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STABILIZED GREASE COMPOSITION CONTAINING A STEROL AND A SELENIUM COMPOUND

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The present invention relates to improvements in grease compositions and more particularly in grease compositions containing a special combination of additive compounds.

Greases comprise a lubricating base gelled to a grease consistency with a gelling agent which may be either an organic material, such as a soap, or an inorganic substance, such as an onium clay, or a colloidal amorphous inorganic oxide or hydroxide, and the like. The presence of the gelling agent complicates research in the determination of the causes of lubrication failure relative to the effect of oxidative breakdown and mechanical influences. Greases have been prepared containing selenium compounds as oxidation inhibitors. However, as the data given hereinafter indicate, the presence of these selenium compounds does not effect satisfactory stabilization of the present compositions.

While many additives are useful at ordinary operation temperatures, certain greases must be stabilized against deterioration and breakdown at temperatures approaching 400-500° F. This is due to the development of machinery containing bearings subject to high temperatures such as in turbo jet engines and in turboprop motors. High temperature greases may be prepared by the gelling of high boiling lubricants with especially favored materials such as the sodium soaps of high molecular weight acids, particularly those having at least 20 carbon atoms. These include the sodium soaps of beeswax acids and of degreas as well as inorganic colloids. Certain materials promote the mechanical stability of such greases at high temperatures such as the salts of aromatic acids of which sodium benzoate is a typical example. In spite of the improved performance of such greases at elevated temperatures over ordinary grease compositions, they have not heretofore had satisfactory life as evidenced by the relatively short bearing tests.

It is an object of the present invention to provide improved lubricating greases. It is another object of the present invention to provide greases exhibiting substantially extended bearing life. It is a particular object of this invention to provide greases useful for high temperature operation and which are not subject to mechanical breakdown over extended periods. Other objects will become apparent during the following discussion.

Now in accordance with the present invention it has been found that greases may be stabilized to an unexpected extent by the synergistic cooperation of minor amounts of polycyclic alco-

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hols and of aliphatic selenium or tellurium compounds as defined hereinafter.

A specific improvement according to the present invention comprises the discovery that high temperature greases comprising a mixture of aliphatic diesters and high boiling petroleum lubricants gelled with sodium soaps of aliphatic acids having at least 20 carbon atoms and containing metallic salts of aromatic acids respond particularly well to the presence of between about 0.25% and about 5% each of wool grease alcohols and dilauryl selenide.

POLYCYCLIC ALCOHOLS

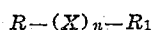
The polycyclic alcohols useful for promoting the stability of the present greases are typified by the sterols. Preferably they are obtained from natural sources and therefore constitute mixtures of alcohols but synthetic materials may be employed if necessary. The following species are typical of the materials which may be employed although natural sources, such as wool fat, are preferred.

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

While amounts of polycyclic alcohols may vary widely with the specific composition contemplated, they will generally be less than about 5% by weight of the total composition but an effective proportion usually greater than about 0.25%. Optimum results are obtained when the alcohols are present in amounts between about 1% and about 4% by weight of the grease.

SELENIUM AND TELLURIUM COMPOUNDS

The selenium and tellurium compounds added for their synergistic stabilizing effect have the general configuration:



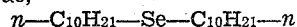
wherein R is an aliphatic radical, R₁ is a substituent of the group consisting of hydrogen atoms and aliphatic radicals, X is an element of the group consisting of selenium and tellurium and n has a value of 1 or 2, said compound containing at least 8 carbon atoms per molecule. Preferably the constituents R and R₁ are aliphatic hydrocarbon radicals and the element X is selenium. The three principal groups of com-

pounds falling within the general formula, as defined above, include dialkyl selenides, dialkyl diselenides and alkyl selenomercaptans as well as the analogous tellurium compounds and substituted or unsaturated analogs of the same. The following description of specific materials meeting the above requirements defines the classes contemplated:

Monoselenides (R_1-Se-R_2)

Normal (straight chain) monoselenides

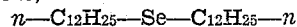
Didecyl selenide,



Dicetyl selenide,

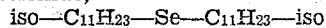


Dilauryl selenide,

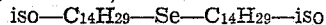


Iso (branched chain) monoselenides

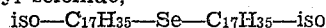
Diundecyl selenide,



Ditetradecyl selenide,

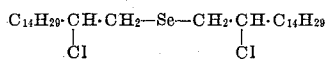


Diheptadecyl selenide,

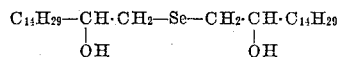


Polar substituted monoselenides

Bis (beta-chlorocetyl) selenide

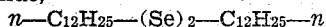


Bis (beta-hydroxy cetyl) selenide

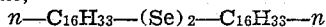


Diselenides

Dilauryl diselenide,

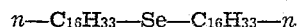


Dicetyl diselenide,



Monotellurides

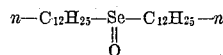
Dicetyl telluride,



Miscellaneous selenides

Diparaffin selenide—prepared by condensing chlorinated paraffin wax with Na_2Se . Most probably a mixture of compounds corresponding to the formula $R-Se-R$, where R is a higher alkyl radical.

Dilauryl selenoxide



As stated, dialkyl selenides and dialkyl tellurides preferably containing at least 8 carbon atoms in an alkyl group, may be employed in accordance with the invention. The alkyl groups R and R_1 may be not only straight and branched chain saturated alkyl groups C_nH_{2n+1} , but also straight and branched chain unsaturated aliphatic groups C_nH_{2n-1} , C_nH_{2n-3} , etc., and also cycloalkyl or cycloaliphatic groups. That is, the groups attached to selenium and tellurium in the compounding agents of the present invention, may be saturated, unsaturated or cyclic aliphatic groups. Also, the groups R and R_1 may be substituted by aromatic groups, such as the phenyl, hydroxy phenyl and amino phenyl groups, provided such groups are spaced at least one carbon atom from the group (X_n). Polar groups, such as chlorine, bromine, hydroxyl, ether, keto, amino, free carboxyl, metallo carboxyl, carboxy ester, mercapto, mercaptide, mono-, di- and polysulfide, etc., may be substituted in the groups R and R_1 of the selenides and tellurides of the present invention. Two or more selenide or tel-

luride groups (X)_n may be present in the molecule.

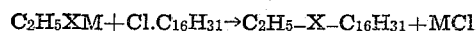
The following specific examples of selenides and tellurides, together with those specifically mentioned hereinabove, will illustrate the selenium and tellurium compounds of the present invention: decyl methyl monoselenide, cetyl ethyl monoselenide, octyl decyl monoselenide, dieicosyl monoselenide; dioctyl diselenide, didecyl diselenide, diheptadecyl diselenide, dieicosyl diselenide; decyl methyl monotelluride, cetyl ethyl monotelluride, octyl decyl monotelluride, didecyl monotelluride, diundecyl monotelluride, dilauryl monotelluride, ditetradecyl monotelluride, dicetyl monotelluride, diheptadecyl monotelluride, dieicosyl monotelluride; dioctyl ditelluride, didecyl ditelluride, dilauryl ditelluride, dicetyl ditelluride; and the various mono- and poly-selenides and mono- and poly-tellurides prepared by reacting sodium or other alkali metal mono- or poly-selenides or mono- or poly-tellurides with halogenated, e. g., chlorinated hydrocarbons, such as decyl chloride, dodecyl chloride, tetradecyl chloride, cetyl chloride, heptadecyl chloride, eicosyl chloride, chlorinated lubricating oil and chlorinated wax.

The selenides are preferred to the tellurides, because they are more stable and more easily prepared. However, the tellurides are highly effective as oil stabilizers and may be preferred in certain cases. Mixtures of selenides or tellurides are suitable, such as those prepared by condensing a metal selenide, polyselenide, telluride or polytelluride with a chlorinated or brominated mixture of hydrocarbons, for example, chlorinated or brominated lubricating oil or paraffin wax. It is not essential that all of the halogen be removed in the condensation reaction; thus a chlorine-containing dialkyl selenide or telluride or mixture of dialkyl selenides or tellurides may be used. Also, a mixture of selenides and tellurides may be used.

Suitable methods of preparing the dialkyl selenides and tellurides of the invention are as follows:

(1) From aliphatic halides and a metal selenide, telluride, polyselenide or polytelluride, by condensation in an inert solvent such as ethyl alcohol. This method is particularly suitable for the preparation of pure, simple selenides and tellurides such as dicetyl selenide and dicetyl telluride, and for the preparation of mixtures of selenides and/or tellurides, as from chlorinated wax.

(2) From the seleno and telluro analogues of the mercaptans; that is, from compounds of the type $RSeH$ and $RTeH$, where R is an aliphatic group. The compound $RSeH$ or $RTeH$, which may be termed a "seleno mercaptan" or a "telluro mercaptan," is converted to a metal "seleno mercaptide" or metal "telluro mercaptide," which is then condensed with a halogenated hydrocarbon, such as cetyl chloride, or a halogenated mixture of hydrocarbons, such as chlorinated wax, in the same manner as the halogenated hydrocarbons are condensed with metal selenides or tellurides. This method is especially suited to the preparation of mixed selenides or tellurides, such as cetyl ethyl selenide and cetyl ethyl telluride; for example, as follows:



where $X=Se$ or Te and M is a metal such as an alkali metal.

(3) Diselenides such as dilauryl diselenide can

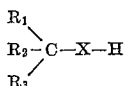
be readily and economically prepared by the following series of reactions:

- (a) $\text{MCN} + \text{Se} \rightarrow \text{MSeCN}$
 (b) $\text{RX} + \text{MSeCN} \rightarrow \text{RSeCN} + \text{MX}$
 (c) $2\text{RSeCN} \rightarrow \text{R}-\text{Se}_2-\text{R} + (\text{CN})_2$

In the above equations, M represents an alkali metal, preferably potassium; R represents an aliphatic group; and X represents a replaceable negative atom or radical, preferably chlorine. In carrying out this process, reaction (a) may be carried out in aqueous solution, reaction (b) may be carried out in ethyl alcohol, and reaction (c) is carried out by reacting the alkyl selenocyanate with caustic alkali in aqueous alcohol. This method does not yield as desirable a product, from the standpoint of lubricant additives, with chlorinated wax as it yields with some of the lower, purer alkyl chlorides, such as lauryl chloride and cetyl chloride.

(4) Selenium is dissolved in strong aqueous or alcoholic caustic soda or caustic potash solution to yield a mixture (in solution) of alkali metal selenides, polyselenides and selenites, possibly also other selenium compounds. It has been found that when this mixture is heated with a halogenated hydrocarbon or mixture of hydrocarbons, such as lauryl chloride or chlorinated wax, the product, comprising a complex mixture of selenides and probably including mono- and diselenides, perhaps also higher polyselenides, is an excellent lubricant additive.

In addition to the mono- and diselenides and their tellurium analogs, seleno- or telluromercaptans are also effective. These selenium compounds are the aliphatic selenomercaptans. Tellurium may be substituted for selenium, although the selenium compounds are preferred. These compounds may be represented by the formula:



wherein R_1 , R_2 and R_3 are hydrogen or organic radicals (any two of which may be joined to form a single, bivalent radical), C is an aliphatic carbon atom (i. e., a carbon atom other than a carbon atom forming part of a benzenoid ring), and X is selenium or tellurium.

The preferred compounds of the invention are those containing 8 to 30 carbon atoms, most advantageous 10 to 30 carbon atoms in the molecule. As stated, the selenium compounds are preferred to the tellurium compounds.

Examples of selenium and tellurium compounds of the invention are 2-ethylhexyl, decyl, lauryl, cetyl, octadecyl, and "paraffin" selenomercaptans and 2-ethylhexyl, lauryl and octadecyl telluromercaptans. Other radicals (e. g., other alkyl radicals such as undecyl and tetradecyl, aralkyl radicals such as cetylbenzyl and cycloaliphatic radicals such as ethylcyclohexyl and butyl cyclohexyl), may be used in place of the above mentioned radicals, and the organic radical attached to selenium may contain an unsaturated group or may be substituted by a non-hydrocarbon substituent such as chlorine, hydroxyl, alkoxy, amino, etc.

By "paraffin" as used herein to designate an organic radical is meant a radical derived from paraffin wax; e. g., paraffin selenomercaptan is a selenomercaptan (actually, a mixing of selenomercaptan), such as can be prepared by using

chlorinated paraffin wax as the organic chloride, R.Cl , in Equation 2 below.

By "aliphatic" as used herein without qualification to designate an organic radical attached to selenium or tellurium, is meant an organic radical whose attachment to selenium or tellurium is through a non-benzenoid carbon atom; e. g., octadecyl, benzyl and cyclohexyl selenomercaptans are all "aliphatic" selenomercaptans as "aliphatic" is herein defined.

The selenomercaptans can be prepared by the following series of reactions:

- (1) $\text{Na}_2\text{Se} + \text{Se} \rightarrow \text{Na}_2\text{Se}_2$
 (2) $\text{Na}_2\text{Se}_2 + 2\text{R.Cl} \rightarrow \text{R.SeSe.R} + 2\text{NaCl}$
 (3) $\text{R.SeSe.R} + 2\text{H} \rightarrow 2\text{R.SeH}$

Sodium diselenide is prepared by reaction 1 and is reacted with an aliphatic chloride (RCl) in accordance with reaction (2) to yield an aliphatic diselenide (R.SeSeR). The aliphatic diselenide is reduced in accordance with reaction 3 to yield an aliphatic selenomercaptan.

In reactions 1, 2 and 3, potassium or other metal may be substituted for sodium, tellurium may be used instead of selenium and bromine or other replaceable element or radical may be substituted for chlorine. The group R is an aliphatic group. If a mixed diselenide is available, e. g., octyl cetyl diselenide



it may be substituted for the symmetrical diselenide of reaction 3, yielding a mixture of selenomercaptans (e. g., octyl and cetyl selenomercaptans).

LUBRICATING BASE

The present invention contemplates the stabilization of greases generally, regardless of their specific lubricating base. As the data given hereinafter show, certain bases respond to the synergistic additives to a greater extent than others but a beneficial effect has been found in a number of different media. While the stabilization of greases in general is therefore considered the following types of lubricating bases have been found to be particularly responsive.

Petroleum lubricants are valued not only because of their lubricating property but because of economic considerations as well. Moreover they are available in a wide variety of boiling ranges. Since the present invention especially contemplates the production of high temperature greases, it is particularly desirable when petroleum lubricants are present that they have relatively high boiling points and viscosities. It has been found that an especially effective type of lubricating oil comprises one having viscosity of between about 1250 and 11,000 SUS at 100° F. In order to promote the stability of such mineral oils it is preferred that they contain less than about 15% by weight of aromatic hydrocarbons.

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 stocks," and particularly 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 are usually subjected to distillation under ordinary 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 steam distillation, usually under a vacuum. 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." The steam refined stock is then deasphalted (if an asphaltic crude is employed) and subjected to dewaxing operations to remove microcrystalline or macrocrystalline waxes. Following this, the raffinate is treated with a solvent for the purpose of reducing or removing the aromatic fractions. 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 reasphalting, dewaxing, extraction, and clay treatment is generally called "bright stock."

The bright stocks suitable for use in the present compositions should have the following ranges of properties:

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
V. I., >+60, preferably +85-110
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
Per cent aromatics, <15, preferably <10 optimum <5
Per cent naphthenes, <35
Per cent paraffines, at least 60

The tables which follow give the properties of typical bright stocks which are useful in the compositions of this invention.

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° F.	210° F.	VI	Ar, per cent	N, per cent	P, per cent			
Mid-Continent Bright Stock:									
Conventional Extraction	3,650	164	77	13	17	70	4.1	685	3.7
Mild Extraction	2,569	141	85	9	19	72	3.8	685	3.4
Heavy Extraction	2,049	131	93	3	21	76	3.62	675	2.9
Pennsylvania Bright Stock	2,109	144	102	5	16	79	4.95	730	3.0
Coastal Bright Stock	1,251	85	63	4	35	61	1.74	515	3.4

¹ Ar=aromatics, N=naphthenes, P=paraffins.

Table III

SPECIFICATIONS FOR TYPICAL MID-CONTINENT BRIGHT STOCKS

	Unfiltered	Filtered
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
SUS °F, 210	200-215	150-160
VI, min.	90	90

It will be understood from the above analyses that the source of 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 of treatment of such oil.

The most important inherent properties of a mineral oil suitable for the present use comprise the volatility, oxidation stability, aromatic content and viscosity characteristics. The aromatic content has a large influence upon the sensitivity of the oil to thermal changes and the viscosity of the oils defines their suitability for their present purpose. Hence, the best definition with respect to essential characteristics of mineral oil suitable for the present compositions comprising those 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, aniline point, and viscosity index usually are largely dependent upon them.

While mineral oils, such as those described above, may be used as the sole lubricating base, it has been found that certain advantages are gained by combining it with synthetic lubricants such as aliphatic diesters or polyorganosiloxanes.

The term "polyorganosiloxane" as used herein embraces those organic polymers having 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 (U. S. Patent No. 2,352,974—Rochow) and cyclic (U. S. Patent No. 2,371,050—Hyde) in structure. For purposes of the present invention, only those polymers which are high boiling liquids within the lubricating oil

viscosity range are suitable, these generally possessing a viscosity of 100° F. within the range of about 10-600 centistokes. These polyorganosiloxane liquids within this viscosity range are generally colorless, odorless and relatively inert, have very low volatility, such that vapor pressure within the lubricating temperature range is substantially negligible, and high viscosity index which means that they undergo relatively little change in viscosity for a given change in temperature.

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, it is contemplated that the silicone polymers produced from higher molecular weight alkyl groups, such as butyl, amyl and above, when economically available, will constitute valuable lubricant bases for purposes of the present invention. In general, these silicone polymers are adapted to specialized 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 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.

Aliphatic diesters are suitable lubricating components in the present greases. The aliphatic diesters to be used in place of, or in combination with, other lubricating bases described herein are preferably those formed by esterification of an aliphatic dicarboxylic acid and of an aliphatic monohydric alcohol having between 2 and 20 carbon atoms. While these are generally of the type described in U. S. Patent 2,481,372, the preferred classification includes especially the aliphatic esters of dicarboxyalkanes wherein said alkane contains between about 4 and 20 carbon atoms and preferably between 4 and 12 carbon atoms. Typical species meeting these requirements include especially the branched chain alkyl diesters such as di(1-ethylpropyl)oxalate, di(2-ethylhexyl)oxalate, di(2-ethylhexyl)sebacate, di(2-ethylhexyl)succinate, di(dodecyl)sebacate and other esters of aliphatic monohydric alcohols with acids such as malonic, succinic, glutaric, adipic, and sebacic acid.

When mineral lubricating oils are combined in the present compositions with synthetic materials such as the aliphatic diesters or the polyorganosiloxanes, the proportion may vary within wide limits. It has been found, however, that certain proportions exhibit optimum response to the particular combination of additives claimed and described herein. It is preferred, therefore, that the proportion of mineral oil to synthetic lubricant be within the limits from about 3:1 to about 1:3. More particularly the ratio should be confined to proportions between about 2:1 and 1:2 if the best results are desired.

In addition to the above types of materials, other lubricants may be used such as organic phosphates and silicates including tricresyl phosphate, trioctyl phosphate and tetraoctyl silicate. Certain other phosphorous additives are indicated such as the phosphonates and phosphinates. Typical species of these include: Bis(3,5,5-trimethylhexyl); 2,4,4-trimethyl pentane phosphonate; tris(3,5,5-trimethylhexyl)phosphate; 2-ethylhexyl bis(4-tetradecyl) phosphinate as well as diphosphorus compounds of which the following are typical: Bis-1,4-(secondary amyl pentane phosphino)butane; 1,6-hexane diol di(bis-butyl phosphate); 1,5-pentane diol di(butyl butane phosphate); bis-1,3-diisobutyl phosphono)pentane.

It will be understood that the lubricant or mixture of lubricants employed in these compositions constitute the major ingredient thereof. The precise amount which is present is not a critical feature of this invention since the stability of the compositions depends upon the presence of the two synergizing additives rather than upon the exact proportion of the lubricating ingredients.

GELLING AGENTS

As stated hereinbefore, the grease may be gelled to an appropriate consistency by the presence of organic or inorganic gelling agents. Usually these will comprise soaps of high molecular weight acids, preferably having at least 20 carbon atoms and being of an aliphatic character. Generally they are saturated or unsaturated aliphatic monocarboxylic acids preferably derived from natural sources such as from beeswax or degreas. The following list of acids is typical of those particularly effective for use in greases to be inserted in machinery operated at relatively high temperatures:

- Phthioic acid
- Tetracosenoic acids (e.g., selacholeic acid)
- Docosenoic acids (e.g., ereicic 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

While acids having more than about 20 carbon atoms are preferred for the special purpose of preparing high temperature greases other high temperature greases may be prepared by the use of inorganic gelling agents and particularly from amorphous colloidal gelling materials such as silica, magnesia, lime and mixtures thereof. The so-called "microgels" having surface areas of at least about 100 square meters per gram may be prepared according to known methods and may comprise mixtures of inorganic gelling agents with organic materials such as soaps or amines. When high temperature requirements are not paramount, soaps of lower molecular weights may be used such as the sodium, potassium or lithium soaps of fatty or hydroxy fatty acids including lithium 12-hydroxy stearate, sodium stearate, calcium oleate and the like. Other metallic soaps include those of amphoteric metals or heavy metals such as copper, aluminum, magnesium, calcium, iron and similar materials

known for their soap-forming properties. Preferably the soaps or other gelling agents are present in amounts between about 2% and 25% by weight of the total grease composition. Usually they are present in amounts between about 5% and 15%.

OTHER INGREDIENTS

In addition to the essential components of the greases, as given in detail hereinbefore, other optional ingredients may be present. One of the most important of these comprises the salts of organic carboxylic acids containing an aromatic ring. The presence of such salts has been found to unaccountably increase the dropping point of greases and, hence, to promote optimum properties in greases for use at high temperatures. The alkali metal salts are especially preferred such as the sodium potassium or lithium salts of benzoic acid or alkyl benzoic acids including phenyl acetic or toluic acids. Similar results are obtained by the use of metallic salts of hydrocinnamic acid, as well as from the sodium salt of aromatic poly basic acid such as sodium phthalate. Such salts are preferably present in amounts between about 0.2% and 5% based on the weight of the total grease.

In order to promote the maximum stability against oxidation, aromatic amines are also employed such as phenyl - alpha - naphthylamine, phenyl-beta-naphthylamine and phenylene diamine. Useful additives for the improvement in corrosion characteristics include especially the reaction products of a phosphorous sulfide and a terpene such as the reaction product of phosphorus pentasulfide and turpentine. Moreover, the metallic salts of substituted thiocarbamic acids also may be included such as the zinc, calcium or magnesium salts of alkyl thiocarbamic acids including zinc dibutyl dithiocarbamate, calcium ethylhexyl dithiocarbamate, magnesium dioctyl dithiocarbamate and the like. These additives should be employed in minor amounts, preferably less than 5% of the total amount of the grease, but at least in amounts of about 0.25%.

In addition to the above materials the compositions may contain thickeners and viscosity index improvers such as the polymeric acids of the acrylic acid series or polymeric olefins having molecular weights greater than about 1,000. Typical species of these substances include the lower alkyl esters (ethyl through octyl) of polymethacrylic acids having molecular weights between about 5,000 and 25,000 and polybutene or polyisobutene having molecular weights of between about 8,000 and 20,000.

The following examples illustrate the advantages to be gained by the use of compositions according to the present invention.

The greases to be described were prepared by the following process which is described as merely typical of a number of means for assembling the constituents into a grease composition. Part of the lubricating base was heated to a temperature of about 195° F. at which temperature beeswax was added and stirred until melted in the lubricant. While heating to a temperature of about 230° F., concentrated sodium hydroxide solution was added with stirring. Water was eliminated by continued heating up to a temperature of about 300° F. at which point the soap and oil were held for a period of about one hour. The blend was then cooled to a temperature of about 195° F., at which point wool grease alcohols or their equivalent were added together with about 1% by weight of water based on the total

grease. Thereafter the mixture was reheated to a temperature of about 450° F. for a period of about thirty minutes. The temperature was then reduced by the addition of the balance of the oil and, if necessary, by the use of external cooling. At a temperature of approximately 160° F. the remainder of the additives, as specified in the following examples, was added and the greases homogenized to obtain smooth products.

It will be appreciated by experts in the art that the steps involved in the above process may be amended to suit the particular composition being prepared. If the actual steps enumerated are employed the temperatures may be varied approximately 50°, suitable to cause either solution of the desired product in the oil or saponification of the particular acid utilized. Moreover the period of heating or cooling and the period of holding at that particular temperature may be varied without departing from the spirit of the present invention. Table IV, given below, illustrates the effect of preparing greases having both dilauryl selenide and wool grease alcohols upon the operating life of the resulting greases. These greases contained a major proportion of equal quantities of a petroleum oil bright stock and of an aliphatic diester wherein the alcoholic radicals contained from 6 to 10 carbon atoms in branched configuration and the acid residue from 6 to 10 carbon atoms. The grease contained approximately 11% of sodium soaps of beeswax acids and about 3% by weight of sodium benzoate. The presence or absence of either dilauryl selenide or of wool grease alcohols is indicated by the table. The Navy test referred to in the specification which follows is described in the Federal Stock Catalogue VV-L-791d, issued November 15, 1948, Method 33.1.

Table IV

Sample	Dilauryl Selenide, Percent	Wool Grease Alcohols, Percent	Navy Test 300° F., 10,000' R. P. M. Hours to Failure
A.....	1	3	>1,700
B.....	0	3	530
C.....	1	0	526

¹ Test discontinued, not failed.

As the data given in Table IV showed, the presence alone of either dilauryl selenide or of wool grease alcohols resulted in a test life to failure of approximately 500 hours. However, when both of these additives were present (sample A) the test life of the resulting grease was greater than 1700 hours, at which point the test was discontinued before failure. This is clear evidence of synergism occurring between these two classes of additives.

The effect of having both of these additives present varies with the specific lubricating base employed. This is demonstrated by the data given in Table V which follows:

Table V

[Dilauryl selenide and wool grease alcohols present]

Sample	Ratio, Petroleum Oil Bright Stock-Aliphatic Diester	300° F., 10,000 R. P. M. Navy Test, Hours to Failure
C.....	1:1	>1,700
D.....	3:1	450
F.....	1:0	280

In the above table it will be found that the greatest response was shown by a lubricating base comprised of equal proportions of a petroleum oil bright stock and of an aliphatic diester. When the proportion of bright stock was increased, the test life of the resulting grease was substantially reduced. In the absence of any aliphatic diester, a still further reduction in the life of the grease occurred.

Table VI illustrates the effect of operating the grease at high temperatures when employing lubricating bases composed entirely, or in part, of a polyorganosiloxane, namely, a dimethyl silicone fluid.

Table VI

Sample	Ratio, Bright Stock-Silicone	Dilauryl Selenide, Percent	Wool Grease Alcohols, Percent	ABEC Test 400° F., 10,000 R.P.M. Hours to Failure
G.....	0:1	1	0	170
H.....	0:1	1	3	238
I.....	0:1	0	3	20
J.....	3:17	1	0	176
K.....	3:17	0	3	100
L.....	3:17	1	3	277

While the above examples illustrate the synergistic effect obtained by the presence of the two required additives, the following examples illustrate other embodiments of this invention:

Example I

Lithium stearate.....	18.0
Mineral oil.....	78.0
Dicetyl diselenide.....	0.5
Cholestanol.....	3.5

Example II

Lithium 12-hydroxy stearate.....	12.5
Poly(propylene oxide) mol. wt. 1250.....	84.2
Ethyl octadecyl selenide.....	0.8
Cholesterol.....	2.5

Example III

Barium stearate.....	15.0
Bis(2-ethylhexyl)sebacate.....	41.0
Bright stock mineral oil.....	41.0
Octadecyl selenomercaptan.....	1.0
Lanyl alcohol.....	2.0

Example IV

Sodium soap of degrass.....	12.0
Diethyl benzene phosphonate.....	30.0
Mineral oil.....	51.0
Didecyl selenide.....	1.5
Allocholesterol.....	3.0
Sodium cinnamate.....	2.5

Example V

Sodium soaps of beeswax acids.....	10.0
Bright stock.....	33.75
Bis(diisononyl)sebacate.....	50.0
Wool grease alcohols.....	1.5
Dilauryl selenide.....	0.25
Zinc dibutyl dithiocarbamate.....	1.5
Sodium benzoate.....	3.0

Example VI

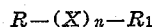
Sodium soaps of beeswax acids.....	10.0
Bis(didecyl)sebacate.....	41.5
Bright stock.....	40.0
Wool grease alcohols.....	3.0
Ditetradecyl selenide.....	1.0
Sodium benzoate.....	3.0
Zinc dibutyl dithiocarbamate.....	0.5
Reaction product of turpentine and P ₂ S ₅	1.0

Example VII

Sodium soaps of beeswax acids.....	10.0
Bis(dodecyl)sebacate.....	40.5
Bright stock.....	40.0
Wool grease alcohols.....	3.0
Didecyl selenide.....	1.0
Sodium benzoate.....	3.0
Zinc dibutyl dithiocarbamate.....	0.5
Reaction product of turpentine and P ₂ S ₅	1.0
Phenyl-alpha-naphthylamine.....	1.0

We claim as our invention:

1. A grease composition comprising a major proportion of a lubricating oil, a grease-forming proportion of a gelling agent, and minor amounts, but sufficient to increase the operating life of said grease, of a sterol and of a compound of the type



2. wherein R is an aliphatic radical, R₁ is a substituent of the group consisting of hydrogen atoms and aliphatic radicals, X is an element of the group consisting of selenium and tellurium, and n is a full integer less than 3, said compound containing at least 8 carbon atoms per molecule.

3. A grease composition comprising a major proportion of a lubricating oil, a grease-forming proportion of a metallic soap, and minor amounts less than about 5%, by weight, each but sufficient to increase the operating life of said grease of a sterol and of a dialkyl monoselenide containing at least 8 carbon atoms per molecule.

4. A grease composition comprising a major proportion of a mixture of an aliphatic diester and of a petroleum lubricating oil having a viscosity between about 1250 and 11,000 SUS at 100° F. and containing less than about 15% by weight of aromatic hydrocarbons, between about 2% and 25% by weight of a soap of an aliphatic monocarboxylic acid, and minor amounts less than about 5% by weight each but sufficient to increase the operating life of said grease of a sterol and of a dialkyl monoselenide containing at least 8 carbon atoms per molecule.

5. A grease composition comprising a major proportion of a mixture of an aliphatic diester and of a petroleum lubricating oil having a viscosity between about 1250 and 11,000 SUS at 100° F., between about 2 and 25% by weight of a sodium soap of an aliphatic monocarboxylic acid having at least 20 carbon atoms per molecule, and minor amounts less than about 5% by weight each but sufficient to increase the operating life of said grease of a sterol and of a dialkyl monoselenide containing at least 8 carbon atoms per molecule.

6. A grease composition comprising a major proportion of a mixture of an aliphatic diester and of a petroleum lubricating oil having a viscosity between about 1250 and 11,000 SUS at 100° F., between about 2% and about 25% by weight of a sodium soap of at least 1 aliphatic monocarboxylic acid having at least 20 carbon atoms per molecule and minor amounts less than about 5% by weight each but sufficient to increase the operating life of said grease of wool grease alcohols and of a dialkyl monoselenide containing at least 8 carbon atoms per molecule.

7. A grease composition comprising a major proportion of a mixture of an aliphatic diester and of a petroleum lubricating oil having a viscosity between about 1500 and 3500 SUS at 100° F. and containing less than about 10% by weight of aromatic hydrocarbons, between about 2% and about 25% by weight of sodium soaps of bees-

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wax acids and minor amounts less than about 5% by weight each but sufficient to increase the operating life of said grease of wool grease alcohols and dilauryl selenide.

7. A grease composition comprising a major proportion of a lubricating oil comprising a mixture of an aliphatic diester and a petroleum lubricating oil having a viscosity between about 1500 and about 3500 SUS at 100° F. and containing less than about 10% by weight of aromatic hydrocarbons, between about 2% and about 25% by weight of sodium soaps of beeswax acids and minor amounts less than about 5% by weight each but sufficient to increase the operating life of said grease of cholesterol, dilauryl selenide, and sodium benzoate.

8. A grease composition comprising a major proportion of a lubricating oil, grease-forming proportions of a metallic soap of a higher aliphatic acid and minor amounts less than about 5% each but sufficient to increase the operating life of said grease of a sterol and of a dialkyl diselenide containing at least 8 carbon atoms per molecule.

9. A grease composition comprising a major

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proportion of a lubricating oil, grease-forming proportions of a metallic soap of a higher aliphatic acid and minor amounts less than about 5% each but sufficient to increase the operating life of said grease of a sterol and of an alkyl selenomercaptan.

10. A grease composition comprising a major proportion of a mixture of lubricating oils comprising a polyorganosiloxane and a petroleum lubricating oil having a viscosity between about 1250 and 11,000 SUS at 100° F., between about 2% and about 25% by weight of sodium soaps of degrass acids and minor amounts less than about 5% by weight each but sufficient to increase the operating life of said grease of octadecyl selenomercaptan, cholesterol and a metallic salt of an aromatic acid.

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