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HIGH-TEMPERATURE GREASE COMPOSITIONS

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This invention is related to improvements in grease compositions and more particularly it is concerned with greases especially designed for high temperature operation.

Greases prepared by the use of the normal soap-forming ingredients, such as the acids derived from animal fats or vegetable oils, exhibit phase changes with increasing temperature up to a point at which the soap dissolves or at least forms a colloidal dispersion in the lubricating oil base. Such greases are unsuitable for use in the lubrication of bearings operating at elevated temperatures such as those used in aircraft mechanisms and the like.

Greases have been proposed to overcome certain disadvantages of this normal type of grease; U. S. Patent No. 2,182,137 to Veron L. Ricketts describes such greases. In the greases described in the Ricketts patent, use in made of certain salts of aromatic acids such as sodium benzoate which apparently form complexes with the normal soap-forming acids. Greases containing these ingredients exhibit exceptionally high dropping points and, hence, are suitable for use at elevated temperatures. However, as Ricketts notes, it was necessary to heat such grease compositions to a temperature of at least 500–600° F., preferably 550–600° F. in order to produce a satisfactory grease structure. The lubricating oil base employed by Ricketts in the production of his greases was a mineral oil. It will be realized that operations involving temperatures in the order of 500–600° F. involves fire hazards necessitating the use of special precautions. This is true even if high flash point mineral oils are employed.

It is an object of the present invention to produce improved greases. It is a particular object of this invention to produce improved greases for use at elevated temperatures. A special object of this invention comprises the production of high temperature greases at temperatures below those involving excessive fire hazards. Other objects will become apparent during the following discussion.

Now, in accordance with the present invention, it has been found that the disadvantages of high temperature grease cooking can be avoided and the life of the grease unexpectedly prolonged by the use of a lubricating oil base comprising a special mineral oil having a viscosity of between about 1250 and about 11,000 SUS at 100° F., said oil containing less than about 15% by weight of aromatic hydrocarbons, combined with a greater amount of a compatible synthetic high boiling

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liquid polyorganosiloxane having a viscosity within the lubricating oil viscosity range.

Still in accordance with the present invention it has been discovered that the addition of high molecular weight alcohols, and particularly polycyclic alcohols, unexpectedly promotes the high temperature operating life of these greases.

Greases prepared according to the present invention comprise as the liquid base a mixture of the special mineral oil and polyorganosiloxane, said mixture containing a major proportion, from about 55% to about 95% by weight of the latter and a minor proportion of at least 5%, from about 5% to about 45% by weight, of said mineral oil, the percentages being based on the mixture. This mixture of lubricating oils is thickened to a grease consistency by means of a soap predominating in sodium soaps of at least one carboxylic acid having 20 or more carbon atoms. These acids may be aliphatic acids or cycloaliphatic, such as fatty acids or naphthenic acids. Moreover the greases must contain an alkali metal salt of an organic carboxylic acid containing an aromatic ring. The description and proportions of these ingredients will be discussed below.

THE MINERAL LUBRICATING OIL

While the present invention is not to be confined to the use of a mineral oil derived from any particular source or by any particular refining process, the usual source of suitable mineral oils comprises the fraction thereof generally termed "bright stock," and bright stocks having a viscosity index of at least 60. The term "bright stock" is one which is well recognized in the art of refining mineral oils. To obtain the desired fraction, crude oils containing lubricating oil components are usually subjected to distillation under ordinary atmospheric pressures in order to obtain a "long residue" comprising the fraction which does not distill under these conditions without substantial decomposition. The long residue is then subjected to distillation under reduced pressure, with or without steam. Under these conditions, gas oil and waxy lubricant fractions distill over, leaving what is normally termed a "short residue" or a "steam refined stock," also known as "cylinder stock." This material is then deasphalted (if an asphalt-containing crude is employed), then solvent extracted to separate paraffinic and naphthenic components from aromatic components, and the raffinate therefrom is then subjected to dewaxing operations to remove microcrystalline and/or macrocrystalline waxes. The solvent extraction and dewaxing operations

may be reversed in order if desired. Clay contact treatment or percolation may be employed to clean up the oil following any one or all of these separate operations. The raffinate which remains after deasphalting, dewaxing, extraction, and clay treatment is generally called "bright stock."

The bright stocks which are suitable for use in the present compositions have the ranges of properties shown in Table I.

TABLE I

Properties of bright stocks

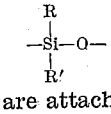
Visc. SUS, 100° F. >1250, usually 1250–11,000, preferably 1500–3500
Visc., SUS, 210° F. >75, usually 125–325, preferably 150–250
Viscosity Index (Dean and Davis) >+60, preferably +85 to 130
Aniline point, °C. >100, preferably >115
Flash, °F. >475, preferably >500
Fire, °F. >550, preferably 600
Pour point, °F. maximum 25, preferably lower than 15
Aromatics, per cent wt. <15, preferably 10 (optimum <5)
Naphthenes, per cent wt. <35
Paraffines, per cent wt. at least 60

The properties of typical bright stocks which are useful in the compositions of this invention are given in Tables II and III.

The most important inherent properties of a mineral oil suitable for the present use comprise the volatility, oxidation stability, aromatic content and the viscosity characteristics. The aromatic content has a large influence upon the sensitivity of the oil to thermal changes and the viscosity of the oil defines its suitability for the present purpose. Hence, the best definition with respect to essential characteristics of mineral oil suitable for the present compositions is that it comprises those oils having an aromatic hydrocarbon content less than about 15% by weight and having a viscosity of between about 1250 and about 11,000 SUS at 100° F. Having defined these particular properties, the other properties such as flash, fire, and aniline points, and viscosity index usually are largely dependent upon them.

THE POLYORGANOSILOXANE

The term "polyhydrocarbylsiloxane" as used herein embraces those organic polymers having as recurrent units the unit structure:



wherein the units are attached through the silicon and oxygen atoms and wherein R and R′ represent alkyl, aryl, alkaryl, aralkyl, and cycloalkyl groups. The method of producing these polymers is well known, and may involve the reaction of a silicon halide with a Grignard reagent to form the corresponding organo silicon halide, followed by hydrolysis of the organo silicon halide to form a silicol, and then condensation of the silicol in the presence of air or oxygen, with the aid of a catalyst or heat to form the polyorganosiloxane or silicone polymer (Kipping, Proc. Chem. Soc. 20, 15–16 (1904)). Depending upon the extent of condensation or polymerization, the resulting products vary from relatively light liquids to solid resins and are reported to be both chain-like (Rochow—U. S. Patent No. 2,352,974) and cyclic (Hyde—U. S. Patent No. 2,371,050) in structure. For purposes of the present invention, only those polymers which are high boiling liquids within the lubricating oil viscosity range and are compatible with mineral lubricating oils are suitable. These generally possess a viscosity at 100° F. within the range of about 10–600 centistokes. The polyorganosiloxane liquids within this viscosity range are usually colorless, odorless and relatively inert, have very low volatility, such that their vapor pressures within the lubricating temperature range are substantially negligible, and high viscosity index which means that they undergo relatively little change in viscosity for a given change in temperature.

TABLE II

Examples of typical bright stocks

	Viscosity SUS at °F		Ring Analysis [1]				Ratio P/N	Av. Mol. Wt.	Av. Rings per Mol.
	100	210	VI	Ar., percent	N, per-cent	P, per-cent			
Mid-Continent Mild Extraction	3,650	164	77	13	17	70	4.1	685	3.7
Mid-Continent Conventional Extraction	2,569	141	85	9	19	72	3.8	685	3.4
Mid-Continent Heavy Extraction	2,049	131	93	3	21	76	3.6	675	2.9
Pennsylvania	2,109	144	102	5	16	79	4.9	730	3.0
Gulf Coastal	1,251	85	63	4	35	61	1.7	515	3.4

[1] Ar.=aromatics, N=napthenes, P=paraffins.

TABLE III

Specifications for typical Mid-Continent bright stocks

	Unpercolated	Clay Percolated
Gravity, °API, min	24.5	25.5
Color, NPA	Dark green	6.7
Pour Pt. °F, max	10	10
Flash, °F, min	580	545
Fire, °F, min	655	610
Visc., SUS 210° F	200–215	150–160
Viscosity Index, min	90	90

It will be understood from the above analyses that the source or treatment of a particular mineral oil is not as important for the present purpose as the final properties of the mineral oil constituent to be used in these compositions. For example, it is possible to vary the extent of solvent extraction dependent upon the original aromatic content and the requirements of the specific use of the final product, as well as upon the necessity or desirability of deasphalting, clay treating, acid treating, and the like. Hence, it will be recognized that the present invention is predicated upon the use of a mineral oil fraction having the above defined ranges of properties and not upon the source or treatment of such oil.

While any of the various types of silicone polymers within the foregoing definition are contemplated for purposes of the present invention, the preferred polymers, from the standpoint of cost, are those which have achieved the greatest commercial production, namely, the dimethyl silicone polymers, the diethyl silicone polymers, and the ethylphenyl or methylphenyl silicone polymers. However, the silicone polymers having higher radical weight alkyl groups, such as butyl, amyl and higher, constitute suitable lubricant bases for purposes of the present invention. In general, these silicone polymers are adapted to speciialized lubrication outside the conventional lubricating temperature ranges, such as ultra low temperature operation found in refrigerator systems and arctic service, or to general purpose lubrication over a wide lubricating temperature range which was previously unattainable through the use of a single mineral lubricating oil because of the latter's high viscosity change over such a wide temperature range. In addition, these silicone materials are compatible with bright stock mineral oils and more resistant at high temperatures where hydrocarbons, esters of carbon chain compounds and similar synthetic lubricant bases of essentially organic structure are subject to carbonization such that they eventually become dry and hard.

THE GREASE-FORMING SOAP

The soda soap comprising the major grease-forming ingredient should constitute from about 2% to about 40% by weight of the composite grease. The term "soda soap," as used in the present specification and claims, designates sodium soaps of carboxylic acids containing at least about 20 carbon atoms. Particularly outstanding results are obtained by the use of acids present in beeswax or degras. While the major grease-forming component should comprise sodium soaps of such acids, minor amounts of other soaps may be present to good advantage for particular purposes.

Acids finding favored use for the formation of soda soaps in the present greases comprise the following:

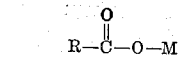
Phthioic acid
Tetracosenoic acids (e. g., selacholeic acid)
Docosenoic acids (e. g., erucic acid)
Eicosenoic acids (e. g., gadoleic acid)
Arachidonic acid
Clupanodonic acid
Lignoceric acid
Selacholeic acid
Celoleic acid
Melissic acid
Montanic acid
Cerotic acid
Behenic acid
n-Octatriacontanoic acid

In addition to the use of higher aliphatic acids, such as those enumerated above, high molecular weight naphthenic acids may be used in place of or in addition to those already specified. Petroleum naphthenic acids having more than 20 carbon atoms per molecule may be employed.

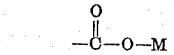
AROMATIC SALTS

Salts of both light and heavy metals may be employed but it is preferred to employ oil soluble salts of alkali or alkaline earth metals and an

organic carboxylic acid containing an aromatic ring. The salt should have the formula:



wherein M is a hydrogen equivalent of the metal and R represents an organic radical containing an aromaic ring which may or may not be substituted with hydrocarbon and/or non-hydrocarbon groups. The carboxylate residue,



may be linked directly to a carbon atom of the aromatic nucleus or it may be linked thereto through an aliphatic or oxyaliphaitc atom or group of atoms, such as a chain of atoms. This chain may be saturated or unsaturated and the acid radical may be substituted with polar radicals such as halogen, amino, hydroxy, keto, or other polar groups. The preferred acids include hydrocarbon monocyclic aromatic and alkylaromatic acids, such as benzoic, o-, m- and p-toluic acids, the xylic acids (e. g., 2,4-, 2,5-, 2,6-dimethylbenzoic acids) hydrocarbon dicyclic aromatic and alkylaromatic acids, that is the naphthoic acids and alkylnaphthoic acids (e. g., α-naphthoic acid, β-naphthoic, 4-butyl-1-naphthoic acid), hydroxy substituted aromatic acids (e. g., salicyclic acid, 3,5-diisopropyl-1-hydroxybenzoic acid) and aryl aliphatic acids such as phenyl acetic acid, cinnamic acid, α-naphthyl acetic acid. Suitable salts made therefrom include sodium benzoate, potassium cinnamate, lithium salicylate, calcium xylate and magnesium vinylate.

Other aromatic acids which may be employed include phenyl acetic, toluic and other alkyl benzoic acids. Phenyl propionic, naphthoic, butyl naphthoic, and phenyl monobasic acids may be employed to form such effective salts as sodium phenyl acetate, sodium toluate, potassium hydrocinnamate, aluminum naphthoate and zinc naphthylacetate.

The salt utilized in the composite greases, according to the present invention, is preferably present in concentrations between 0.1% and about 6% by weight although higher concentrations may be employed. The salt may be formed apart from the step of saponification of the aliphatic material employed for the grease base, and added to the soap either before or after the admixture with the special mineral oil and polyorganosiloxane while the mixture is being heated; it may, however, also be formed in the same operation as explained below in the specific examples.

HIGH MOLECULAR WEIGHT ALCOHOLS

In addition to the essential ingredients enumerated hereinbefore, outstanding mechanical stability is obtained by the addition of high molecular weight alcohols, and particularly monohydric alcohols, to these compositions. These alcohols should have at least 12 carbon atoms and include aliphatic alcohols such as lauryl, cetyl, stearyl, heptadecyl, and monodecyl alcohols; the corresponding mono-olefinic alcohols such as oleyl alcohol and poly olefinic alcohols such as linoleyl alcohol, and cyclic alcohols including mono- and polycyclic alcohols, such as naphthenic alcohols. The preferred type of alcohol for use in these compositions comprises the polyalicyclic alcohols (such as those found in wool fat) which contain at least about 17 and up to about 30 carbon atoms. The principal component of wool fat alcohols is believed to be

cholestanol. Other suitable polycyclic alcohols promoting the mechanical stability of the present greases include the following:

Allochlolesterol
Ostreasterol
Lanosterol
Lanyl alcohol
Lano-octadecyl alcohol
Cholesterol
7-dehydrocholesterol
Alpha-spinasterol
Fucasterol
Stigmasterol
Beta-sitosterol
Ergosterol
Ergostanol

Alcohols such as those described above may be used in amounts of about 1–5%, based upon the weight of the total grease composition. Preferably they are present in amounts of from about 1.5 to about 3% based on the total grease but this proportion will vary with the specific requirements of the grease and the other ingredients present. The presence of these alcohols, such as wool fat alcohols, reduces the granularity of the grease, prevents bleeding and depresses slumpability. All of these properties enhance the mechanical life of the grease during its utilization for such purposes as bearing lubrication. These properties will be evident from the data presented hereinafter.

Summarizing the compositions, as described above, the preferred greases contain the following ingredients in the stated proportions:

	Weight percent
Soda soap	2–40
Salt of aromatic acid	0.15–5
Alcohol	0–5
Polyorganosiloxane 55–95% of mixture Special mineral oil 5–45% of mixture	Balance

In addition to the above essential or optional ingredients, other materials may be present. For example, the lubricating oil base (comprising 5–45% of the special mineral oil and 55–95% of the polyorganosiloxane) may be supplemented by the presence of other types of lubricants in minor amounts such as aliphatic diesters, e. g., bis(2-ethylhexyl) sebacate; phosphate esters such as tricresyl phosphate; phosphonates such as diethyl benzene phosphate and the like.

The soda soap may be supplemented by the presence of less than about 5% based on the total soap content of other soaps such as the potassium or calcium soaps of the same or different acids including the potassium soaps of beeswax acids or the calcium soaps of degras. The presence of such minor amounts of non-sodium soaps promotes the mechanical stability of the greases.

Supplementing the beneficial action of the salts of aromatic acids and the high molecular weight alcohols, various types of antioxidants, anti-corrosion agents and extreme pressure agents may be present. A particularly effective type of antioxidant comprises aromatic amines preferably containing at least 10 carbon atoms. These may be either monocyclic or polycyclic although the naphthalamines are preferred. Typical species of these include phenyl alpha-naphthylamine, phenyl beta-naphthylamine and benzyl phenyl naphthylamine. Other suitable amines include di(p-aminophenyl) phenyl methane, and polyalkyl diamino diaryl alkanes such as P,P'(N,N' tetra-methyl) diamino diphenyl methane.

A synergistic action has been observed to occur when both an aromatic amine and a reaction product of a terpene with a phosphorous sulfide are present. The latter type of reaction product is described in the patent literature and comprises the product obtained by heating a phosphorous sulfide and a dicyclic terpene together at a temperature above about 212° F. Suitable sulfides include the mixtures of various phosphorous sulfides but phosphorous pentasulfide is especially preferred and pinene or turpentine are effective species to be reacted therewith. The reaction is carried out usually between temperatures of 212–320° F. with a ratio of 1 mol of phosphorous sulfide to about 3–5 mols of the dicyclic terpene.

In addition to these especially effective ingredients, another class still further improving the compositions comprises the metallic salts of carbamic acid or its analogs. Species of these materials include the zinc or calcium salts of dibutyl dithiocarbamic or of dihexyl dithiocarbamic acid as well as the strontium, zinc or lithium salts of dibenzyl mono- or dithiocarbamic acid. Generally these additives are present in an amount less than 5% by weight of the composition and if present in effective quantities comprise at least about 0.1% by weight of the total composition.

Other additives which may be present include pour point depressants, viscosity index improvers, and alkali metal soaps of hydroxy fatty acids having more than 12 carbon atoms per molecule such as 0.1–2.5% lithium-12-hydroxy stearate.

The following compositions illustrate the basic compositions of the present invention. In preparing these compositions, it has been found, as noted already, that the combination of the two essential oils makes possible the use of much lower "cooking" temperatures than was possible heretofore. While the exact reason for this is somewhat obscure, it is believed that the presence of substantial quantities of polyorganosiloxane promotes melting or dissolution of the soap and salt at lower temperatures than are required when the lubricating oil is entirely composed of a petroleum base. While the individual steps may be altered in accordance with well-known variations in the art, the following procedure is preferred since it produces greases having maximum mechanical stability both under dynamic and static conditions: Part of the mixture of special mineral oil and polyorganosiloxane is heated to a temperature of approximately 195° F. At this initial elevated temperature the high molecular weight acids, such as beeswax acids, are added and stirred until melted. The mixture is then warmed to about 230° F. The acids are saponified at about this temperature by the addition of 33% aqueous sodium hydroxide solution. The resulting mixture is heated (to gradually eliminate water and complete saponification) to a temperature of about 300° F. and held at this temperature for approximately one hour. Thereafter the composition is cooled to about 195° F., while being stirred, after which high molecular weight alcohols, e. g., wool grease alcohols, and aromatic acids are added together with a minor amount of water, such as about 1% based on the finished grease. The mixture is again heated to about 450° F. and held at this temperature for approximately thirty minutes. The batch is then cooled by the addition of the remainder of the

mixture of oils to a temperature of about 250° F. and the alkalinity adjusted to approximately 0.1–0.3% sodium hydroxide by adding either sodium hydroxide or benzoic acid. Other additives, as desired, are incorporated at this point. The final grease is then homogenized and cooled to obtain the completed product.

As noted hereinbefore, each of these steps is subject to variation dependent upon the identity of the ingredients employed. For example, the initial period of heating may be to temperatures between about 170° and 225° F. in order to melt the particular species of acids utilized or to increase or depress the rate of melting of said acids. The temperature of saponification also may be varied from approximately 200° to about 250° F.; the rate of caustic addition may be used as one means of controlling this temperature. The heat of saponification, as well as external heat, may be used for this effect. The maximum saponification temperature will vary according to the species of acid used but will ordinarily be between about 275° to 325° F. This maximum temperature may be held for periods from about thirty minutes to about four hours. The temperature following maximum cooking temperature may be lowered to 175–275° F. The salts of benzoic acids, or other aromatic acids, may be added in pre-formed state or the acids can be saponified during or after their addition to the grease-forming ingredients. Hence, sufficient caustic may be added in the previous saponification step to saponify the aromatic acid or additional caustic may be supplied during or subsequent to the acid addition. The maximum cooking temperature will vary with the exact proportion of polyorganosiloxane and special mineral oil but in all instances it will be found that this usually is from 50° to 150° F. lower than that required if the lubricating oil base were all mineral oil. This maximum cooking temperature will be between about 400° and 475° F. and will be held for a period varying from about 15 minutes to about 2 hours.

Addition of the balance of the oil may be at such a rate and in such proportions as to cool the composition to a temperature between about 150° and about 250° F. in order to blend in any other additional ingredients. It will be understood that the proportion of oil initially added to the cooking vessel will be selected depending upon the degree of ease required in stirring or otherwise working the batch. With the greases given in the following examples approximately one-half of the oil mixture was initially employed although quantities between one-fourth and all of the oil may be added initially to the cooking kettle. Using the method as outlined about the following greases can be prepared and are found to have exceptionally high mechanical stability as well as exhibiting the property of being formed satisfactorily by the use of maximum cooking temperatures in the order of about 400–475° F.

Example 1:
- 10% sodium beeswax soaps
- 3% sodium benzoate
- 3% cetyl alcohol
- 74% dimethyl silicone fluid
- 10% bright stock

Example 2:
- 10% sodium degras soaps
- 3% potassium cinnamate
- 3% branched C_{13}–C_{18} aliphatic alcohols
- 67% dimethyl silicone
- 17% bright stock

Example 3:
- 15% sodium cerotate
- 2.5% lithium salicylate
- 2.5% cholestanol
- 60% dimethyl silicone
- 20% bright stock

Example 4:
- 9% sodium beeswax soaps
- 1% potassium beeswax soaps
- 80% dimethyl silicone
- 10% bright stock

Example 5:
- 19% sodium beeswax soaps
- 1% calcium beeswax soaps
- 68% dimethyl silicone
- 12% bright stock

Example 6: Greases were prepared using the procedure outlined above and in accordance with the ingredients specified in Table IV. These were tested in two accepted dynamic test rigs as follows: The Annular Bearing Engineers Committee Test (ABEC Test) at 400° F. and the Navy Engineering Experiment Station Test at 392° F. The first of these is described in detail in Technical Bulletin No. 5 of the National Lubricating Grease Institute Cooperative Committee dated November 1944. The latter test is described in the Federal Stock Catalogue dated November 15, 1948, Serial No. V V–L–791*d* and is Method No. 33.1. This test is used by the Navy Experiment Station in grease investigations. While it is operated at a somewhat lower temperature than the first test, the grease is exposed to a greater quantity of air and is therefore subject to more stringent conditions in regard to evaporation and oxidation.

TABLE IV

Grease	Wt. Percent Bright Stock	Wt. Percent Dimethyl Silicone	Wt. Percent Na Beeswax	Wt. Percent Na Benzoate	Wt. Percent Wool Grease Alcohols	ABEC Test, Hours at 400° F.	Navy E. E. S. Bearing Test Hours at 392° F.
A	86		11	3		100	32
B		86	11	3		172	
C	12.5	73.5	11	3		176	92
D	83		11	3	3		35
E		83	11	3	3	238	132
F	12	71	11	3	3	277	184

According to Table IV, it will be found that the use of both dimethyl silicone and bright stock resulted in a grease having a Navy Bearing Test life nearly three times as great as when bright stock alone was employed. However, the major improvement gained by the combination of silicone with bright stock comprised the substantially lower temperature (in the order of about 75° F. lower) required for the maximum cooking temperature in order to obtain satisfactory

greases as compared with the much higher temperatures required when bright stock alone was the lubricating oil base. Attention is directed to the outstanding improvements obtained by the addition of wool grease alcohols and particularly to the response as illustrated by the Navy Bearing Test for grease "F." It would be expected by examination of greases "D" and "E" that the Navy Bearing Test life of grease "F" would have been about 100 hours or less. However, it was found that the test life was about 184 hours. Hence, this is a clear demonstration of a synergistic effect apparently occurring when bright stock and silicone fluid are combined with wool grease alcohols in addition to the benzoic acid salt and soaps of beeswax acids. Similar unexpected properties can be demonstrated with the compositions of Examples 1 to 5.

Other specific compositions which are preparable in accordance with the present invention include the following:

Example 7:

	Weight percent
Dimethyl silicone fluid	70
Bright stock	12
Sodium soap of beeswax acids	11
Sodium benzoate	3
Phenyl alpha-naphthylamine	1
Wool grease alcohols	3

Example 8:

Dimethyl silicone fluid	69.5
Bright stock	12
Sodium soap of beeswax acids	11
Sodium benzoate	3
Phenyl alpha-naphthylamine	0.5
P_2S_5 reaction product with turpentine	1
Wool grease alcohols	3

Example 9:

Dimethyl silicone fluid	69
Bright stock	12
Sodium soap of beeswax acids	11
Sodium benzoate	3
Phenyl alpha-naphthylamine	0.5
P_2S_5 reaction product with turpentine	1
Zinc dibutyl dithiocarbamate	0.5
Wool grease alcohols	3

Example 10:

Dimethyl silicone fluid	68
Bright stock	12
Sodium soap of beeswax acids	11
Sodium benzoate	3
Phenyl alpha-naphthylamine	0.5
P_2S_5 reaction product with turpentine	1
Zinc dibutyl dithiocarbamate	0.5
Dilauryl selenide	1
Wool grease alcohols	3

The aromatic amines to be used as antioxidants in the above compositions are unexpectedly supplemented by the presence of selenium containing compounds selected from the groups consisting of dialkyl selenides, alkyl seleno mercaptans, and dialkyl diselenides. It appears from the data at hand that the selenides act in a synergistic manner to promote the mechanical stability of the grease when said grease also contains high molecular weight alcohols. Suitable selenium containing materials are described in U. S. Patents 2,528,346; 2,398,415, and 2,543,735.

We claim as our invention:

1. A lubricating grease composition comprising as the lubricating base thereof a mixture of from 55% to about 95% by weight of a synthetic high boiling liquid polyhydrocarbylsiloxane having a viscosity within the lubricating oil viscosity range and from about 5% to about 45% by weight of a mineral oil having a viscosity of between about 1250 and about 11,000 SUS at 100° F., said mineral oil containing less than about 15% by weight of aromatic hydrocarbons, the lubricating base being thickened to a grease consistency by a sodium soap of a carboxylic acid having at least 20 carbon atoms per molecule, said grease containing a minor proportion of an alkali metal salt of an organic carboxylic acid containing an aromatic ring.

2. A lubricating grease composition comprising as the lubricating base thereof a mixture of from 55% to about 95% by weight of a high boiling liquid dialkyl silicone polymer having a viscosity within the lubricating oil viscosity range and from 5% to about 45% by weight of a mineral oil having a viscosity of between 1250 and about 11,000 SUS at 100° F., said oil containing less than about 10% by weight of aromatic hydrocarbons and having a viscosity index greater than about 60, the lubricating base being thickened to a grease consistency by a sodium soap of an aliphatic monocarboxylic acid having at least 20 carbon atoms per molecule, said grease containing a minor proportion of a sodium soap of an organic carboxylic acid containing an aromatic ring and a polycyclic alcohol.

3. A lubricating grease composition comprising as the lubricating base thereof a mixture of from 55% to about 95% by weight of a high boiling liquid dimethyl silicone polymer having a viscosity within the lubricating oil viscosity range and from about 5% to about 45% by weight of a mineral oil having a viscosity of between about 1250 and 11,000 SUS at 100° F., said oil containing less than about 10% by weight of aromatic hydrocarbons and having a viscosity index greater than 60 and an aniline point higher than about 100° C., the lubricating base being thickened to a grease consistency by a sodium soap of a monocarboxylic aliphatic acid having at least 20 carbon atoms per molecule, said grease containing a minor proportion of a sodium salt of an organic carboxylic acid containing an aromatic ring and a minor proportion of at least one sterol.

4. A lubricating grease composition comprising as the lubricating base thereof a mixture of from 55% to about 95% by weight of a high boiling dimethyl silicone polymer having a viscosity within the lubricating oil viscosity range and from about 5% to about 45% by weight of a mineral oil having a viscosity between about 1500 and about 3500 SUS at 100° F., said oil containing less than about 10% aromatic hydrocarbons and having a viscosity index greater than about 85 and an aniline point higher than about 115° C., the lubricating base being thickened to a grease consistency by a sodium soap of beeswax acids, said grease containing a minor proportion of sodium benzoate and of wool fat alcohols.

5. A lubricating grease composition comprising as the lubricating base thereof a mixture of from 55% to about 95% by weight of a synthetic high boiling polyhydrocarbylsiloxane having a viscosity within the lubricating oil viscosity range and from about 5% to about 45% by weight of a mineral oil having a viscosity of between about 1250 and 11,000 SUS at 100° F., said lubricating oil containing less than about 15% by weight of aromatic hydrocarbons, the lubricating base being thickened to a grease consistency by a sodium soap of an organic carboxylic acid having at least 20 carbon atoms per molecule and containing minor proportions of an alkali metal salt

of an organic carboxylic acid containing an aromatic ring and an alcohol having at least 12 carbon atoms per molecule.

6. A lubricating grease composition comprising as the lubricating base thereof a mixture of from about 55% to about 95% by weight of a synthetic high boiling dialkyl silicone polymer having a viscosity within the lubricating oil viscosity range and from about 5% to about 45% by weight of a mineral oil having a viscosity of between about 1250 and 11,000 SUS at 100° F., said oil containing less than about 10% by weight of aromatic hydrocarbons and having a viscosity index greater than about 60, the lubricating base being thickened to a grease consistency by a sodium soap of an aliphatic carboxylic acid having at least 20 carbon atoms per molecule and containing a minor proportion of a sodium salt of an organic carboxylic acid containing an aromatic ring.

7. A lubricating grease composition comprising as the lubricating base thereof a mixture of from 55% to about 95% by weight of a liquid high boiling dimethyl silicone polymer having a viscosity within the lubricating oil viscosity range and from about 5% to about 45% by weight of a mineral oil having a viscosity of between about 1250 and about 11,000 SUS at 100° F., said oil containing less than about 10% by weight of aromatic hydrocarbons and having a viscosity index greater than 60 and an aniline point above about 100° C., the lubricating base being thickened by sodium soaps of beeswax acids, the grease containing a minor proportion of sodium benzoate.

8. A lubricating grease composition comprising as the lubricating base thereof a mixture of from 55% to about 95% by weight of a high boiling liquid dimethyl silicone polymer having a viscosity within the lubricating oil viscosity range and from about 5% to about 45% of a mineral oil having a viscosity of between about 1500 and about 3500 SUS at 100° F., said oil containing less than about 10% by weight of aromatic hydrocarbons and having a viscosity index greater than about 85 and an aniline point above about 115° C., the lubricating base being thickened to a grease consistency by sodium soaps of degras, said grease also containing a minor proportion of a sodium salt of an organic carboxylic acid containing an aromatic ring.

9. A lubricating grease composition comprising as the lubricating base thereof a mixture of 55% by weight to about 95% by weight of a high boiling liquid dimethyl silicone polymer having a viscosity within the lubricating oil viscosity range and from about 5% to about 45% by weight of a mineral oil having a viscosity of between about 1500 and about 3500 SUS at 100° F., said oil containing less than about 10% aromatic and having a viscosity index greater than about 85 and an aniline point higher than about 115° C., the lubricating base being thickened to a grease consistency by a sodium soap of beeswax acids, said grease also containing minor proportions of sodium benzoate and cholestanol.

10. A lubricating grease composition comprising as the lubricating base thereof a mixture of from about 55% to about 95% by weight of a synthetic high boiling liquid dimethyl silicone polymer having a viscosity within the lubricating oil viscosity range and from about 5% to about 45% by weight of a mineral oil having a viscosity of between about 1250 and about 11,000 SUS at 100° F., said oil containing less than about 10% aromatic hydrocarbon and having a viscosity index greater than about 60, the lubricating base being thickened to a grease consistency by a mixture of sodium and potassium soaps of higher aliphatic monocarboxylic acids wherein the potassium soaps constitute less than about 5% by weight of the total soap content, said sodium soaps being soaps of acids containing at least 20 carbon atoms per molecule, said grease also containing minor proportions of an alkali metal salt of an organic carboxylic acid containing an aromatic ring and of at least one sterol.

11. A lubricating grease composition comprising as the lubricating base thereof a mixture of from about 55% to about 95% by weight of a synthetic high boiling liquid dimethyl silicone polymer having a viscosity within the lubricating oil viscosity range and from about 5% to about 45% by weight of a mineral oil having a viscosity of between about 1250 and about 11,000 SUS at 100° F., said oil containing less than about 10% aromatic hydrocarbon and having a viscosity index greater than about 60, the lubricating base being thickened to a grease consistency by a mixture of sodium and calcium soaps of higher aliphatic monocarboxylic acids wherein the calcium soaps constitute less than about 5% by weight of the total soap content, said sodium soaps being soaps of acids containing at least 20 carbon atoms per molecule, said grease also containing minor proportions of an alkali metal salt of an organic carboxylic acid containing an aromatic ring and of at least one sterol.

12. The process for the preparation of grease compositions which comprises heating a synthetic high boiling liquid dimethyl silicone polymer having a viscosity within the lubricating oil viscosity range and a mineral oil having a viscosity of between about 1250 and 11,000 SUS at 100° F., said oil containing less than about 10% aromatic hydrocarbons and having a viscosity index greater than about 60 together with beeswax and benzoic acid to a temperature between about 170 and 225° F., saponifying the beeswax and benzoic acid with a sodium alkali base at a temperature below 250° F., dehydrating the resulting mixture at temperatures between about 275° F. and about 325° F. for a period between about one-half and about four hours, cooling to a temperature of between about 175° F. and about 275° F., adding wool grease alcohols at a temperature within the latter range, heating the resulting composition to a temperature between about 400° F. and 475° F. for a period between about one-fourth and two hours and cooling the resulting grease composition, the silicone polymer and mineral oil mixture being present in the final grease compositions in proportions between about 55–95 parts by weight of the polymer and about 45–5 parts by weight of the mineral oil for each 100 parts by weight of the mixture.

13. The process for the preparation of grease compositions which comprises heating a synthetic high boiling liquid polyhydrocarbylsiloxane having a viscosity within the lubricating oil viscosity range and a mineral oil having a viscosity of between about 1250 and 11,000 SUS at 100° F., said oil containing less than about 15% aromatic hydrocarbons and having a viscosity index greater than about 60 together with a carboxylic acid having at least 20 carbon atoms per molecule and an organic carboxylic acid containing an aromatic ring to a temperature between about 170 and 225° F., saponifying the carboxylic acid and organic carboxylic acid with a sodium alkali

base at a temperature below about 250° F., dehydrating the resulting mixture at temperatures between about 275° F. and about 325° F. for a period between about one-half and about four hours, cooling to a temperature of between about 175° F. and about 275° F., adding wool grease alcohols at a temperature within the latter range, heating the resulting composition to a temperature between about 400° F. and 475° F. for a period between about one-fourth and two hours and cooling the resulting grease composition, the silicone polymer and mineral oil mixture being present in the final grease compositions in proportions between about 55–95 parts by weight of the polymer and about 45–5 parts by weight of the mineral oil for each 100 parts by weight of the mixture.

14. A lubricating grease composition comprising as the lubricating base thereof a mixture of from 55% to about 95% by weight of a synthetic high boiling liquid polyhydrocarbylsiloxane having a viscosity within the lubricating oil viscosity range and from about 5% to about 45% by weight of a mineral oil having a viscosity of between about 1250 and about 11,000 SUS at 100° F.; said mineral oil containing less than about 15% by weight of aromatic hydrocarbons, the lubricating base being thickened to a grease consistency by a sodium soap of a carboxylic acid having at least 20 carbon atoms per molecule, said grease containing a minor proportion of an alkaline earth metal salt of an organic carboxylic acid containing an aromatic ring.

15. A lubricating grease composition comprising as the lubricating base thereof a mixture of from 55% to about 95% by weight of a synthetic high boiling liquid polyhydrocarbylsiloxane having a viscosity within the lubricating oil viscosity range and from about 5% to about 45% by weight of a mineral oil having a viscosity of between about 1250 and about 11,000 SUS at 100° F.; said mineral oil containing less than about 15% by weight of aromatic hydrocarbons, the lubricating base being thickened to a grease consistency by a sodium soap of a carboxylic acid having at least 20 carbon atoms per molecule, said grease containing a minor proportion of an alkali metal salt of an organic monocyclic aromatic carboxylic acid wherein the carboxyl radical is directly attached to a carbon atom of the aromatic ring.

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