

UNITED STATES PATENT OFFICE

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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 pronounced 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.

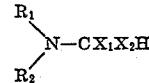
Generally, to inhibit bleeding and improve the texture of greases special precautionary measures are taken, such as employing slow or rapid means of cooling, or extensively working the grease in special homogenizers, e. g., the Cornell homogenizer and the like. Such procedures are usually time-consuming and add to the cost of the grease. Other ways of producing stable, non-bleeding greases have been attempted by either reducing the soap content generally to less than

5 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 costly and such products generally possess an undesired consistency.

10 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 non-bleeding 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.

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

20 Broadly stated, this invention comprises a lubricating grease composition containing in addition to the gel-forming agent and/or agents, two particular types of additives in amounts much less than that of the gelling agent used to form the grease; the combination of which produces a synergistic effect resulting in a grease composition possessing the properties enumerated above. The two additives are: (a) a high molecular weight organic amine and (b) an organic salt the acid portion of which contains nitrogen, carbon and the elements from the group of oxygen and the elements of the sulfur family, and may be represented by the formula:

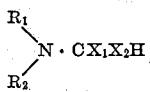


25 where R₁ and R₂ can be hydrogen and/or an oil-solubilizing organic group such as normal or iso-alkyl; alicyclic, aryl; aralkyl; alkaryl and heterocyclic group; X₁ and X₂ may be oxygen or an element selected from the sulfur family or mixtures thereof. The cationic portion of the molecule may be a mono- or polyvalent metal such as Na, K, Li, Ca, Ba, Sr, Mg, Zn, Al, Cu, Co, Sn, Ni and the like.

30 35 40 45 50 55 60 The first additive (a), namely, a high molecular weight organic amine, may include the aromatic amines, aliphatic amines, alkylarylamines, cyclic amines, heterocyclic amines and the like and their mixtures. The following amine compounds

are applicable as stabilizing agents for metal coating compositions of this invention: para-phenylenediamine, alpha-naphthylamine, ortho-phenylenediamine, beta - naphthylamine, 5 - di-beta-naphthyl para-phenylenediamine, 2,4-di-amino diphenylamine, meta-toluylenediamine, 2-amino-1,4-naphthohydroquinone, 4 - amino - 1,2-naphthohydroquinone, thiodiphenylamine, mono-benzyl para-aminophenyl, 2,4-diamino toluene, 2,4-diamino diphenylamine, para-amino ozobenzene, octadecyl benzylamine, beta-phenylamine-alpha - naphthylamine, phenyl-alpha-naphthylamine, phenyl-beta-naphthylamine, N,N'-dibutyl para-phenylenediamine, tetramethyl diamino-diphenylmethane, p,p'diamino-diphenylmethane, 4,4-diamino-diphenylmethane, tetraethyl diamino - diphenylmethane, diisoamyl - diamino - diphenylmethane, bis - (beta - naphthyl amino methyl) - p-tert-amyl-phenol; 3,3,5-tricyclohexylamine, dicyclohexylamine; N-phenyl morpholine, N-(para-hydroxyphenyl) morpholine; octadecyl 3-methyl-2-pentylamine, N-octadecyl-2-ethylhexylamine, hexadecylamine, octadecylamine, octadecylamine, octadecadienylamine, paraffin waxamine, cocoamine prepared from cocoanut oil acids, N,N'-dimethyl triglycoldiamine; disalicyl ethylenediamine; N-salicylal-N'-ethanol-ethylenediamine; 5-methyl,2,4-diamino anisole; ketone diarylamine, ketone amine; ketone amine condensation products; butyraldehyde aniline derivatives; condensation products of acetone and aniline, reaction products of acetone and para-amino diphenyl. In addition to the above amine compounds the following mixtures of amines produce good stabilizers. Mixtures of diphenyl para-phenylenediamine and isopropoxy - diphenylamine, phenyl-alpha-naphthylamine and meta-toluylenediamine, mixture of di-para-methoxy diphenylamine, diphenylamine, diphenyl para-phenylenediamine and phenyl-beta-naphthylamine, mixtures of phenyl-beta-naphthylamine and meta-toluylenediamine mixture of diphenyl para-phenylenediamine and para-phenylenediamine, mixture of stearic acid, meta-toluylenediamine and phenyl-alpha-naphthylamine, mixture of ditolylamine and petroleum wax and the like. The amines which are particularly preferred are: phenyl - alpha - naphthylamine, phenyl-beta-naphthylamine, beta-phenylamine-alpha-naphthylamine, tetra-methyl diamino diphenylmethane, meta-toluylenediamine and their mixtures.

The second additive (b) as defined above and the acid portion of which has been represented by the general formula:



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
 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(ethyl piperidyl) mono- and dithiocarbamic acid
 Zn, Ca, Na, salts of dihexyl mono- and diselenocarbamic 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 amount of both the amine or the carbamate 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 and/or other gelling agents and the like. Generally, the carbamates and their derivatives are used in amounts varying from 0.01% to 2% and preferably from 0.1% to 1%. The amines are used in amounts varying from 0.01% to 5% and preferably from 0.25% to 2%. Depending upon the type of grease produced, the ratio of the two additives (a) amine and (b) carbamate can vary over wide limits of from 1:4 to 4:1, respectively.

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, palmitoleic, 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-hydroxy-stearic acid, hydroxy palmitic acid, ricinoleic acid, ricinelaic acid, linusic 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 10 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 pre-made

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soaps can be used to form the grease. Specific examples of preferred soaps or mixtures thereof are: lithium stearate, lithium 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 sap 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.

Instead of using only soaps as the gelling agent mixtures of soaps and other gelling agents, such as organic or inorganic aerogels, e. g. silica aerogels, can be used or aerogels can replace the soap entirely as the gelling agent.

The soap content of grease compositions of this invention may vary over wide limits and may be as high as 50%. In practice, grease compositions of this invention containing from 5 to 25% by weight of soap.

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 SUV at 100° F. to about 2000 SUV 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., 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-ethyl-hexyl sebacate, dioctyl phthalate, trioctyl phosphate; polymeric tetrahydrofuran; polyalkyl silicon polymers, e. g., dimethyl silicon polymer, etc. Under some conditions of lubrication, minor amounts of a fixed oil such as castor oil, lard oil, etc., may be admixed with the hydro-

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carbon oil and/or synthetic oil used in making grease compositions of this invention.

Highly desirable greases may be prepared by using formulations within the following range:

		General Range	Preferred Range
10	Gelling agent, e. g., soaps, aerogels, etc.	5 to 50.....	15-25
	<i>Primary Additives:</i>		
	Carbamates and their thio derivatives.....	0.01 to 2.....	0.1-1.5
	Amine.....	0.01 to 5.....	0.25-1
	<i>Secondary Additives:</i>		
	Ca octyl phenolformaldehyde condensation product.....	0 to 2.....	0.1-1
	Base (mineral oil and/or synthetic oil).....	Balance.....	Balance

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% and 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 homogeneous 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.

50 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.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Components:																				
Li stearate	x	x	---		x	---		x	x		x	---				x	x	x		
Li 12-hydroxy stearate																				
Li soap of hydrogenated fish oil fatty acids						x														
Na soap of hydrogenated fish oil fatty acids									x		x							x		
K ricinoleate																				
Ca stearate			x	x											x		x			
Ca soap of tallow and hog fat																				
Ba stearate												x	x						x	
Al stearate	x		x	x	x		x							x	x	x	x	x	x	
Zn dibutyl dithiocarbamate	x		x	x			x		x		x			x		x	x	x	x	
Zn-dihexyl dithiocarbamate																				
Zn dibenzyl dithiocarbamate						x			x											
Zn dibenxyl monothiocarbamate																				
Ca dibutyl dithiocarbamate											x		x							
Zn dicyclohexyl dithiocarbamate											x			x						
Zn dicyclohexyl carbamate	x	x	x	x		x	x	x	x		x	x	x		x	x	x	x	x	
Phenyl-alpha-naphthylamine					x				x						x					
Phenyl-beta-naphthylamine															x					
Ca octylphenol-formaldehyde condensation product									x											
2,4-Dibutyl-6-methylphenol	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
Mineral oil																				
Diocetyl sebacate														x	x		x	x	x	

Grease compositions of this invention were compared with greases in which one of the additive components was omitted by subjecting them to the performance test of the Army-Navy Aero-nautical Specification AN-G-5a, and the results were as follows:

Composition	1	1A	1B
Li.stearate	20	20	20
Phenyl-alpha-naphthylamine	0.25		0.25
Zn dibutyl dithiocarbamate	1.0	1.0	
Mid.-Cont. oil, 400 SUS at 100° F.	Balance	Balance	Balance
(Oxidation Tests Results Time for 5 lb. pressure drop (hrs.))	500	20	
(High speed, high temperature ball bearing performance test (hrs.))	300	176	

Composition	2A
Formulæ, percent wt.:	
Sodium soap—	
Hydrogenated castor oil, 10	27.5% wt.
Stearic acid, 40	
Beef tallow fatty acids, 50	
Phenyl-alpha-naphthylamine	0.5% wt.
Zn dibutyl dithiocarbamate	0.5% wt.
Ca salt of octyl phenol-formaldehyde condensation product	0.5% sulfated ash.
Mineral oil (85 SUS at 210° F., 55 V. I. naphthenic oil)	Balance.
Test Results:	
Worked penetration, ASTM	287.
Spec. AN-G-5a performance, hours	362 av.

The synergistic effects which are obtained by the combination of the two additive agents of this invention are illustrated by subjecting a lithium stearate grease to a modified Dornte oxidation test using an iron wire catalyst at 300° F. The results were as follows:

Composition	Additive, Per Cent Wt.	Oxygen Absorption (hrs., 1500 ml.)
Lithium stearate grease		
Li stearate grease	0.25% phenyl-alpha-naphthylamine.	4.3
Do	0.5% Zn di.utyl dithiocarbamate.	5.2
Do	0.25% phenyl-alpha-naphthylamine.	19.6
Do	0.50% Zn di.utyl dithiocarbamate.	63.0

Minor amounts of secondary additives can be admixed with greases of this invention such as extreme pressure agents can be added to such greases and the preferred comprise esters of phosphorus acids such as triaryl, alkylhydroxy, ary, 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 diphenol 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 oils, acids, 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 ester 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, e. g., Ca octylphenol 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, volatilized 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.

The amount of the above additives can be added to grease compositions of this invention in around about 0.01% to less than 10% by weight, and preferably 0.1 to 5.0% by weight.

20. Greases of this invention are applicable for general automotive uses and are excellent aircraft greases, industrial greases and the like.

This application is a continuation-in-part of our co-pending application Serial No. 93,635, filed May 16, 1949.

We claim as our invention:

1. A grease composition comprising a major amount of mineral lubricating oil having incorporated therein an amount sufficient to form a grease of lithium soap and from about 0.01 to 5% of an oil-soluble aryl amine and from about 0.1 to 2% of an oil-soluble polyvalent metal salt of an alkyl dithiocarbamic acid.

2. A grease composition comprising a major amount of mineral lubricating oil having incorporated therein an amount sufficient to form a grease of a sodium soap and from about 0.01 to 5% of an oil-soluble aryl amine and from about 0.1 to 2% of an oil-soluble polyvalent metal salt of an alkyl dithiocarbamic acid.

3. A grease composition comprising a major amount of mineral lubricating oil having incorporated therein an amount sufficient to form a grease of a lithium stearate and from 0.25 to 1% of phenyl-alpha-naphthylamine and from 0.1 to 1.5% of zinc dibutyl dithiocarbamate.

4. A grease composition comprising a major amount of mineral lubricating oil having incorporated therein an amount sufficient to form a grease of sodium stearate and from 0.25 to 1% of phenyl-alpha-naphthylamine and from 0.1 to 1.5% of zinc dibutyl dithiocarbamate.

5. A grease composition comprising a major amount of mineral lubricating oil having incorporated therein an amount sufficient to form a grease of lithium stearate and from 0.25 to 1% of phenyl-alpha-naphthylamine and from 0.1 to 1.5% of zinc dihexyl dithiocarbamate.

6. A grease composition comprising a major amount of mineral lubricating oil having incorporated therein an amount sufficient to form a grease of sodium stearate and from 0.25 to 1% of phenyl-alpha-naphthylamine and from 0.1 to 1.5% of zinc dihexyl dithiocarbamate.

7. A grease composition comprising a major amount of mineral lubricating oil having incorporated therein in an amount sufficient to form a grease of lithium 12-hydroxy stearate and from 0.25 to 1% of phenyl-alpha-naphthylamine and from 0.1 to 1.5% of zinc dibutyl dithiocarbamate.

8. A grease composition comprising a major amount of a lubricating oil having incorporated therein a minor amount of an alkali metal soap and from about 0.01 to 5% of an oil-soluble aryl amine and from about 0.01 to 2% of an oil-sol-

ble polyvalent metal salt of an alkyl dithiocarbamic acid.

9. A grease composition comprising the following ingredients in the following proportions:

Li stearate	20
Phenyl-alpha-naphthylamine	0.25
Zn dibutyl dithiocarbamate	1.0
Mineral lubricating oil	Balance

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