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GREASE COMPOSITION

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This invention relates to improved lubricating grease compositions. More particularly, this invention pertains to improved grease compositions which are capable of resisting oxidation under both static and dynamic conditions, bleeding, age-hardening and possess outstanding mechanical stability and are thermally reversible.

It is well established that oxidation has a profound deteriorating effect upon lubricants and lubricating compositions. The rapidity of this deterioration varies with different lubricants and depends in part upon the source of the base oil, the presence of additives therein as well as on the conditions to which the lubricant is exposed. Once oxidation has started in a lubricant, the deterioration caused thereby appears to be an autocatalytic phenomenon which results in further deterioration of the lubricant.

A general deficiency encountered in greases is their lack of resistance to shear as well as other types of mechanical forces which are generally exerted upon greases under various working conditions. Thus, in the lubrication of ball and roller bearings, greases are often subjected to temperatures in excess of 250° to 300° F., which temperatures accelerate oxidation, and coupled with high shearing stresses, the greases break down in structure and are incapable of adhering to the lubricating surfaces, resulting in bearing corrosion, wear and failure. It is essential of good greases, therefore, to resist shearing stresses and oxidation, particularly over wide temperature ranges.

The cause or causes of age-hardening of greases at present is not understood. It is believed to be caused by the soap fibers which in storage tend to form cross layers due to the presence of an active group associated with the soap micelles, and thereby increases the consistency of the grease. Such hardening is extremely undesirable for it introduces numerous lubricating difficulties such as in pumping equipment and the like.

Bleeding is another phenomenon which is frequently encountered in grease compositions. Bleeding is primarily due to the fact that the soaps present in grease compositions have a marked tendency to synerize, thereby causing a separation of the soap from the oil or synthetic base lubricant in which it is dispersed.

Generally, to inhibit bleeding and improve the texture of greases special precautionary measures are taken, such as employing slow or rapid means of cooling, or extensively working the grease in special homogenizers, e. g., the Cornell homogenizer and the like. Such procedures are usually time-consuming and add to the cost of

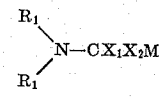
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the greases. Other ways of producing stable, non-bleeding greases have been attempted by either reducing the soap content generally to less than about 5% by weight or by increasing the soap content to a maximum. These methods of stabilizing greases against bleeding have also proved to be unsatisfactory because in the case of reducing the soap content to less than 5% such greases become limited in their use due to the low soap content, while increasing the soap content to a maximum makes the grease too clostly and such products generally possess an undesired consistency.

It is an object of this invention to produce grease compositions having outstanding mechanical stability under dynamic and static conditions. It is another object of this invention to produce greases having good thermal reversibility and which are capable of resisting shearing stresses over wide temperature ranges. Still another object of this invention is to produce nonbleeding greases. Still another object of this invention is to produce novel greases of this invention by conventional grease-making techniques either by batch or continuous processes. Furthermore, it is an object of this invention to produce a multi-purpose grease of outstanding lubricating properties.

These and other objects of this invention will be apparent from the following description and the appended claims.

Broadly stated, this invention comprises a lubricating grease composition containing in addition to the lubricating oil and gel-forming agent, a combination of two, and preferably three, particular types of additives in amounts much less than that of the gelling agent used to form the grease. The combination of additives produces a synergistic effect resulting in a grease composition possessing the properties enumerated above and exhibiting in particular outstanding and unexpected resistance to oxidation. The two additives present in combination are (1) a high molecular weight naphthyl amine and (2) a reaction product of a phosphorus sulfide with a dicyclic terpene. Still better results are obtained both from corrosion and oxidation standpoints if to this combination is also added a metallic salt of carbamic acid or its analogs, represented by the formula:



wherein R_1 and R_2 can be hydrogen and/or an

oil-solubilizing organic group such as normal or iso-alkyl, alicyclic, aryl, aralkyl, alkaryl and/or heterocyclic group; X_1 and X_2 may be oxygen or an element selected from the sulfur family (i. e., S, Se, Te) or mixtures thereof; and M is a metallic radical. The metallic portion of the molecule may be a mono- or polyvalent metal such as Na, K, Li, Ca, Ba, Sr, Mg, Zn, Al, Cu, Co, Sn, Ni and the like.

The reaction product

The primary oxidation inhibitors contemplated herein are phosphorus- and sulfur-containing reaction products obtained by reaction, at a temperature of above about 100° C., of a phosphorus sulfide and a dicyclic terpene or a material predominantly comprised of a dicyclic terpene.

All of the phosphorus sulfides, such as P_3S_5 (or PS_2), P_4S_6 (or P_2S_3), P_2S_5, P_4S_7, P_4S_{10}, etc., are contemplated as reactants in the preparation of primary oxidation inhibitors, but P_2S_5 is particularly preferred. As used herein, the designation "dicyclic terpene" refers to those terpenes which are characterized by the presence of one double bond in the molecule and are built up of two ring systems. Illustrative of such compounds are pinene, camphene and fenchene. Also contemplated as coming within this particular designation are those materials which are predominantly comprised of one or more dicyclic terpenes, representative of which materials are the essential or volatile oils, which are predominantly comprised of such a terpene or terpenes and are typified by turpentine oil, the major constituent of which is pinene. Particular preference is accorded to pinene and turpentine oil.

It is to be undertsood that the aforesaid designation, "dicyclic terpene," is not inclusive of such terpenes as those known in the art as monocyclic terpenes, which are typified by dipentene and terpinolene. It is also to be understood that the dicyclic terpenes should not be confused with the olefin hydrocarbon terpenes such as myrcene.

Although a complete understanding of the chemical composition of the reaction products of phosphorus sulfide and dicyclic terpenes has not been achieved at this time, a partial understanding of their composition may be obtained by noting the characteristics involved in the reaction. For example, the reaction of phosphorus pentasulfide and pinene commences at about 100° C. and is exothermic in nature. During the reaction, the reaction mixture increases appreciably in viscosity and little, if any, hydrogen sulfide is evolved therefrom. The reaction product obtained contains phosphorus and sulfur in substantially the same amounts as in the particular phosphorus sulfide reacted with the pinene. It would therefore appear that the reaction is one of addition; that is, addition of phosphorus sulfide to the one unsaturated bond present in pinene.

Although the reaction temperature for the reaction described above should be one of at least about 100° C., the preferred temperatures fall within the range of about 100° C. to about 160° C. or higher.

The proportions of reagents used in the preparation of the primary oxidation inhibitors may be varied in order to prepare reaction products having different degrees of oil-solubility. In this regard, it is preferred that about one mol of phosphorus sulfide be reacted with four mols of a dicyclic terpene in order to obtain a reaction product relatively soluble in petroleum oils. For example, when more than one mol of P_2S_5 is used with 3–5 mols of pinene, a viscous gel-like reaction product is obtained, and this product is definitely insoluble in petroleum oils. When less than one mol of P_2S_5 is used with 3–5 mols of pinene, a viscous oil also somewhat insoluble in mineral oil is obtained, after the unreacted pinene has been removed by distillation. Accordingly, it is to be understood that although effective primary oxidation inhibitors can be obtained by using different ratios of reactants, particularly preferred inhibitors are those obtained by using approximately one mol of a phosphorus sulfide for about 3.5 to 4.5 mols of a dicyclic terpene, while the most suitable ratio is 1 mol P_2S_5 to 4 mols terpene.

There is, however, still another desirable procedure for preparing the primary oxidation inhibitor. In order to obtain a relatively non-viscous reaction product, the dicyclic terpene, such as pinene, may be blended with a comparatively inert solvent, such as petroleum oil, and then treated as described above to yield an oil blend of the reaction product. The preferred procedure of this latter type involves the use of a 1:1 blend of dicyclic terpene and petroleum oil with the phosphorus sulfide, the molar ratio of said terpene to said sulfide being about 3:1 to 5:1.

When used in viscous mineral oil fractions in small amounts, the aforesaid primary oxidation inhibitors effect improvement of several of the oxidation characteristics thereof by preventing, for example, corrosion of hard metal bearings, by inhibition of acid formation, by inhibition of formation of gummy deposits in engines, by preventing increase in viscosity, etc.

The organic amines

The aromatic amines may be either monocyclic or polycyclic. The naphthyl amines include primary, secondary or tertiary alkyl, aryl or aralkyl amines such as phenyl-alpha-naphthyl amine, phenyl-beta-naphthylamine, tetraline naphthylamine, alpha,alpha-, alpha-beta-, or beta,beta-dinaphthylamines, benzyl phenyl naphthylamine and diphenyl naphthylamine.

The amount of both the amine or the terpene reaction product which can be added to grease compositions of this invention depends upon various factors, such as the lubricating base used to form the grease, the amount and type of soap or inorganic gelling agent and the like. Generally, the amines are used in amounts varying from .01% to 5% and preferably from .25% to 2%. The phosphorus sulfide-terpene reaction products are also to be used in like amounts. Depending upon the type of grease produced, the ratio of the two additives can vary over wide limits, preferably of from one part amine and five parts terpene reaction product to five parts amine and one part terpene reaction product.

The gelling agent

The gelling agent used to form the grease may be soaps of fatty acids and/or their glycerides. The saponifiable material may be fatty acids having from 12 to 32 carbon atoms and they may be saturated, unsaturated or polar substituted fatty acids, such as: capric, lauric, myristic, palmitic, stearic, arachidic, behenic, lignoceric, myristoleic acids, cottonseed oil fatty acid, palm oil fatty acids, linoleic, hydrogenated fish oil fatty acids, palmitolic, oleic, linoleic, ricinoleic, erucic acids and their mixtures and/or their glycerides, such as lard, beef, rapeseed, palm, menhaden, herring oils, etc. Other acids may be included among which are: acids produced by oxidation of petroleum oil and waxes, rosin acids, tall oil

acids, abietic acids, naphthenic acids, petroleum sulfonic acids and the like.

A particularly preferred class of saponifiable materials is the hydroxy fatty acids and their glycerides, such as: dimethyl hydroxy caprylic acid, dimethyl hydroxy capric acid, 12-hydroxy stearic acid, 9,10-dihydroxy-stearic acid, hydroxy palmitic acid, ricinoleic acid, ricinelaidic acid, dihydroxy behenic acid and the like. The preferred hydroxy fatty acids are those in which the hydroxy group is at least 12 carbon atoms removed from the carboxyl group. Also, it is preferable to use hydroxy fatty acids having at least 12 carbon atoms and up to about 32 carbon atoms and preferably those having between 14 and 32 carbon atoms in the molecule. Instead of using the free fatty acids containing a hydroxy radical, their glycerides can be used such as castor oil, or hydrogenated castor oil or mixtures of free hydroxy fatty acids and their glycerides can be used. Mixtures of hydroxy and non-hydroxy fatty acids can be used to form soap.

The saponifying agent used to make the soap may be any oxide or hydroxide of one or several of metals selected from groups I, II, III, VI, VII, and VIII. Specifically, the cation portion of the soaps may be Na, K, Li, Cs, Ca, Sr, Ba, Cd, Zn, Al, Pb and Co. Mixtures of soaps can be used, and the soap can be made in situ or premade soaps can be used to form the grease. Specific examples of preferred soaps or mixtures thereof are: lithium stearate, lithium 12-hydroxy stearate, lithium castorate, lithium soap of hydrogenated fish oil fatty acids, lithium soap of mixed stearic and hydroxy stearic acid, sodium stearate, sodium hydroxy stearate, sodium oleate, potassium oleate, potassium rosinate, calcium stearate, calcium hydroxy stearate, aluminum stearate, aluminum soap of fish oil fatty acids, barium hydroxy stearate, barium stearate, sodium soap of mixed stearic and hydroxy stearic acids, lithium soap of mixed oleic and hydroxy stearic acid, aluminum castorate, mixed soaps of lithium stearate and sodium stearate, mixed soaps of lithium hydroxy stearate and sodium stearate, mixed soaps of lithium hydroxy stearate and calcium stearate, etc.

In addition to greases gelled by the presence of soaps, greases thickened or gelled by the presence of inorganic colloids may be utilized as the base composition containing the combination of additives of the present invention. In particular, the inorganic colloidal materials useful for this purpose include the inorganic oxides and hydroxides of alkali metals, alkaline earth metals, silica, and combinations of the same. Silica greases, for example, may be prepared either by incorporating a silica aerogel in a suitable lubricant or by transferring an unshrunken gel from the medium in which it is originally formed either directly or indirectly into the lubricating medium. The latter process specifically contemplates the formation of a hydrogel such as silica hydrogel, addition of a hydrophobic surface-active agent, and incorporation of the compositions so formed with lubricating oil followed by elimination of water and homogenizing the grease so formed.

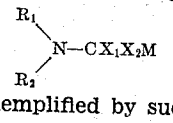
Another suitable method for the preparation of such greases comprises utilizing the ion-exchange capacity of naturally occurring or synthetic zeolites and swelling-type clays such as bentonite to form gelling agents bearing hydrophobic radicals. A specific instance of this comprises forming a hydrosol of hectorite (a magnesium bentonite), adding thereto a quaternary ammonium salt such as dimethyl dioctadecyl ammonium chloride to cause the formation of a hydrogel of the amino clay products; incorporating the hydrogel in mineral oil and eliminating water therefrom by distillation. Other suitable inorganic colloiding agents include especially, alumina, magnesia, lime, copper sulfide, and similar inorganic substances capable of colloid formation.

The content of gelling agent in grease compositions of this invention may vary over wide limits and may be as high as 50% by weight of the total grease. In practice, grease compositions containing soaps, normally comprise from 5% to 35% by weight of soap, while in the case of greases gelled with inorganic colloids the latter is normally present in amounts from about 2% to about 20% by weight.

Lubricating oil bases

The grease-forming lubricant bases used in preparing the greases of the present invention may vary widely in character and include mineral oil of wide viscosity, the range varying from about 150 SUS at 100° F. to about 2000 SUS at 100° F. The viscosity index of the oil can vary from below zero to about 100 and have an average molecular weight ranging from about 250 to about 600. It may be highly refined and solvent treated, if desired, by any known means. A preferred mineral oil is one which has a viscosity of 300 to 700 SUS at 100° F., or a viscosity of 65 to 100 SUS at 210° F. and a viscosity index of from 40 to 70 and an average molecular weight of 350 to 750. Instead of using straight mineral oil as the base, synthetic oils and lubricants may be substituted in part or wholly for the mineral oil. Among the synthetic lubricants which can be used are: polymerized olefins; copolymers of alkylene glycols and alkylene oxides; organic esters, e. g., 2-ethylhexyl sebacate dioctyl phthalate, trioctyl phosphate; polymeric tetrahydrofuran; polyalkyl silicone polymers, e. g., dimethyl silicone polymer, etc. Under some conditions of lubrication, minor amounts of a natural animal or vegetable oil such as castor oil, lard oil, etc., may be admixed with the hydrocarbon oil and/or synthetic oil used in making grease compositions of this invention.

In addition to the essential combination of ingredients described hereinbefore, a further improvement may be made in the grease compositions by the addition thereto of the metallic salts of carbamic acid or its analogs. This class of materials is represented by the general formula:



which can be exemplified by such specific compounds as:

Ca, Ba, Na, Zn, Cu, Ni, salts of dibutyl mono- and dithiocarbamic acid

Na, Ca, Zn, Cu, Ni, salts of diethyl mono- and dithiocarbamic acid

Na, Ca, Zn, Cu, Ni, Co salts of diamyl mono- and dithiocarbamic acid

Na, Ca, Zn, Cu, Ni, Co salts of dihexyl mono- and dithiocarbamic acid

Na, Ca, Zn salts of dioctyl mono- and dithiocarbamic acid

Ca, Zn, Cu, Ni salts of N-ethyl-N-phenyl mono- and dithiocarbamic acid

wherein R_1 and R_2 are hydrogen atoms or oil-

solubilizing organic radicals such as normal alkyl, isoalkyl, alicyclic, aryl, aralkyl, alkaryl and/or heterocyclic groups. X_1 and X_2 are oxygen, sulfur, selenium or tellurium; and M is a metallic radical.

Ba, Ca, Zn, Na salts of dicyclohexyl mono- and dithiocarbamic acid

Zn, Ca salts of monocetyl mono- and dithiocarbamic acid

Zn, Ca, Ni salts of di(cetyl phenyl) mono- and dithiocarbamic acid

Sr, Zn, Li salts of dibenzyl mono- and dithiocarbamic acid

Zn and Ni salts of di(amyl piperidyl) mono- and dithiocarbamic acid

Zn, Ca, Na salts of dihexyl mono- and diseleno carbamic acid

Zn salt of dicyclohexyl mono- and diselenocarbamic acid

Na, Zn, Ni, Cu salts of dibutyl carbamic acid

Na, Ca, Zn salts of dihexyl carbamic acid

Ca and Zn salts of dicyclohexyl carbamic acid

Co salts of monocetyl carbamic acid

Zn salts of dibenzyl carbamic acid.

The preferred class of the above materials comprises the metallic salts of dialkyl dithiocarbamic acid, and specifically the zinc salts of dialkyl dithiocarbamic acids, wherein the alkyl radicals each contain from about 2 to about 12 carbon atoms. These carbamates may be present in amounts from about .01% to 2% and preferably from .1% to 1% by weight based on the total composition.

Greases of this invention may be made by conventional or special methods and either by the batch or continuous process. In the case of lithium soap grease made by the conventional method, a calculated amount of lithium soap of between about 5 and 25% or higher is charged into a suitable grease kettle together with about half of the required amount of oil. The oil-soap mixture is heated to around about 350 to 450° F. under agitation until a homogeneous mass is obtained. The balance of the oil is then slowly added with stirring. Stirring is continued until a homogenous mass is formed at which point the grease is allowed to cool either in the grease kettle or in pans to the ambient temperature. The grease thus formed is generally lumpy and requires reworking by milling or homogenizing to produce a smooth and relatively stable grease. If soda soap or alkaline earth greases are made, they may be cooled slowly in the kettle, whereas if lithium or aluminum soap greases of this invention are made it is preferred that they be cooled uniformly and rapidly either in tubes of small diameter or in their layers by feeding the hot grease onto a steel belt and subjecting the grease to a current of air or other cooling medium so as to cool the grease in a uniform fashion, free from shearing stresses. The primary additives and, if desired, the secondary additives, can be added to the grease at any convenient time. A preferred time for adding the additives of this invention is while the grease is in a hot liquid state.

The following table illustrates specific grease compositions of this invention, each component of which may be used in the range indicated above in the general formulations.

Components	1	2	3	4	5	6	7	8	9	10	11	12	13
Soaps:													
Al ricinoleate	---	---	---	X	---	---	---	---	---	X	---	---	---
Li-12-hydroxy stearate	X	---	---	---	---	---	X	---	---	---	---	---	---
Li soaps of hydrogenated fish oil fatty acids	---	---	X	---	---	---	---	X	---	---	---	---	---
Sodium stearate	---	X	---	---	---	---	---	---	X	---	---	---	---
Ca stearate	---	---	---	---	---	X	---	---	---	---	---	---	---
Ba Stearate	---	---	---	---	X	---	---	---	---	---	---	---	---
Li stearate	---	---	---	---	---	---	---	---	---	---	X	X	X
Amines:													
Phenyl alpha-naphthylamine	X	---	---	X	---	---	X	---	---	X	X	X	X
Phenylenediamine	---	---	X	---	---	X	---	---	X	---	---	---	---
Phenyl beta-naphthylamine	---	X	---	---	X	---	---	X	---	---	---	---	---
Condensation Products:													
Pinene-P_2S_5	X	---	---	X	---	---	---	X	---	---	X	X	X
Turpentine-P_2S_5	---	---	X	---	X	---	X	---	---	---	---	---	---
Dipentene-P_2S_5	---	X	---	---	---	X	---	---	X	---	---	---	---
Carbamates:													
Zn dibutyl dithiocarbamate	---	---	---	---	---	---	X	---	---	X	X	---	X
Ca dihexyl dithiocarbamate	---	---	---	---	---	---	---	X	---	---	---	---	---
Zn dicyclohexyl dithiocarbamate	---	---	---	---	---	---	---	---	X	---	---	---	---
Lubricating Oils:													
Mineral oil	X	X	X	X	X	X	X	---	---	X	X	X	---
Di-(2-ethylhexyl) sebacate	---	---	---	---	---	---	---	X	X	---	---	---	X

Grease compositions of this invention were compared with greases in which one or more of the additive components was omitted by subjecting them to a modified Dornte oxidation test using an iron wire catalyst at 300° F. In this test 1% by weight of sodium stearate was dissolved in 99% by weight of mineral lubricating oil having a 400 SUS viscosity at 100° F. and a viscosity index of 55. This composition was tested both in the presence and absence of the additives described below using the Dornte oxidation test apparatus. The results were as follows:

Sample	Additive, percent wt.	Oxygen absorption (hrs.), 1,500 cc.
A	None	2.7
B	0.25% phenyl alphanaphthylamine	15.5
C	1.5% P_2S_5-turpentine reaction product	78.9
D	0.25% phenyl alpha napththylamine+0.5% Zn dibutyl dithiocarbamate.	62.7
E	0.25% phenyl alphanaphthylamine+1.5% P_2S_5-turpentine reaction product.	138
F	0.25% phenyl alphanaphthylamine+1.5% P_2S_5-turpentine reaction product+0.5% Zn dibutyl dithiocarbamate.	170

Minor amounts of secondary additives can be admixed with greases of this invention such as extreme pressure agents and can be added to such greases and the preferred comprise esters of phosphorus acids such as triaryl, alkylhydroxy, aryl, or aralkyl phosphates, thiophosphates, or phosphites, etc., neutral aromatic sulfur compounds such as diaryl sulfides and polysulfides, e. g., diphenyl sulfide, dicresol sulfide, dibenzyl sulfide, methyl butyl diphenyl sulfide, etc., diphenyl selenide and diselenide; dicresol selenide and polyselenide, etc., sulfurized fatty oils or esters of fatty acids and monohydric alcohols, e. g., sperm oil, jojoba oil, etc. in which the sulfur

is tightly bound; sulfurized long-chain olefins obtained by dehydrogenation or cracking of wax; sulfurized phosphorized fatty acids, oils, esters and ketones, phosphorus acid esters having sulfurized organic radicals, such as esters of phosphoric or phosphorus acids with hydroxy fatty acids; chlorinated hydrocarbons such as chlorinated paraffins, aromatic hydrocarbons, terpenes, mineral lubricating oils, etc., or chlorinated esters of fatty acids containing the chlorine in positions other than alpha position.

Additional ingredients which can be added are anti-wear agents such as oil-soluble salts of alkylphenol - aldehyde condensation products, e. g., Ca octyl phenol-formaldehyde condensation product Ca diwax phenol sulfide, urea or thiourea derivatives, e. g. urethanes, allophanates, carbazides, carbazones, etc.; or rubber, polyisobutylene, polyvinyl esters, esters of fatty acids, e. g., butyl stearate, etc., VI improvers such as polyisobutylene having a molecular weight above about 800, voltolized paraffin wax, unsaturated polymerized esters of fatty acids and monohydric alcohols, etc.; anti-oxidants, e. g., alkyl phenols, oiliness agents such as stearic and oleic acids and pour point depressors such as chlorinated naphthalene to further lower the pour point of the lubricant.

Example I

The following composition represents a high temperature anti-friction bearing grease:

	Per cent
Sodium soaps of	25.0
Hydrogenated castor oil 10%	
Stearic acid 40%	
Beef tallow fatty acids 50%	
Phenyl alpha-naphthylamine	0.5
P_2S_5-turpentine condensation product	1.5
Medium VI lubricating oil	73

This composition had an ASTM worked penetration of 287 and an average high temperature performance (Army/Navy specification AN G-5*a* method) of 316 hours.

Example II

A soda-base grease was prepared containing the following ingredients, the grease being stabilized with the combination of the recited additives.

	Per cent
Sodium soaps of	30.0
Hydrogenated castor oil 10%	
Stearic acid 40%	
Beef tallow fatty acids 50%	
Phenyl alpha-naphthylamine	0.5
P_2S_5-turpentine reaction product	1.0
Zinc dibutyl dithiocarbamate	0.5
85 SSU at 210° F. naphthenic base lubricating oil having a V. I. of 55	68.0

This grease had the following properties:

Melting point, °F	417
Water resistance, loss per cent by weight	35
Unworked penetration	205
Worked penetration 500 strokes	280
High temperature performance at 10,000 R. P. M. and 300° F.—time to failure in hours	329
Oxidation (Norma Hoffman)—	
Pressure drop at 100 hours p. s. i	3
Pressure drop at 500 hours p. s. i	11

Example III

A lithium hydroxy fatty acid grease was prepared using the following components:

	Per cent
Hydrogenated castor oil	9.28
Lithium hydroxide monohydrate	1.31
Phenyl alpha-naphthylamine	0.25
P_2S_5-turpentine reaction product	1.0
Zinc dibutyl dithiocarbamate	0.5
Tributyl phosphite	0.25
High V. I. lubricating oil, 100 SSU at 100° F.	50.65
High V. I. lubricating oil, 250 SSU at 100° F.	36.76

The above grease had the following properties:

Unworked penetration at 77° F	255
Worked penetration 500 strokes	275
Dropping point, °F	386
High temperature performance at 10,000 R. P. M. and 250° F.—time to failure in hours	longer than 1900

Example IV

The following grease was prepared using hydrogenated castor oil fatty acids instead of the hydrogenated castor oil as in Example III.

	Percent
Hydrogenated castor oil fatty acids	6.95
Lithium hydroxide monohydrate	1.0
Phenyl alpha-naphthylamine	.25
P_2S_5-turpentine reaction product	1.0
Zinc dibutyl dithiocarbamate	.5
Tributyl phosphite	.25
High V. I. lubricating oil 100 SSU at 100° F.	52.23
High V. I. lubricating oil 250 SSU at 100° F.	37.82

The following properties were obtained on the above grease:

Unworked penetration at 77° F	250
Worked penetration 500 strokes	302
Dropping point, °F	386
High temperature performance at 10,000 R. P. M. and 250° F.—time to failure in hours	985

The invention claimed is:

1. A grease composition comprising the following ingredients:

	Percent
Lubricating oil, 100–250 SSU at 100° F.	87.5
Phenyl alpha-naphthylamine	.25
P_2S_5-turpentine reaction product	1.0
Zinc dibutyl dithiocarbamate	0.5
Tributyl phosphite	0.25
Lithium soap of hydrogenated castor oil acids	Balance

2. A grease composition comprising the following ingredients:

	Percent
Sodium soap of higher fatty acids	30.0
Lubricating oil	68.0
Phenyl alpha-naphthylamine	0.5
P_2S_5-turpentine reaction product	1.0
Zinc dibutyl dithiocarbamate	0.5

3. A grease composition comprising a major amount of a mineral lubricating oil having incorporated therein an amount sufficient to form a grease of a sodium soap and minor amounts at least 0.01% by weight each, sufficient to stabilize said grease of phenyl alpha-naphthylamine and the reaction product of phosphorus pentasulfide and turpentine, and zinc dibutyl dithiocarbamate.

4. A grease composition comprising a major amount of a mineral lubricating oil having incorporated therein an amount sufficient to form a

grease of a sodium soap and minor amounts at least 0.01% by weight each, sufficient to stabilize said grease of phenyl alpha-naphthylamine and the reaction product of phosphorus pentasulfide and turpentine.

5. A grease composition comprising a major amount of a lubricating oil having incorporated therein an amount sufficient to form a grease of a gelling agent and 0.01 to 5% each of an aromatic naphthyl amine and the reaction product of phosphorus pentasulfide and a dicyclic terpene.

6. A grease composition comprising a major amount of a lubricating oil having incorporated therein an amount sufficient to form a grease of a gelling agent and minor amounts at least 0.01% by weight each, sufficient to stabilize said grease of a naphthyl amine and a reaction product of turpentine and a phosphorus sulfide.

7. A grease composition comprising a major amount of a lubricating oil having incorporated therein an amount sufficient to form a grease of a gelling agent and minor amounts at least 0.01% by weight each, sufficient to stabilize said grease of an aromatic naphthyl amine and a phosphorus- and sulfur-containing reaction product obtained by reaction of a dicyclic terpene and a phosphorus sulfide.

8. A grease composition comprising a major amount of a lubricating oil having incorporated therein an amount sufficient to form a grease of colloidal silica and minor amounts at least 0.01% by weight each, sufficient to stabilize said grease of a naphthyl amine and a phosphorus- and sulfur-containing reaction product obtained by reaction of a dicyclic terpene and a phosphorus sulfide.

9. A grease composition comprising a major amount of a lubricating oil having incorporated therein an amount sufficient to form a grease of colloidal siliceous gelling agent and minor amounts at least 0.01% by weight each, sufficient to stabilize said grease of a naphthyl amine and a phosphorus- and sulfur-containing reaction product obtained by reaction of a dicyclic terpene and a phosphorus sulfide.

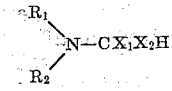
10. A grease composition comprising a major amount of a lubricating oil having incorporated therein an amount sufficient to form a grease of an inorganic colloidal gelling agent and minor amounts at least 0.01% by weight each, sufficient to stabilize said grease of a naphthyl amine and a phosphorus- and sulfur-containing reaction product obtained by reaction of a dicyclic terpene and a phosphorus sulfide.

11. A grease composition comprising a major amount of a lubricating oil having incorporated therein an amount sufficient to form a grease of sodium soap and minor amounts at least 0.01% by weight each, sufficient to stabilize said grease of a naphthyl amine and a phosphorus- and sulfur-containing reaction product obtained by reaction of a dicyclic terpene and a phosphorus sulfide.

12. A grease composition comprising a major amount of a lubricating oil having incorporated therein an amount sufficient to form a grease of a soap and minor amounts at least 0.01% by weight each, sufficient to stabilize said grease of a naphthyl amine and a phosphorus- and sulfur-containing reaction product obtained by reaction of a dicyclic terpene and a phosporus sulfide.

13. A grease composition comprising a major amount of a mineral lubricating oil having incorporated therein an amount sufficient to form a grease of a gelling agent and minor amounts at least 0.01% by weight each, sufficient to stabilize said grease of a naphthyl amine and a phosphorus- and sulfur-containing reaction product obtained by reaction of a dicyclic terpene and a phosphorus sulfide.

14. A grease composition comprising a major amount of a lubricating oil having incorporated therein an amount sufficient to form a grease of a gelling agent and minor amounts at least 0.01% by weight each, sufficient to stabilize said grease of a naphthyl amine and a phosphorus- and sulfur-containing reaction product obtained by reaction of a dicyclic terpene and a phosphorus sulfide, and a metal salt of an organic acid represented by the formula:



wherein R_1 and R_2 are selected from the group consisting of hydrogen, alkyl, alicyclic, aryl, aralkyl, alkaryl and heterocyclic radicals and X_1 and X_2 are elements of the group consisting of oxygen, sulfur, selenium and tellurium.

15. A grease composition comprising a major amount of a lubricating oil having incorporated therein an amount sufficient to form a grease of a gelling agent and minor amounts at least 0.01% by weight each, sufficient to stabilize said grease of a naphthyl amine and a phosphorus- and sulfur-containing reaction product obtained by reaction of a dicyclic terpene and a phosphorus sulfide, and a metal salt of a carbamic acid.

16. A grease composition comprising a major amount of a lubricating oil having incorporated therein an amount sufficient to form a grease of a gelling agent and minor amounts at least 0.01% by weight each, sufficient to stabilize said grease of a naphthyl amine and a phosphorus- and sulfur-containing reaction product obtained by reaction of a dicyclic terpene and a phosphorus sulfide, and a zinc salt of a carbamic acid.

17. A grease composition comprising a major amount of a lubricating oil having incorporated therein an amount sufficient to form a grease of a gelling agent and minor amounts at least 0.01% by weight each, sufficient to stabilize said grease of a naphthyl amine and a phosphorus- and sulfur-containing reaction product obtained by reaction of a dicyclic terpene and a phosphorus sulfide.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,289,748	Beerbower et al.	July 14, 1942
2,316,085	Kelso et al.	Apr. 6, 1943
2,379,453	Noland	July 3, 1945
2,400,106	Denison et al.	May 14, 1946
2,409,799	Roberts	Oct. 22, 1946
2,417,876	Lewis	Mar. 25, 1947
2,486,188	May	Oct. 25, 1949
2,504,672	Farrington et al.	Apr. 18, 1950
2,546,552	Loane et al.	Mar. 27, 1951