

UNITED STATES PATENT OFFICE

2,351,384

LITHIUM SOAP GREASE

Harold A. Woods and Jacobus M. Plantfeber,
Martinez, Calif., assignors to Shell Develop-
ment Company, San Francisco, Calif., a cor-
poration of Delaware

No Drawing. Application November 18, 1942,
Serial No. 466,068

12 Claims. (Cl. 252-42)

This invention relates to a stable low tempera-
ture grease. More particularly, it deals with a
lithium soap grease comprising a small amount
of an oxidation inhibitor, and a low viscosity and
low pour point mineral oil having a viscosity

5

gravity constant (V. G. C.) of greater than .84.
The V. G. C. is an arbitrary constant calcu-
lated from the Saybolt Universal viscosity of an
oil and its specific gravity, the value of which
constant increases with the naphthenicity, and
decreases with the paraffinicity of the oil (see the
article by Hill and Coats in vol. 22, 1928, pp. 641-4,
Ind. Eng. Chem., entitled "Viscosity Gravity Con-
stant of Petroleum Lubricating Oils"). Pennsylv-
ania oils, typical of paraffinic oils, have V. G. C.'s
of about .80, while typical naphthenic oils have
V. G. C.'s above about .84 up to about .90.

10

15

20

25

30

35

40

45

50

55

Investigations into the flow properties of
greases at low temperatures have revealed in the
past that the flow of greases is primarily a func-
tion of the viscosity of the oil at that tempera-
ture and, to a lesser extent, of the amount and
type of soap employed. Since oils of low V. G. C.
change less in viscosity of a given temperature
range than oils of higher V. G. C., such oils have
in the past been employed for low temperature
operation. Concerning the influence of the soap,
it is known that relatively small amounts of soap
are preferred to preserve the flow properties of
the oil, and that lithium soap greases have bet-
ter flow properties at low temperatures than com-
parable greases made with other soaps.

Lithium soap greases must contain free fatty
acid to prevent excessive gelling. Such low tem-
perature greases as were produced heretofore
employing oils having S. U. viscosities below 100
sec. at 100° F. normally contain at least about
.5% free acid calculated as stearic acid.

It is usually considered that low temperature
greases should have consistencies of between
about 200 and 370 A. S. T. M. penetration at 77°
F. By low temperatures as herein stated, we
mean temperatures low as about -100° F.

It has now been discovered that an improved
low temperature lithium soap grease can be pro-
duced by using a naphthenic oil rather than a
paraffinic oil. The new lithium soap grease of
this invention differs from the previous lithium
soap greases having the same consistency and
equally good physical properties in that the
grease of this invention requires only about ½
the amount of soap and less than ¼ the amount
of free fatty acid used in previous lithium soap
low temperature greases.

The reduced amount of lithium soap employed

in the grease of this invention is of material eco-
nomic advantage, since lithium soap is very ex-
pensive. Also, the reduced amount of soap coun-
teracts the advantage of low V. G. C. oils em-
ployed in other lithium soap greases, because the
more soap a grease contains the less it preserves
the flow properties of the oil contained in it.

Furthermore, the amount of free fatty acid in
this new grease is critical in that an excess of
acid over the amount later specified causes the
grease to become too soft, and when the grease
is too soft, more soap must be added—which de-
feats one of the main advantages of this inven-
tion, namely, that of employing a smaller amount
of soap.

These differences and advantages of the lith-
ium soap grease of this invention are based upon
the peculiar and unexpected influence of naph-
thenic mineral oils having a V. G. C. greater than
.84 on the ability of the lithium soap to produce
a grease of a given consistency.

It is a primary purpose of this invention to
produce an economical low temperature lithium
soap grease which meets the rigid Army and Navy
Aeronautical Specification AN-G-3. Another
purpose is to produce a stable lithium soap grease
having an effective lubricating temperature range
of between about -100° F. and +300° F. A fur-
ther purpose is to produce a smooth homogeneous
lithium soap grease having a low soap content
and a low free fatty acid content.

The composition of the grease of this invention
may be summarized as follows:

Component	Broad range	Preferred range
	Per cent by weight	* Per cent by weight
Lithium soap	3-10	6-9
Free fatty acid	.01-.5	.03-.2
Oxidation inhibitor	.01-2.0	.1-1.0
Light naphthenic mineral oil	Balance	Balance

Greases of the above composition have con-
sistencies as measured by the A. S. T. M. pen-
etrometer of between about 200 and 370+.

Suitable lithium soaps consist essentially of or
comprise predominantly salts of lithium with
fatty acids having 12 or more carbon atoms. In
addition, the lithium soap may contain minor
amounts of fatty acid salts of other metals, par-
ticularly Na, K, Ca, Ba, Zn, Al, etc.

Saturated fatty acids preferred in the manu-
facture of the lithium soap, as well as for mak-
ing up the free fatty acid content of the grease,
are, for example, lauric, myristic, palmitic,

stearic, arachic, behenic, hydroxy stearic, etc. Unsaturated fatty acids which may be present comprise oleic, ricinoleic, etc.

Lithium soaps may be manufactured by conventional methods, e. g. by saponification of various fats or fatty acids with lithium oxide or hydroxide, if desired, in the presence of oxides or hydroxides of one or several of the above-enumerated metals.

The free fatty acid may be contained in the soap if the latter was produced by the reaction of a fatty acid with an amount of lithium oxide or hydroxide slightly insufficient to effect neutralization of the fatty acid; or else the free acid may be added later either to the soap, or to the grease after compounding the oil with the soap.

An oxidation inhibitor is essential to produce an oxidation-stable grease. Some lubricating oil oxidation inhibitors are more effective than others in this grease. Specifically, it has been discovered that N-alkyl para-phenylene diamine inhibitors and condensed polynuclear aromatic mono-amine inhibitors are the most effective. The N-alkyl para-phenylene diamine inhibitors have the advantage of very materially increasing the oxidation stability and life of the grease. Such inhibitors are N-butyl para-phenylene diamine, N-N'-dibutyl para-phenylene diamine, etc. The condensed polynuclear aromatic mono-amine inhibitors do not produce a grease having quite so long a life as the same amount of the N-alkyl para-phenylene diamine. Such inhibitors are alpha or beta naphthylamine, phenyl alpha or beta naphthylamine, alpha-alpha, beta-beta, or alpha-beta dinaphthylamine, etc. Several of these inhibitors have the advantage of slightly increasing the consistency of the grease. Other suitable inhibitors are mixed petroleum alkyl phenols boiling from about 200° C.-240° C.

Some oxidation inhibitors which are less effective in the grease of this invention are: diphenyl amine, tetra-methyl-aminol diphenyl methane, 2,4-di-tertiary butyl 6-methyl phenol, and some sulfur- and phosphorus-containing inhibitors.

The naphthenic mineral oils suitable for making the low temperature lithium soap grease of this invention, as stated above, are those having a low viscosity, low pour point and a V. G. C. of greater than .84. Such oils are generally lubricating oils obtained from Gulf Coast, California, Venezuela and similar crudes. The pour point must be below about -60° F. and the S. U. V. at 100° F. usually less than 100 seconds and preferably between about 50 and 90 seconds. Oils of S. U. V. of about 30 seconds at 100° F. are too light to be considered lubricating oils.

Other ingredients which may be added include various corrosion inhibitors, extreme pressure additives, anti-wear agents, stabilizers, V. I. improvers, and the like, provided they do not interfere with the low temperature operation and oxidation stability of the grease.

Some extreme pressure additives which may be used comprise: esters of phosphorus acids such as triaryl, alkyl hydroxy aryl, or aralkyl phosphates, thiophosphates, or phosphites, etc.; neutral aromatic sulfur compounds of relatively high boiling temperatures such as diaryl sulfides, diaryl disulfides, alkyl aryl disulfides, e. g. diphenyl sulfide, diphenol sulfide, dicresol sulfide, dixylenol sulfide, methyl butyl diphenol sulfide, dibenzyl sulfide, corresponding di- and tri-sulfides, etc.; sulfurized fatty oils or esters of fatty acids and monohydric alcohols, e. g. sperm oil, jojoba oil, etc., in which the sulfur is strongly bonded; sul-

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

Additional ingredients other than extreme pressure additives may comprise anti-wear agents such as oil-soluble urea or thio-urea derivatives, e. g. urethanes, allophanates, carbazides, carbazones, etc.; or rubber, poly-isobutylene, polyvinyl esters, or other high molecular weight oil-soluble polymers to improve the stability of the grease; or pour point depressors to further lower the pour point of the oil; or stabilizer to reduce bleeding such as glycerine (less than .1% by weight); and V. I. improvers such as poly-isobutylenes of molecular weights above about 800, volatilized paraffin wax, unsaturated polymerized esters of fatty acids, and monohydric alcohols and other high molecular weight oil-soluble compounds.

Example I

A low temperature grease according to this invention was prepared by a process comprising making a slurry in an open kettle of lithium stearate and distillate oil having a Saybolt Universal viscosity at 100° F. of 62 sec., a pour point of -75° F. and a V. G. C. of .8468. The slurry was continuously agitated and heated to a temperature of about 375° F. At this temperature phenyl alpha naphthylamine was added to the grease. The temperature of the resulting mixture was then brought up to between about 385° F. and 400° F. for a period of about 15 minutes and then the grease was drawn from the kettle and cooled as quickly as possible in open pans one inch deep. The cooled grease was then worked to remove any lumps that might be present therein. Amounts of the ingredients were such that the composition of this grease was as follows:

	Per cent by weight
Lithium stearate	7.00
Free stearic acid	.02
Phenyl alpha naphthylamine	.20
Mineral oil	92.78
	100.00

This grease was a smooth, non-corrosive, light-colored, homogeneous grease having a consistency of about 275 as measured by the A. S. T. M. grease penetrometer. At the end of 50 hours it bled less than 1.5% and was tested to be an effective lubricant at temperatures as low as -67° F.

Example II

Eight other samples of such lithium soap greases were similarly prepared, containing (1) no amine, (2) .1% and (3) .25% phenyl alpha naphthylamine; (4) .1% and (5) .25% phenyl beta naphthylamine; (6) .1% N-N'-dibutyl para-phenylene diamine; (7) .1% and (8) .25% alkyl phenols boiling between 200° C. and 220° C.; which eight samples were tested for oxidation stability by the 100-hour Norma-Hoffmann oxidation test. This test is as follows: A sample of the grease is charged into a bomb under an initial pressure of 110 pounds p. s. i. of oxygen and the bomb is placed in a bath at 210° F. A pressure

gauge measures the pressure. The time required is recorded for the pressure to drop due to adsorption of the oxygen by the grease. The following table shows the results obtained on these samples:

Sample No.	Inhibitor used	Per cent wt. amt. inhibitor	Consistency	Lbs./in. ³ pres. drop	Hours time
1	Phenyl alpha naphthylamine.	.1	290	5	3
2	do.	.1	266	0	100
3	do.	.25	268	5	210
4	Phenyl beta naphthylamine.	.1	262	0	100
5	do.	.1	262	5	450
6	do.	.25	282	5	85
7	N-N'-dibutyl para-phenylene diamine.	.1	244	0	100
8	Alkyl phenols, B. P. 200° C.-220° C.	.1	241	0	610
	do.	.25	250	5	1,030
			279	2.5	78
				5	100
					130

The oxidation stability limits allowed by the Army and Navy Aeronautic Specification AN-G-3 for low temperature grease are 5 pounds p. s. i. drop in pressure after 100 hours of oxidation. Thus, samples 2, 3, 5, 6 and 8 meet these requirements.

The low temperature greases of this invention are particularly applicable for lubricating mechanisms, including ball bearings, that are used in cold climates as well as mechanisms of transportation including aircraft which operate within short periods of time between tropical temperatures at sea level and subzero temperatures at high altitudes.

We claim as our invention:

1. A low temperature grease consisting essentially of a hydrocarbon oil having a V. G. C. greater than .84 and a pour point below -60° F., and containing between about 3% and 10% by weight of a lithium soap of a fatty acid of 12 or more carbon atoms, between about .01% and .5% by weight of free fatty acid having 12 or more carbon atoms and between about .01% and 2% by

weight of an oxidation inhibitor selected from the class consisting of N-alkylated para-phenylene diamines and polynuclear aromatic amines.

2. The grease of claim 1 wherein the soap is lithium stearate.

3. The grease of claim 1 containing between about 6% and 9% by weight of said lithium soap.

4. The grease of claim 1 containing between .03% and .2% by weight of said free fatty acid.

5. A low temperature grease stable to oxidation consisting essentially of a hydrocarbon oil having a V. G. C. greater than .84, a pour point below -60° F. and an S. U. V. at 100° F. of less than 100 seconds, and containing between about 3% and 10% by weight of a lithium soap of a fatty acid of 12 or more carbon atoms, between .01% and .5% by weight of free fatty acid having 12 or more carbon atoms, and between about .01% and 2% by weight of an oxidation inhibitor.

6. The grease of claim 5 wherein the oxidation inhibitor is selected from the class of N-alkylated para-phenylene diamines and polynuclear aromatic amines.

7. The grease of claim 5 wherein the oxidation inhibitor is phenyl alpha naphthylamine.

8. The grease of claim 5 wherein the oxidation inhibitor is phenyl beta naphthylamine.

9. The grease of claim 5 wherein the oxidation inhibitor is N-N'-dibutyl para-phenylene diamine.

10. The grease of claim 5 containing between .1% and 1% by weight of said oxidation inhibitor.

11. The grease of claim 5 wherein the hydrocarbon oil has an S. U. V. at 100° F. of between about 50 and 90 seconds.

12. A low temperature grease consisting essentially of a hydrocarbon oil having a V. G. C. greater than .84 and a pour point below -60° F., and containing between about 6% and 9% by weight of a lithium soap of a fatty acid of 12 or more carbon atoms and between about .01% and .5% by weight of free fatty acid having 12 or more carbon atoms.

HAROLD A. WOODS.

JACOBUS M. PLANTFEBER.