, are unstable at temperatures above about 200° F. Attempts have been made ot obtain a grease composition having a high dropping point and a high resistance to the effects of water by blending together a soda base grease and a lime base grease. Unfortunately,

when soda base and lime base greases are blended together the ratio of lime soap to soda soap required to obtain good water resistance is so high that the dropping point of the grease is reduced below the limits desired for a high-temperature grease.

It is known in the art that high-temperature greases having good water resistance can be obtained by thickening lubricating oils to the consistency of a grease with various combinations of calcium soaps and calcium salts as disclosed in U.S. Pat. No. 2,197,263 dated Apr. 16, 1940 to E. S. Carmichael. While grease compositions having improved high-temperature and water resistant characteristics have been obtained by utilizing soap-salt complexes of calcium, difficulty has been encountered in manufacturing such grease compositions by conventional grease-making procedures because of excessive foaming which has been encountered. Also, difficulty has been encountered in producing a calcium soap-salt grease composition which does not vary in physical characteristics from batch to batch. Special methods of preparing smooth-textured high-temperature calcium soap-calcium salt grease compositions which do not vary in physical characteristics from batch to batch are disclosed in U.S. Pat. No. 3,466,245 dated Sept. 9, 1969 to C. M. Peck, but such methods are economically unattractive for manufacturing an inexpensive all purpose grease composition.

Some degree of commercial success has been obtained in the preparation of high-temperature grease compositions utilizing lithium soaps to thicken the oil. While lithium soap compositions have met with some success in lubricating surfaces exposed to atmospheric conditions, their use as an all purpose lubricant has been hampered because they do not possess all of the properties required of such lubricants. In particular, the lithium soap greases have not had the desired mechanical and chemical stability in the presence of water which is required of all purpose lubricants. The mechanical and chemical characteristics of lithium soap grease compositions in the presence of water has been improved by incorporating a small amount of a calcium soap of a saturated fatty acid having from 12 to 24 carbon atoms in the compositions as disclosed in U.S. Pat. No. 3,402,615 dated July 3, 1962 to L. U. Franklin et al. but such grease compositions are more expensive to prepare than are grease compositions prepared from a single metal component.

Aluminum soaps and particularly certain aluminum complex soaps have been utilized in producing grease compositions and thus the use of aluminum soaps broadly in formulating grease compositions is not new. For example, a detailed description of one such type of material is disclosed in U.S. Pat. No. 2,599,553 to B. W. Hotten and in U.S. Pat. No. 2,768,138 to B. W. Hotten, et al., wherein an aluminum salt is coprecipitated with an aqueous solution of mixtures of water-soluble soaps to obtain aluminum complex soaps such as aluminum benzoate stearate and aluminum toluate stearate which are then blended with an oil to form a grease composition. Other complex aluminum soap greases in the art are disclosed in U.S. Pats. Nos. 2,654,710; 2,719,826; 3,345,291; 3,511,781; 3,574,111 and 3,591,505. The aluminum complex soap grease compositions disclosed in the above patents are generally recognized as having higher dropping points and better water resistance than conventional sodium, calcium and lithium soap greases, and thus are suitable for use in rollers and bearings where high temperatures and water are frequently encountered. However, it has been found difficult to prepare aluminum complex soap grease compositions which are uniform in physical characteristics from batch to batch. Frequently, an aluminum complex soap grease will possess one or two desirable qualities and it will be deficient in another

respect. In U.S. Pat. No. 3,591,505, an improved grease composition is obtained by a procedure wherein an aluminum alkoxide is reacted sequentially with two different carboxylic acids in the presence of an oil base. The aluminum alkoxide is reacted first with the carboxylic acid of lesser reactivity, e.g., stearic acid, and then with the carboxylic acid of greater reactivity, e.g., benzoic acid. This produces a grease having good physical characteristics but the procedure is rather exacting.

We have discovered that an aluminum complex soap grease composition which has a high dropping point and which is resistant to the effects of water, as well as having good resistance to oxidation, can be uniformly obtained from batch to batch by thickening a mineral lubricating oil base having an aniline point below about 230° F. with an aluminum complex soap of benzoic acid and a saturated fatty acid having from 20 to 22 carbon atoms or a fatty acid mixture which contains at least 50 percent by weight of the C_{20} and/or C_{22} fatty acids. The molar ratio of benzoic acid to C_{20}–C_{22} fatty acids is about 1.25:1 to about 2:1, benzoic acid to C_{20}–C_{22} fatty acids, respectively. When a saturated C_{14} to C_{22} fatty acid mixture which contains about 50 to about 60 percent by weight of C_{20} and/or C_{22} fatty acids is employed, the molar ratio of the benzoic acid to saturated C_{14} to C_{22} fatty acid mixture is about 0.7:1 to about 1:1, benzoic acid to saturated fatty acid mixture, respectively. The latter ratio of benzoic acid to fatty acid mixture is sufficient to give a benzoic acid to C_{20}–C_{22} fatty acid molar ratio of about 1.25:1 to about 2:1. The improved lubricating composition of our invention therefore comprises a mineral lubricating oil base having an aniline point below about 230° F. thickened to the consistency of a grease with an aluminum complex soap of benzoic acid and a saturated fatty acid having from 20 to 22 carbon atoms or a fatty acid mixture containing at least 50 percent by weight of the C_{20} and/or C_{22} fatty acids, the molar ratio of said benzoic acid to said C_{20} and/or C_{22} fatty acids being between about 1.25:1 and about 2:1. We have found, for example, that the physical characteristics of a lubricating oil having an aniline point below about 230° F. thickened to the consistency of a grease with an aluminum complex soap of benzoic acid and a fatty acid mixture containing at least 50 percent by weight of the C_{20} to C_{22} fatty acids is markedly improved over the corresponding characteristics of an aluminum complex soap grease prepared from an oil having an aniline point above about 230° F. and from an aluminum complex soap of benzoic acid and a fatty acid mixture wherein the C_{16} and/or C_{18} fatty acids predominate.

The term "aluminum complex soap" as used herein and in the appended claims is intended to mean a mixture of aluminum soap molecules containing at least one hydroxyl anion for each aluminum cation and one or more carboxylic acid anions, and preferably two dissimilar acid anions such as one aromatic, i.e., benzoate anion and one saturated aliphatic, i.e., arachidate or behenate anion. It is to be understood that all individual soap molecules in a given complex soap are not the same. For example, one soap molecule may contain two hydroxyl anions and only one carboxylic acid anion such as an aluminum monoarachidate, an aluminum monobehenate or an aluminum monobenzoate; another may contain one hydroxyl anion and two carboxylic acid anions which are the same, as for example, an aluminum diarachidate, dibehenate or dibenzoate; while a third molecule may contain two dissimilar carboxylic acid anions such as aluminum benzoate arachidate, aluminum benzoate behenate or aluminum arachidate behenate. It will thus be recognized that any given aluminum soap preparation may contain a mixture of all three types of molecules and that the properties of any given aluminum soap preparation may be the average properties of the mixture of molecules present.

While the applicants do not wish to be limited to any particular theory with respect to their invention, they believe that the improved properties obtained in the aluminum complex soap greases of this invention are due to the presence of a substantial preponderance of soap molecules containing two dissimilar carboxyllic acid anions. The term "dissimilar anions" as used hereinabove refers to two homologous saturated aliphatic anions such as arachidate and behenate as well as two unlike anions such as saturated aliphatic, i.e., arachidate or behenate, and aromatic, i.e., benzoate anions.

The method by which the aluminum complex soap is prepared for use in the grease composition of the present invention is not new per se. Essentially, the soap is prepared in the presence of all or a portion of the base mineral oil by reacting a lower alkoxy-substituted cyclic aluminum oxide trimer, e.g., tri-oxy-aluminum tri-isopropoxide or tri-oxy-aluminum tri-butoxide, with a mixture of benzoic acid and a saturated aliphatic (fatty) acid in which C_{20} and/or C_{22} acids predominate at moderate temperatures. The preparation of a similar material is described in Bulletin 7013 issued by Agrashell, Inc. Easton, Pa., (now The Ayers Co., Martin's Creek, Pa.) relating to "Kolate 7013." As disclosed in the publication, all of the mineral oil base and acids are weighed into a vessel and heated to 180° F. Then "Kolate 7013" is added to the vessel whereupon an aluminum complex soap is formed. Because of the trimeric structure of the alkoxy-substituted cyclic aluminum oxide, only one more alcohol is released for each mole of aluminum. When "Kolate 7013" is used to form the soap, no water is required to effect the reaction. Since "Kolate 7013" is in oil solution, the oil itself becomes a part of the overall grease composition and aids in incorporating the soap in the mineral oil base.

In preparing the aluminum complex soap for use in the grease composition of the present invention, it is important that the ratio of benzoic acid to C_{20}–C_{22} fatty acids be carefully controlled so that the molar ratio of benzoic acid to C_{20} and/or C_{22} fatty acids is about 1.25:1 to about 2:1. If the molar ratio is less than about 1.25:1, for example, 1.15 to 1, the water stability and dynamic oxidation stability of the resulting grease composition is substantially reduced.

The amount of the aluminum complex soap which we use in the grease composition of the present invention may vary depending upon the particular lubricating oil base employed and upon the characteristics desired in the ultimate composition. In any event, the aluminum complex soap is used in an amount sufficient to thicken the lubricating oil to a grease consistency. In general, this amount comprises about 2 to about 25 percent by weight of the total composition. When producing a grease corresponding of an NLGI No. 2, grade, the aluminum complex soap comprises about 4 to about 10 percent by weight of the total composition, and preferably about 5 to about 7 percent by weight of the total composition.

The mineral lubricating oil base employed in preparing the grease composition of the present invention may be any of the hydrocarbon oils of lubricating grade customarily used in compounding greases provided the oil or blend of oils has an aniline point below about 230° F. and preferably within the range of about 175° to about 230° F. The oil may be a refined or semirefined oil having a viscosity of about 100 to about 4000 SUS at 100° F. However, an aluminum complex soap grease having maximum shear stability for a given amount of soap is usually obtained with a paraffinic oil or blend of oils having a viscosity of about 300 to about 3000 SUS at 100° F. In producing a multi-purpose lubricant, it is generally preferred to employ an oil or blend of oils having a viscosity within the range of about 500 to about 1200 SUS at 100° F. and an aniline point within the range of about

180° to about 200°, for example, 190° F. The oil content of the composition of the invention comprises about 75 to about 98 percent by weight of the total composition. The particular oil or oil blend as well as the exact amount of oil employed depends upon the characteristics desired in the finished grease.

Benzoic acid which is used in the preparation of the aluminum complex soap is available commercially so that neither benzoic acid per se nor the process by which it is made constitutes any portion of the invention. Benzoic acid, for example, can be prepared by the air oxidation of toluene, or it can be made by chlorinating toluene to obtain benzotrichloride which is then hydrolyzed to produce benzoic acid. While benzoic acid is marketed in USP, technical and industrial grades, we prefer to use the industrial grade from economic reasons. The amount of benzoic acid used in preparing a grease composition of the invention depends at least in part upon the amount of the fatty acid component employed and vice versa. In any event, the benzoic acid is employed in an amount such that the molar ratio of benzoic acid is employed in an amount such that the molar ratio of benzoic acid to C_{20} and/or C_{22} fatty acids is about 1.25:1 to about 2:1.

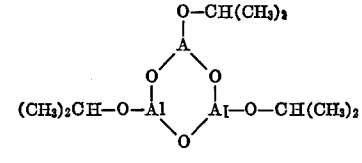
The saturated aliphatic (fatty) acid which is employed in preparing the aluminum complex soap for use in the composition of the invention can be either a substantially pure fatty acid such as arachidic acid or behenic acid or a mixture of saturated fatty acids containing at least 50 percent by weight of archidic or behenic acid or mixtures of aracchidic and behenic acids. An example of a saturated fatty acid mixture wherein arachidic and behenic acids are present in an amount of at least 50 percent by weight is "Hydrofol 2022–55" which comprises a hydrogenated fish oil fatty acid mixture containing 55 percent by weight of arachidic and behenic acids. The number of carbon atoms in the fatty acids used in preparing the aluminum complex soap is critical. We have found, for example, that the aluminum complex soaps of fatty acids containing less than 20 carbon atoms per molecule or mixtures of fatty acids wherein acids containing less than 20 carbon atoms per molecule predominate when used in conjunction with benzoic acid do not produce greases having the desirable characteristics which can be obtained with the aluminum complex soaps of the C_{20} and C_{22} fatty acids. The amount of fatty acid used in preparing a grease composition of the invention depends at least in part upon the amount of the benzoic acid component employed and vice versa. In any event, the fatty acid is employed in an amount such that the molar ratio of benzoic acid to C_{20} and/or C_{22} fatty acids is about 1.25:1 to about 2:1.

The lubricating grease composition of the present invention can contain other lubricant additives, if desired, to improve other specific properties thereof. Thus, the grease composition can contain a filler, an antioxidant, a dispersant, an anticorrosion agent, a rust inhibitor, a metal deactivator, an extreme pressure agent, a tackiness agent, a dye and the like. Whether or not such additives are employed and the amounts thereof depend to a large extent upon the severity of the conditions to which the composition is subjected. When such additives are employed, they are generally added in amounts between about 0.01 and about 10 percent by weight based on the weight of the total composition. They may be added prior to, during or after the heating steps depending upon the thermal stability of the particular additive employed as will be apparent to those skilled in the art.

We have found that a grease composition of the present invention is surprisingly improved in its torque stability as evidenced by its improved antiwear properties as a ball joint lubricant when a sulfurized hydrocarbon, zinc dialkyl dithiophosphate and a chlorinated paraffin are admixed with the grease composition. When these three additives are used together, the antiwear property of the grease composition is improved synergistically. The sulfurized hydrocarbon which we employ is preferably one which contains at least 25 percent by weight of sulfur. Exemplary of such sulfurized hydrocarbons are dibenzyl disulfide (26% S) and ditertiary nonyl polysulfide (37% S). The chlorinated paraffin which we employ is preferably one which contains at least 50 percent by weight of chlorine. The sulfurized hydrocarbon and the zinc dialkyl dithiophosphate are each used in amounts of about 2 to about 4 percent by weight based on the weight of the grease composition. The chlorinated paraffin is used in an amount of about 0.4 to about 2 percent by weight based on the weight of the grease composition. The total amount of the three additives (sulfurized hydrocarbon, zinc dialkyl dithiophosphate and chlorinated paraffin) comprises about 4.4 to about 10 percent by weight of the grease composition. While the weight ratio of these three additives can vary over wide range, we prefer to use a ratio of about 1:1:0.2, sulfurized hydrocarbon:zinc dialkyl dithiophosphate:chlorinated paraffin, respectively. In a preferred embodiment of the invention, we have used 6 percent by weight of a mixture of dibenzyl disulfide (26% S), zinc dialkyl dithiophosphate and chlorinated paraffin (60% Cl) in a weight ratio, respectively, of 1.0:0.84:0.16. In another preferred embodiment, we have used 5.1 percent by weight of a mixture of ditertiary nonyl polysulfide (37% S), zinc dialkyl dithiophosphate and chlorinated paraffin (60% Cl) in a weight ratio, respectively, of 1.0:1.2:0.23.

In preparing the composition of the present invention, various compounding and blending procedures can be employed in either a batch or a continuous process. For example, the aluminum complex soap can be prepared separately and then blended into the mineral lubricating oil or the complex soap can be made in a small amount of oil to form an oil concentrate of the soap which is then blended with the mineral lubricating oil base. In a preferred embodiment, the aluminum complex soap is formed in the presence of a 500 Texas mineral lubricating oil at a temperature of about 320° F. Thereafter, a more viscous mineral lubricating oil is added slowly with stirring while gradually increasing the temperature to about 380° F. The mixture, with stirring, is then allowed to cool to about 220° F. at which time addition agents, if desired, can be added. The cooled grease composition is then milled in a paint mill or colloid mill until the desired degree of dispersion is obtained.

In order to illustrate the preparation of a grease composition of the invention more particularly, 74.9 grams of benzoic acid, 188.8 grams of "Hydrofol Acids 2022–25" and 1991 grams of a Texas mineral lubricating oil having a viscosity of about 500 SUS at 100° F. and about 55 SUS at 210° F. and an aniline point of about 178° F. are charged to an open kettle. "Hydrofol Acids 2022–55" is a saturated fatty acid mixture which contains 55 percent by weight of C_{20} and C_{22} saturated fatty acids. The remainder of the acids in "Hydrofol Acids 2022–55" comprises myristic (2%), palmitic (13%) and stearic (30%). The contents of the kettle are then heated with stirring to 205° F. To the heated oil-acid mixture are added 126.4 grams of "Kolate 7013." "Kolate 7013" contains tri-oxy-aluminum tri-isopropoxide as the active component and has the following structural formula



As manufactured, "Kolate 7013" has an aluminum content of at least 12.5% and is a 55% solution of the active

component in a naphthenic base stock having a viscosity of about 82 SUS at 100° F. and a viscosity index of 29.

After addition of "Kolate 7013," the temperature of the batch is increased to 320° F. at which point the addition of a 150 Mid-Continent Bright Stock mineral oil having a viscosity of about 2600 SUS at 100° F. and about 150 SUS at 210° F. and an aniline point of about 255° F. is initiated. While the aniline point of the Bright Stock oil per se is above the maximum desired where only one oil is used in compositions of the invention, the aniline point of the oil blend which is obtained when 1991 grams of the Texas oil (aniline point of 178° F.) and 1630 grams of the Bright Stock oil (aniline point of 255° F.) and mixed is 190° F. The Bright Stock oil is added slowly while the temperature of the batch is increased to 380° F. At this point, the heat is turned off and additional Bright Stock oil is added until a total of 1630 grams of such Bright Stock oil has been used. The batch is then stirred and allowed to cool to a temperature of about 220° F. At this point, an antioxidant comprising 40 grams of the condensation product of formaldehyde and N,N-dimethylaniline are incorporated into the composition. If desired, other additives such as sulfurized hydrocarbons, chlorinated hydrocarbons, zinc dialkyl dithiophosphate, etc. can also be added at this point. After cooling the batch to a temperature of about 160° to 180° F., homogenization of the grease composition is accomplished by milling the grease in a grease mill such as a Premier mill with a mill setting of 0.006 to 0.008 inch clearance.

The formulation of the finished grease resulting therefrom together with its properties when using the above procedure are as follows:

Composition:
- 500 Texas Oil
  - wt. percent (grams) — 49.16 (1991)
- 150 MC Bright Stock ——do—— 40.23 (1630)
- "Hydrofol Acids 2022–55" ——do—— 4.66 (188.8)
- Benzoic acid ——do—— 1.85 (74.9)
- "Kolate 7013" ——do—— 3.12 (126.4)
- Condensation product of formaldehyde and N,N-dimethylaniline ——do—— 0.99 (40.0)

Molar ratio:
- Benzoic acid to fatty acid mixture — 1:1
- Benzoic acid to C_{20}–C_{22} fatty acid — 1.92:1

Thickener content: percent (total soap) — 7.0

Base oil:
- Viscosity, SUS at 100° F. — 1100
- Aniline Point, ° F. — 190

Inspections of finished grease:
- Dropping Point, ASTM D–2265, ° F. — 571
- Penetration, ASTM D–217, 77° F.:
  - Unworked — 274
  - Worked 60 strokes — 279
  - Worked 100,000 strokes — 304
- Penetration change 60 vs. 100,000 strokes — +25
- Water stability, 90% grease, 10% water:
  - Worked 100,000 strokes, penertation — 299
  - Penetration change 60 vs. 100,000 strokes — +20
- Oil separation, nickel cone, 50 hours:
  - 220° F., percent separation — 0.40
  - 250° F., percent separation — 0.60
- Dynamic oxidation stability, 20 grams grease, rolled at 50 r.p.m., 110 p.s.i. oxygen, 72 hours, 210° F. (stainless steel roller):
  - Pressure drop: p.s.i.:
    - 24 hours — 2
    - 48 hours — 2
    - 72 hours — 5
  - Penetration change 60 srokes vs. 72 hours shearing — +45

In order to illustrate the importance of using an aluminum complex soap of benzoic acid and a fatty acid mixture in which the C_{20} and C_{22} fatty acids comprise at least 50 percent by weight of the mixture, grease compositions containing aluminum complex soaps of benzoic acid in combination with fatty acid mixtures in which the C_{20} and C_{22} fatty acids comprise 55 percent by weight of the mixture were compared with similar compositions containing aluminum complex soaps of benzoic acid in combination with fatty acid mixtures in which the C_{16} and C_{18} fatty acids predominate. An important consideration in a grease composition is its yield (worked penetration) and shear stability as indicated by the change in penetration which occurs between working for 60 strokes and working for 100,000. These evaluations are made in accordance with ASTM D–217. The formulation of the compositions and their respective characteristics are shown in Table 1.

TABLE 1

	A	B	C	D	E
Composition, percent by weight:					
Texas mineral oil (500 SUS at 100° F.)	49.91	49.16	48.42	48.39	48.05
150 MC Bright Stock	40.84	40.23	39.61	39.60	39.31
"Hydrofol acids 2022–55" [1]	4.00	4.66	5.32		
"Hydrofol acids 1880" [2]				5.17	
12-hydroxy stearic acid [3]					5.64
Benzoic acid	1.59	1.85	2.11	2.24	2.24
"Kolate 7013" [4]	2.68	3.12	3.56	3.62	3.78
Combined antioxidant, antitrust agent and detergent [5]	0.49	0.49	0.49	0.49	0.49
Antioxidant [6]	0.49	0.49	0.49	0.49	0.49
Molar ratio:					
Benzoic acid to fatty acid mixture	1:1	1:1	1:1	1:1	1:1
Benzoic acid to C_{20}–C_{22} fatty acids	1.92:1	1.92:1	1.92:1		
Thickener content: percent (total soap)	6.0	7.0	8.00	8.00	8.93
Base oil:					
Viscosity, SUS at 100° F.	1,100	1,100	1,100	1,100	1,100
Aniline point, ° F	190	190	190	190	190
Inspections of finished grease:					
Dropping point, ASTM D–2265: ° F	545	577	587	542	506
Penetration, ASTM D–217:					
Unworked	315	298	234	339	319
Worked, 60 strokes	313	285	233	341	324
Worked, 100,000 strokes	322	316	243	404	444
Penetration change 60 vs. 100,000 strokes	+9	+31	+10	+63	+120

[1] [2] [3] Composition of acids; percent by weight:

	Unsat.	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{18}–12 OH
1. "Hydrofol acids 2022–55"	2	13	30	30	25		
2. "Hydrofol acids 1880"		20	80				
3. 12–OH stearic acid		2	10				88

[4] Physical and Chemical Data on "Kolate 7013": Aluminum content, percent by weight, 12.5; Molecular weight, 306; Tri-oxy aluminum triisopropoxide, percent by weight, 55; Naphthenic mineral oil (82 SUS at 100° F.), weight percent, 45.

[5] One part by weight of the reaction product of lime (1 mol), primary cocoamine (2 mols) and phthalic anhydride (2 mols) in one part by weight of Texas mineral oil (1,900 SUS at 100° F.) per U.S. Pat. No. 2,378,442.

[6] Condensation product of formaldehyde and N, N-dimethylaniline.

From the comparative data shown in Table 1, it will be noted that those compositions (Compositions A, B and C) prepared from acid mixtures containing 55 percent by weight of arachidic (C_{20}) and behenic (C_{22}) acids are superior to those prepared from acid mixtures predominating in palmitic (C_{16}) and stearic (C_{18}) acids or

palmitic (C_{16}), stearic (C_{18}) and 12-hydroxystearic (C_{18}-12OH) acids.

In order to illustrate the importance of maintaining the benzoic acid to C_{20}–C_{22} fatty acids in molar ratios of about 1.25:1 to about 2:1, benzoic to C_{20}–C_{22} fatty acids, respectively, comparative grease compositions were prepared from the same components except the molar ratio of benzoic acid to C_{20}–C_{22} fatty acid was varied from 1.15:1 to 2:1. An important consideration in a grease composition is its yield (worked penetration) and the shear stability as indicated by the change in penetration which occurs between working for 60 strokes and working for 100,000 strokes according to ASTM D–217. Another important consideration in a grease composition is its water stability as determined by subjecting the grease composition (90%) mixed with water (10%) to the conditions of ASTM D–217. A still further important consideration in a grease composition is its shear stability when subjected to high pressure in a roller bearing under oxidizing conditions. Such a test is the one which is referred to in Tables 2 and 3 as the "Dynamic Oxidation Stability" evaluation. In conducting the "Dynamic Oxidation Stability" test, a 20-gram sample of the grease composition to be evaluated is placed in a bomb as described in ASTM D–942. A metal roller 3.42" x 1⅝" diameter is placed in the bomb so that the roller will turn in a rolling manner as the bomb is rotated. The roller can be made from stainless steel or brass. The bomb containing the grease and the roller is charged with oxygen at a pressure of 110 p.s.i. The oxygen-charged bomb containing the grease and metal roller is then placed in an oven maintained at 243° F. The bomb temperature is 210° F. The bomb is rotated at 50 r.p.m. The pressure drop within the bomb is recorded periodically. At the end of the test period, the penetration value of the grease is measured and compared with the penetration at the start of the test. The formulation of the compositions and their respective characteristics are shown in Table 2.

TABLE 2

	F	G	H	I
Composition, percent by weight:				
Texas mineral oil (500 SUS at 100° F.)	49.16	49.26	49.31	49.35
150 MC bright stock	40.22	40.31	40.34	40.37
"Hydrofol acids 2022–55" [1]	4.66	4.88	5.13	5.30
Benzoic acid	1.85	1.65	1.43	1.26
"Kolate 7013" [2]	3.12	2.91	2.80	2.73
Antioxidant [3]	0.99	0.99	0.99	0.99
Molar ratio:				
Benzoic acid to fatty acid mixture	1:1	0.85:1	0.70:1	0.60:1
Benzoic acid to C_{20}–C_{22} fatty acids	1.92:1	1.65:1	1.35:1	1.15:1
Thickener content, percent (total soap)	7.0	7.0	7.0	7.0
Base oil:				
Viscosity, SUS at 100° F	1,100	1,100	1,100	1,100
Aniline point, ° F	190	190	190	190
Inspections of finished grease:				
Dropping point, ASTM D2265, ° F.	571	568	529	516
Penetration, ASTM D–217:				
Unworked	274	245	248	204
Worked, 60 strokes	279	254	252	223
Worked, 100,000 strokes	304	321	305	280
Penetration change 60 vs. 100,000 strokes	+25	+67	+53	+57
Water stability; 90% grease, 10% water:				
Worked 100,000 strokes	299	285	309	345
Penetration change 60 vs. 100,000 strokes	+20	+31	+57	+122
Oil separation, nickel cone, 50 hours:				
220° F., percent separation	0.40	0.0	0.10	1.10
250° F., percent separation	0.60	0.35	0.40	1.00
Dynamic oxidation stability, 20 grams grease rolled at 50 r.p.m., 110 p.s.i. oxygen, 72 hours, 210 °F. (stainless steel roller) pressure drop, p.s.i.:				
24 hours	2	3	0	0
48 hours	2	3	3	5
72 hours	5	3	5	5
Penetration change (72 hours)	+45	+41	+56	+229

[1] Composition of acid, percent by weight:

	Unsat.	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{18}–12 OH
1. "Hydrofol acids 2022–55", wt. percent.		2	13	30	30		25

[2] Physical and chemical data on "Kolate 7013": aluminum content, percent by wt., 12.5; molecular wt., 306; Tri-oxy aluminum tri-isopropoxide, percent by wt., 55; Naphthenic mineral oil (82 SUS at 100° F.), wt. percent 45.

[3] Condensation product of formaldehyde and N,N-dimethylaniline.

TABLE 3

	J	K	F	L	M	N
Composition, percent by weight:						
Texas mineral oil (500 SUS at 100° F.)	89.38	49.16	49.16			
Paraffinic Texas mineral oil (500 SUS at 100° F.)				89.38	17.88	
150 MC bright stock			40.22			
Paraffinic Texas mineral oil (1,200 SUS at 100° F.)					71.50	
Paraffinic Texas mineral oil (1,900 SUS at 100° F.)		40.22				
Hydrofinished heavy neutral mineral oil						89.38
"Hydrofol acids 2022–55" [1]	4.66	4.66	4.66	4.66	4.66	4.66
Benzoic acid	1.85	1.85	1.85	1.85	1.85	1.85
"Kolate 7013" [2]	3.12	3.12	3.12	3.12	3.12	3.12
Antioxidant [3]	0.99	0.99	0.99	0.99	0.99	0.99
Molar ratio:						
Benzoic acid to fatty acid mixture	1:1	1:1	1:1	1:1	1:1	1:1
Benzoic acid to C_{20}–C_{22} fatty acids	1.92:1	1.92:1	1.92:1	1.92:1	1.92:1	1.92:1
Thickener content: percent (total soap)	7.0	7.0	7.0	7.0	7.0	7.0
Base oil:						
Viscosity, SUS at 100° F	509	900	1,100	509	1,020	606
Aniline point, ° F	178	188	190	216	226	243
Inspections of finished grease:						
Dropping Point, ASTM D–2265: ° F	564	561	571	592	589	493
Penetration, ASTM D–217:						
Unworked	305	289	274	285	284	383
Worked 60 strokes	314	278	279	300	287	414
Worked 100,000 strokes	336	311	304	356	330	Fluid
Penetration change 60 vs. 100,000 strokes	+22	+33	+25	+56	+43	
Water stability, 90% grease, 10% water:						
Worked 100,000 strokes	297	283	299	312	290	Fluid
Penetration change 60 vs. 100,000 strokes	−17	+5	+20	+12	+3	
Oil separation, nickel cone, 50 hours:						
220° F., percent separation	2.00	0.20	0.40	3.00	0.60	19.8
250° F., percent separation	2.85	2.40	0.60	3.85	1.95	23.1
Dynamic oxidation stability, 20 grams grease, rolled at 50 r.p.m., 100 p.s.i. oxygen, 72 hours, 210° F. (stainless steel roller) pressure drop: p.s.i.:						
24 hours	1	0	2	2	0	
48 hours	3	3	2	2	0	
72 hours	3	5	5	2	2	
Penetration change (72 hours)	−7	+15	+45	−5	+8	

[1] Composition of acid, percent by weight:

	Unsat.	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{18}–12 OH
1. "Hydrofol acids 2022–55," wt. percent		2	13	30	30	25	

[2] Physical and chemical data on "Kolate 7013": Aluminum content, percent by weight, 12.5; Molecular weight, 306; Tri-oxy aluminum tri-isopropoxide, percent by weight, 55; Naphthenic mineral oil (82 SUS at 100° F.), wt. percent, 45.

[3] Condensation product of formaldehyde and N,N-dimethylaniline.

It will be noted from Table 2 that those grease compositions (Compositions F, G and H) prepared from benzoic and C_{20}–C_{22} fatty acid mixtures in molar ratios of 2:1 to 1.25:1 (benzoic: C_{20}–C_{22} fatty acid) are considerably more stable than the composition (Composition I) prepared from benzoic acid and C_{20}–C_{22} fatty acid mixtures in a molar ratio of 1.15 to 1. It will be noted from the "Water Stability" and "Dynamic Oxidation Stability" evaluation that the penetration change was considerable with composition I. It is thus evident that the benzoic acid to C_{20}–C_{22} fatty acid molar ratio should be maintained within the range of 1.25:1 to 2:1.

In order to illustrate the importance of maintaining the aniline point of the base oil below about 230° F. comparative grease compositions were prepared in which the aniline point of the base oil varied from 178° to 243° F. The yield (worked penetration) and shear stability of the comparative compositions as well as their water stability and "Dynamic Oxidation Stability" were determined by the procedures referred to hereinabove. The formulation of the compositions and their respective characteristics are shown in Table 3.

It will be noted that compositions of the invention (Compositions F, J, K, L and M) prepared from base oils having aniline points below 230° F. are considerably more stable than Composition N which was prepared from a base oil whose aniline point was 243° F. Whereas Compositions F, J, K, L and M had only moderate changes in penetration upon being worked, Composition N became fluid upon being worked so that a penetration measurement could not be obtained.

As indicated hereinabove, the grease composition of the present invention can contain other additives, if desired. We have found in certain instances that some additives cooperate with each other so as to give enhanced overall properties. This is illustrated by the compositions shown in Table 4 wherein a sulfurized hydrocarbon, zinc dialkyl dithiophosphate and a chlorinated paraffin were added to an aluminum complex soap grease composition to improve its antiwear characteristics. The grease compositions were evaluated according to a Ball Joint Grease Test procedure. This procedure provides a measure of the frictional and antiwear properties of a grease composition when subjected to load and prolonged working under oscillating motions in ball joints. According to this procedure, a lubricated automotive ball joint stud and bearing confined in a relatively fixed, motionless housing is rocked through an arc under prescribed conditions of rocking frequency, rocking amplitude, load and time. The torque stability of the grease composition is reported in terms of "Housing Weight Loss". In the evaluations reported in Table 4, the ball joint was packed with 13.5 grams of the grease composition to be evaluated. The ball joint was then subjected to a load of 1300 pounds, a rocking amplitude of ±12° and a rocking frequency of 150 cycles per minute for a period of 65 hours. The make-up of the grease compositions and their respective characteristics are summarized in Table 4.

TABLE 4

Base grease composition, percent by weight:	
Texas mineral oil (500 SUS at 100° F.)	48.72
150 MC bright stock	39.86
Benzoic acid	1.93
"Hydrofol acids 2022-55" [1]	4.86
"Kolate 7013" [2]	3.13
Combined antioxidant, antirust agent and detergent [3]	0.50
Antioxidant [4]	1.00
Molar ratio:	
Benzoic acid to fatty acid mixture	1:1
Benzoic acid to C_{20}–C_{22} fatty acids	1.92:1
Thickener content, percent (total soap)	7.29
Base oil:	
Viscosity, SUS at 100° F	1,100
Aniline point, ° F	190

	O	P	Q	R	S	T	U	V	W
Composition, percent by weight:									
Base grease	100.0	94.0	94.0	94.0	94.0	94.0	94.0	94.0	94.9
Dibenzyl disulfide [5]		6.0			3.26	5.17		3.00	
Zinc dialkyl dithiophosphate [6]			6.0		2.74		5.04	2.52	2.52
Chlorinated paraffin [7]				6.0		0.83	0.96	0.48	0.48
Ditertiary nonyl polysulfide [8]									2.10
Ball joint test: Torque stability, 65 hours; housing weight loss, mg	54.6	57.5	89.4	138.0	49.8	67.6	107.8	5.4	7.4

[1] Composition of acid, percent by weight:

	Unsat.	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{18}–12 OH
1. "Hydrofol acids 2022-55", wt. percent		2	13	30	30	25	

[2] Physical and Chemical Data on "Kolate 7013:" Aluminum content, percent by wt., 12.5; Molecular weight, 306; Tri-oxy aluminum tri-isopropoxide, percent by wt., 55; Naphthenic mineral oil (82 SUS at 100° F.), wt. percent, 45.

[3] One part by weight of the reaction product of lime (1 mol), primary cocoamine (2 mols) and phthalic anhydride (2 mols) in one part by weight of Texas mineral oil (1,900 SUS at 100° F.) per U.S. Pat. No. 2,378,442.

[4] Condensation product of formaldehyde and N,N-dimethylaniline.

[5 6 7 8] Composition of additives:

Percent of	Sulfur	Phosphorus	Zinc	Chlorine
5. Dibenzyl disulfide	26.0	Nil	Nil	Nil
6. Zinc dithiophosphate	20.0	9.5	10.6	Nil
7. Chlorinated paraffin	Nil	Nil	Nil	60.0
8. Ditertiary nonyl polysulfide	37.3	Nil	Nil	Nil

The data in Table 4 show that the torque stability of a grease composition of the invention can be further improved if a sulfurized hydrocarbon [e.g., dibenzyl disulfide (26% S) or ditertiary nonyl polysulfide (37% S)], zinc dialkyl dithiophosphate and chlorinated paraffin (60% Cl) are added to the base grease. It is interesting to note that the dibenzyl disulfide, zinc dialkyl dithiophosphate and chlorinated paraffin are shown to cooperate with each other to give a housing weight loss which is considerably less than would be expected from an observation of the results obtained with the additives individually. As a matter of fact, it will be noted that with only one exception (Composition S), the individual additives and combination of two such additives gave less stable compositions, as measured by the Ball Joint Grease Test, than the base grease, per se.

The lubricating grease compositions of the present invention are useful in lubricating ball and roller bearings, wheel bearings, water pumps, universal joints, automobile chassis, springs, steering gears, pipe threads, aircraft and the like.

While our invention has been described with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such examples and embodiments and may be variously practiced within the scope of the claims hereinafter made.

We claim:

1. A lubricating grease composition comprising a major proportion of a mineral lubricating oil bas having an aniline point below about 230° F. and a small amount, sufficient to thicken the lubricating oil to a grease consistency, of an aluminum complex soap of benzoic acid and a saturated fatty acid having from 20 to 22 carbon atoms per molecule wherein the molar ratio of benzoic acid to C_{20}–C_{22} fatty acid is about 1.25:1 to about 2:1, benzoic acid to C_{20}–C_{22} fatty acid, respectively.

2. The lubricating grease composition of claim 1 wherein the aniline point of the mineral lubricating oil base is within the range of about 175° to about 230° F.

3. The lubricating grease composition of claim 1 wherein the fatty acid is a fatty acid mixture which contains at least about 50 percent by weight of the C_{20} and/or C_{22} fatty acids.

4. A lubricating grease composition comprising a major proportion of a mineral lubricating oil base having an aniline point within the range of about 175° to about 230° F. and about 2 to about 25 percent by weight of an aluminum complex soap of benzoic acid and a saturated fatty acid mixture which contains at least 50 percent by weight of a mixture of arachidic and behenic acids, wherein the molar ratio of benzoic acid to arachidic and behenic acids is about 1.25:1 to about 2:1, benzoic acid to arachidic and behenic acids, respectively.

5. A lubricating grease composition comprising a major proportion of a mineral lubricating oil base having an aniline point within the range of about 175° to about 230° F. and about 4 to about 10 percent by weight of an aluminum complex soap of benzoic acid and a saturated fatty acid mixture which contains at least 50 percent by weight of a mixture of arachidic and behenic acids, wherein the molar ratio of benzoic acid to arachidic and behenic acids is about 1.25:1 to about 2:1, benzoic acid to arachidic and behenic acids, respectively.

6. The lubricating grease composition of claim 5 which also contains about 2 to about 4 percent by weight of a sulfurized hydrocarbon containing at least 25 percent by weight of a sulfur, about 2 to about 4 percent by weight of zinc dialkyl dithiophosphate and about 0.4 to about 2 percent by weight of chlorinated paraffin containing at least 50 percent by weight of chlorine.

7. The lubricating grease composition of claim 6 wherein the weight ratio of sulfurized hydrocarbon:zinc dialkyl dithiophosphate:chlorinated paraffin is about 1:1:0.2, respectively.

8. A lubricating grease composition comprising a major proportion of a mineral lubricating oil base having an aniline point within the range of about 175° to about 230° F. and about 4 to about 10 percent by weight of an aluminum complex soap of benzoic acid and a saturated fatty acid mixture which consists of about 55 percent by weight of a mixture of arachidic and behenic acids and about 45 percent by weight of a mixture of myristic, palmitic and stearic acids, wherein the molar ratio of benzoic acid to mixture of arachidic and behenic acids is about 1.25:1 to about 2:1, benzoic acid to arachidic and behenic acid mixture, respectively.

9. The lubricating grease composition of claim 8 which also contains about 2 to about 4 percent by weight of a sulfurized hydrocarbon containing at least 25 percent by weight of sulfur, about 2 to about 4 percent by weight of zinc dialkyl dithiophosphate and about 0.4 to about 2 percent by weight of chlorinated paraffin containing at least 50 percent by weight of the chlorine.

10. The lubricating grease composition of claim 9 wherein the sulfurized hydrocarbon is dibenzyl disulfide which contains about 26 percent by weight of sulfur and chlorinated paraffin contains about 60 percent by weight of chlorine and wherein the weight ratio of dibenzyl disulfide:zinc dialkyl dithiophosphate:chlorinated paraffin is about 1.0:0.84:0.16, respectively.

11. The lubricating grease composition of claim 10 wherein the aniline point of thhe lubricating oil base is about 190° F.

12. The lubricating grease composition of claim 9 wherein the sulfurized hydrocarbon is ditertiary nonyl polysulfide which contins about 37 percent by weight of sulfur and the chlorinated paraffin contains about 60 percent by weight of chlorine and wherein the weight ratio of ditertiary nonyl polysulfide:zinc dialkyl dithiophosphate:chlorinated paraffin is about 1.0:1.2:0.23, respectively.

13. The lubricating grease composition of claim 12 wherein the aniline point of the lubricating oil base is about 190° F.

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U.S. Cl. X.R.

252—37.7, 45

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,776,846 **Dated** December 4, 1973

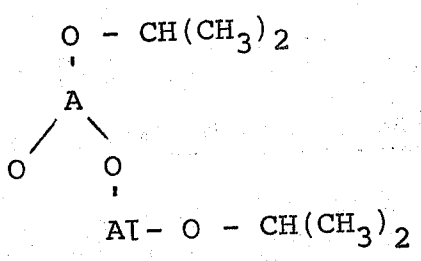
Inventor(s) Wayne W. Bailey and Paul R. McCarthy

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

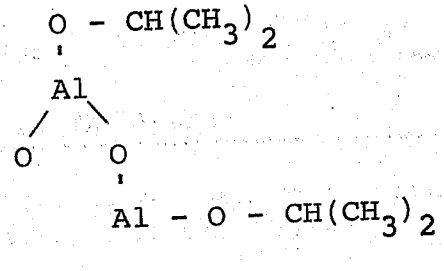
Column 1, line 69, "ot" should read -- to --.

Column 5, line 16, "from" should read -- for --;
lines 20 and 21, delete "is employed in an amount such that the molar ratio of benzoic acid";
line 29, "archidic" should read -- arachidic --;
line 30, "aracchidic" should read -- arachidic --.

Column 6, line 68, that portion of the formula reading



should read



Column 7, line 14, "and" should read -- are --.

Column 10, Table 2, Footnote 1 should read

Unsat.	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{18}-12 OH
--	2	13	30	30	25	--

Column 13, line 7, "bas" should read -- base --;
Line 45, delete "a".

Column 14, line 31, "contins" should read -- contains --.

Signed and sealed this 16th day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents