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LITHIUM SOAP GREASE CONTAINING RUST AND COPPER CORROSION INHIBITORS

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This invention relates to an improved greases composition and more particularly relates to an improved lithium soap grease having a synthetic oil base.

With world-wide use of military equipment, the need for lubricants which can be used over a wide temperature range and under greatly different climatic conditions has become increasingly important. The grease product acceptable for such use must possess properties which will permit its use at temperatures ranging from as low as −65° F. to temperatures as high as 250° F. In addition, the product must be capable of inhibiting rust and at the same time be non-corrosive toward copper and other non-ferrous metals.

It is an object of the present invention to provide a stable lubricant grease composition which is suitable for use over a wide temperature range. Another object of the invention is to provide a grease composition which can be used at subzero temperatures as well as at temperatures in excess of 200° F. Another object of the invention is to provide a grease composition which is capable of inhibiting rusting and which is non-corrosive to non-ferrous metals. Other objects and advantages of this invention will become apparent from the following description thereof.

In accordance with the herein described invention, the foregoing objects can be attained by the use of a grease product having the following composition in the following approximate proportions by weight:

Component	Weight percent
Lithium Soap	5.0–20.0.
Sperm Oil	0.5–3.0.
Petroleum Oxidation Product	0.5–3.0.
Oil-soluble Polyvalent salt of Dialkyl Dithiocarbamic Acid	0.1–0.5.
Metal Deactivator	0.05–0.25.
Synthetic Lubricating Oil	Remainder.

The lithium soap component can be the lithium soap of a high molecular weight carboxylic acid such as stearic acid, palmitic acid, hydrogenated fish oil fatty acids, tallow acids, animal fatty acids, as well as hydroxy fatty acids such as a hydroxy stearic acid, particularly the 12-hydroxy stearic acid and hydrogenated castor oil. Mixtures of such lithium soaps can be used.

The petroleum oxidation product used in the formula is a mixture of aliphatic oxygen-containing compounds of petroleum origin obtained by the controlled oxidation of hydrocarbons, or mixtures of hydrocarbons, such as occur in or associate with petroleum oils. The controlled oxidation is carried out in the liquid phase at elevated temperatures under super-atmospheric pressures. The resultant oxidation product is a mixture of aliphatic alcohols, ketones, alcohol-ketones, lactones, and esters together with some unoxidized hydrocarbons. The method of obtaining these oxygen-containing aliphatic compounds and the compositions thereof are described in U. S. Patents 1,690,768, 1,690,769, 1,863,004, and others issued to

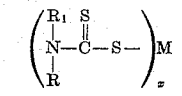
A. W. Burwell. As shown in U. S. 1,863,004, a typical analysis of such oxidation products shows the following approximate composition:

	Weight percent
Saturated aliphatic carboxylic acids	23–40
Neutral lactones and esters from said acids	7–50
Unsaponifiable, non-acidic oxygen-containing aliphatic compounds	25–40

Products of the type suitable for use in the present invention are marketed by the Alox Corporation under the trade name of "Alox" compounds. Compounds marketed as "Alox 100," "Alox 102," "Alox 125," "Alox 325," and "Alox 600" are suitable for this purpose. For the purpose of identifying these compounds, it will be referred to hereinafter in this specification and in the appended claims as "petroleum oxidation products." Of the Alox compounds, it is preferred to use the product marketed as "Alox 125" having the following properties:

Mean molecular weight	450–500.
Acid number	35–70.
Saponification number	150–200.
Unsaponifiable	35–40% by weight.
Ash	0.2% maximum.
Specific gravity at 158° F	0.86–0.89.
Weight per gallon	7.0–7.5 lbs.
Melting pt. (ASTM–D–127–45)	111–114° F.
Flash (O. C.)	275° F. (min.).
Fire	330° F. (min.).

The oil-soluble polyvalent salt of the dialkyl dithiocarbamic acid employed have the general formula



in which R_1 and R are alkyl groups of at least about 4 carbon atoms and preferably from 4 to about 20 carbon atoms and M is a polyvalent heavy metal such as zinc, copper, tin, cobalt, nickel, lead, cadmium, etc. and x is the valence of M. Examples of suitable thiocarbamates are: zinc diamyl dithiocarbamate, zinc dibutyl dithiocarbamate, zinc dioctyl dithiocarbamate, zinc dilauryl dithiocarbamate, zinc amyl-decyl dithiocarbamate, cobalt dioctyl dithiocarbamate, copper amyl-octyldecyl dithiocarbamate, nickel diamyl dithiocarbamate, chromium octyllauryl dithiocarbamate, etc.

While the above defined dialkyl dithiocarbamates are all suitable for use in the herein described grease composition, they are all not equivalent in their effectiveness, some being more effective than the other under certain conditions. Of the dialkyl dithiocarbamates, it is preferred to employ the zinc dialkyl dithiocarbamate.

As noted above, one of the components of the grease composition described herein is a metal deactivator. The metal deactivator used in the present invention is a reaction product of an aromatic ortho-hydroxy aldehyde such as 2-hydroxy benzaldehyde or salicylaldehyde and an alkylene polyamine. Examples of these reaction products which may be termed di-(2-hydroxybenzal)-alkylene-polyamines are di-(2-hydroxybenzal)-ethylenediamine, di-(2-hydroxybenzal)-diethylenetriamine, di-(2-hydroxybenzal)-triethylenetetramine, di-(2-hydroxybenzal)-propylenediamine, di-(2-hydroxybenzal)-dihexylenetriamine, N:N'-disalicylidene-1:2 diaminopropane, etc.

The synthetic oil bases used in the grease composition of this invention are synthetic oleaginous compounds such as the dialiphatic esters of di-basic carboxylic acids such as sebacic acid, adipic acid, azelaic acid, alkenyl acid, succinic acid, etc. wherein the alkyl radical can contain from 5 to 20 or more carbon atoms and preferably from 5 to 12 carbon atoms. The ester can be used singly or

mixtures of 2 or more esters can be employed. Examples of such esters are di-(2-ethylhexyl)-adipate, di-(2-ethylhexyl)-sebacate, di-octyl-adipate, di-octyl-sebacate, di-(2-ethylhexyl)-azelate, etc.

Other synthetic lubricating oils which can be used as the oil base are the aliphatic monoethers of polyoxyalkylene glycols obtained by the addition of an alkylene oxide or a mixture of alkylene oxide to a monohydroxy alcohol such as one described in U. S. 2,425,755, issued to F. H. Roberts et al. August 19, 1947, U. S. 2,425,845, issued to W. J. Toussaint August 19, 1947, U. S. 2,448,664, issued to H. R. Fife et al. September 7, 1948, and others. Still another type of synthetic oil base which can be used is the dihexoate or dioctoate ester of triethylene on tetraethylene glycol such as are described in U. S. 2,585,182 issued to S. Sterman February 12, 1952. Synthetic oils of the type described in this paragraph are marketed by Carbide and Carbon Chemicals Corporation as "Ucon" oils.

The grease composition may, if desired, contain from 0.01 to about 2.0% of an antioxidant such as an aryl amine, for example, phenylene diamine and phenyl alpha naphthylamine. Anti-wear additives such as tricresyl phosphate can also be incorporated in the composition.

The following formulations are illustrative of the grease product of this invention:

Component	Weight Percent	
	I	II
Di-isooctyl azelate		86.15
Di-octyl adipate+di-octyl sebacate (1:1)	85.16	
Lithium 12-hydroxy stearate	11.0	10.0
"Alox 125" [1]	1.0	1.0
Sperm Oil	1.0	1.0
Metal Deactivator [2]	0.14	0.15
Zinc dibutyl dithiocarbamate	0.2	0.2
Phenyl alpha naphthylamine	1.0	1.0
Tricresyl phosphate	0.5	0.5

[1] See supra.
[2] Condensation product of salicylal and an alkylene polyamine; N:N'-disalicylidene-1:2 diaminopropane (du Pont Metal Deactivator) can be used.

In place of the azelate or the mixture of adipate and sebacate, other esters can be used such as di-2 ethyl hexyl sebacate or the di-hexoate or di-octoate esters of triethylene or tetraethylene glycol; or the monoethers of the polyoxyalkylene glycols.

The antioxidant, e. g. phenyl alpha naphthylamine and/or the anti-wear agent, e. g. tricresyl phosphate may be omitted from the formulation. However, the "Alox" compound must be used in combination with the sperm oil since the grease composition with either alone will not pass the anti-rust test. Likewise, the metal deactivator must be used in conjunction with the dialkyl dithiocarbamate since the use of either alone will not result in a grease product which will pass the copper corrosion test. The anti-rust test and the copper corrosion test referred to are carried out as follows:

Anti-rust test

The corrosion preventive properties of the greases are evaluated by means of a humidity cabinet test similar to that described in Specification MIL-G-4343. The humidity cabinet conditions are 100° F.±1° F. and 95%±2% relative humidity.

New 204-type ball bearings, used as test pieces, are carefully cleaned by a prescribed procedure with petroleum naphtha and isopropanol and dried. The test grease is then worked in and around the balls and races and over the bearing surface to provide a uniform grease film over all parts of the bearing. Grease distribution is facilitated by a couple two minute run-ins at 1750 R. P. M. A matter of 1.0±0.1 g. of grease is left in the bearing. The bearings are then suspended from suspension rods in the cabinet by means of glass hooks. The test is continued for 28 days and no corrosion is permitted for a passing test.

Copper corrosion test

The copper corrosion test referred to above is described in detail in Military Specification MIL-G-3278 which covers a grease intended for general use on aircraft and for instruments (for low and high temperatures). Small copper strips are degreased and bent midway between the ends to form an angle of approximately 45°. The strips are then chemically cleaned by a definite prescribed procedure which includes immersion in a solution of 25% by volume of sulfuric and nitric acids, rinsing, immersion in a potassium dichromate-sulfuric acid solution, rinsing and drying.

A cleaned copper strip is then placed on edge in each of two glass sample dishes containing 4 g. of grease. The bottom edge of each strip is in contact with the dish and the top part is exposed to the atmosphere above the grease. The dishes are placed in an oxidation bomb such as described in ASTM D942-50. The bomb copper corrosion test is then carried out for a period of 20 hrs. at 210° F. under 110 lbs. oxygen pressure. The pressure drop shall not exceed 0.5 p. s. i. and there shall be no decomposition of the grease and no stain or corrosion of the copper strip beyond that obtained in a blank test under the same conditions without grease.

Having described the invention by way of specific examples, it is to be understood the present invention embraces such other variations and modifications as come within the spirit and scope of the appended claims.

I claim:

1. A grease composition consisting essentially of the following:

	Approximate weight percent
Lithium 12-hydroxy stearate	5.0 to 20.0
Sperm oil	0.5 to 3.0
Petroleum oxidation product	0.5 to 3.0
Zinc dibutyl dithiocarbamate	0.1 to 0.5
N:N'-disalicylidene-1:2 diaminopropane	0.05 to 0.25
Aliphatic esters of dibasic carboxylic acids	Remainder

said petroleum oxidation product being a mixture of saturated aliphatic oxygen-containing compounds including alkyl esters, lactones, ketones, alcohols, and alcohol-ketones obtained by controlled partial oxidation of petroleum hydrocarbons, and having the following properties:

Mean molecular weight	450–500.
Acid number	35–70.
Saponification number	150–200.
Unsaponifiable	35–40% by weight.
Ash	0.2% maximum.
Specific gravity at 158° F	0.86–0.89.
Weight per gallon	7.0–7.5 lbs.
Melting Pt. (ASTM-D-127-45)	111–114° F.
Flash (O. C.)	275° F. (min.).
Fire	330° F. (min.).

2. A grease composition consisting essentially of the following:

	Approximate weight percent
Lithium 12-hydroxy stearate	11.0
Petroleum oxidation product	1.0
Sperm oil	1.0
N:N'-disalicylidene-1:2 diaminopropane	0.14
Zinc dibutyl dithiocarbamate	0.2
Di-octyl adipate+di-octyl sebacate	Remainder

said adipate and said sebacate being used in equal proportions, said petroleum oxidation product being a mixture of saturated aliphatic oxygen-containing compounds including alkyl esters, lactones, ketones, alcohols, and alcohol-ketones obtained by controlled partial oxidation of

petroleum hydrocarbons, and having the following properties:

Mean molecular weight	450–500.
Acid number	35–70.
Saponification number	150–200.
Unsaponifiable	35–40% by weight.
Ash	0.2% maximum.
Specific gravity at 158° F	0.86–0.89.
Weight per gallon	7.0–7.5 lbs.
Melting Pt. (ASTM–D–127–45)	111–114° F.
Flash (O. C.)	275° F. (min.).
Fire	330° F. (min.).

3. A grease composition consisting essentially of the following:

	Approximate weight percent
Lithium 12-hydroxy stearate	10.0
Petroleum oxidation product	1.0
Sperm oil	1.0
N:N'-disalicylidene-1:2 diaminopropane	0.15
Zinc dibutyl dithiocarbamate	0.2
Phenyl alpha naphthylamine	1.0
Di-isooctyl azelate	Remainder

said petroleum oxidation product being a mixture of saturated aliphatic oxygen-containing compounds including alkyl esters, lactones, ketones, alcohols, and alcohol-ketones obtained by controlled partial oxidation of petroleum hydrocarbons, and having the following properties:

Mean molecular weight	450–500.
Acid number	35–70.
Saponification number	150–200.
Unsaponifiable	35–40% by weight.
Ash	0.2% maximum.
Specific gravity at 158° F	0.86–0.89.
Weight per gallon	7.0–7.5 lbs.
Melting Pt. (ASTM–D–127–45)	111–114° F.
Flash (O. C.)	275° F. (min.).
Fire	330° F. (min.).

4. A grease composition consisting essentially of the following:

	Approximate weight percent
Lithium soap	5.0 to 20.0
Sperm oil	0.5 to 3.0
Petroleum oxidation product	0.5 to 3.0
Oil-soluble polyvalent metal-dialkyl dithiocarbamate	0.1 to 0.5
Metal deactivator	0.05 to 0.25
Synthetic lubricating oil	Remainder

said lithium soap being a soap of a high molecular weight fatty acid, said petroleum oxidation product being a mixture of saturated aliphatic oxygen-containing compounds obtained by the partial oxidation of petroleum hydrocarbons and comprising about 23–40% (wt.) saturated aliphatic carboxylic acids, about 7–50% (wt.) neutral lactones and esters from said acids and about 25–40% (wt.) unsaponifiable non-acidic oxygen-containing aliphatic compounds, said dialkyl dithiocarbamate containing from 4 to about 20 carbon atoms in the alkyl radicals, said metal deactivator being the condensation product of ortho-hydroxy benzaldehyde and an alkylene polyamine, and said synthetic lubricating oil being selected from the class consisting of an alkyl diester of a dicarboxylic having from about 5 to about 20 carbon atoms, an aliphatic monoether of a polyoxyalkylene glycol, and a member of the class consisting of triethylene glycol dihexoate, tetraethylene glycol, dihexoate, triethylene glycol dioctoate, tetraethylene glycol dioctoate, and mixtures thereof.

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