

UNITED STATES PATENT OFFICE

2,506,906

STABILIZED LUBRICATING GREASE
COMPOSITIONS

Herschel G. Smith, Wallingford, and Troy L. Cantrell, Lansdowne, Pa., assignors to Gulf Oil Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

No Drawing. Application May 19, 1949,
Serial No. 94,252

10 Claims. (Cl. 252-42.4)

1

This invention relates to stabilized lubricating grease compositions, and more particularly to grease compositions having increased stability against oil separation and structural breakdown at high and low temperatures, and improved resistance to oxidation.

This application is a continuation-in-part of our prior copending application Serial No. 44,578, filed August 16, 1948.

In general, when greases are employed under operating conditions for extended periods of time, they have a tendency to become oxidized, resulting in the formation of gummy substances which prevent satisfactory lubricating action. When this occurs, it necessitates complete change of the lubricating grease which has become fouled due to oxidative deterioration. Accordingly, it is highly desirable to increase the resistance of greases to such deterioration.

Another serious problem encountered in the use of grease compositions is that of "bleeding." The tendency of a mineral lubricating oil base to separate or bleed from a grease composition in which the oil has been compounded is well known in the art. Excessive bleeding will tend to result in a complete breakdown of the grease involved, to the detriment of any mechanism lubricated thereby.

Still another serious problem is encountered when greases are employed at either relatively high or relatively low temperatures, which tend to promote structural breakdown of grease compositions.

Accordingly, it is an object of this invention to provide improved lubricating grease compositions characterized by their resistance to oxidation.

A further object of this invention is the provision of improved lubricating grease compositions having increased stability against oil separation and structural breakdown at relatively high and low temperatures.

These and other objects are accomplished by the present invention wherein we provide improved grease compositions comprising a mineral lubricating oil thickened to the consistency of a grease by a soap, and relatively small stabilizing amounts of substantially neutral condensation products of formaldehyde and higher fatty mono-carboxylic acid esters of a mono-alkylated phenol, the higher fatty acid being a saturated or mono-olefinic fatty acid having at least 8 carbon atoms, and the alkyl substituent of the mono-alkylated phenol having from 4 to 12 carbon atoms.

Such esters, which are added to grease compositions in accordance with our invention, are described and claimed in our copending application hereinabove identified. As shown therein, the condensation products are prepared by first esterifying a mono-alkylated phenol with a

2

higher fatty mono-carboxylic saturated or mono-olefinic acid containing at least 8 carbon atoms. In general, the esterification reaction is conducted at a temperature not in excess of 220° F., employing conventional esterification catalysts and techniques. The esterified mono-alkylated phenol is then condensed with formaldehyde at a moderately elevated temperature of about 210° F., the mol ratio of alkylated phenol ester to formaldehyde varying from 1:1 to 1:2.

As stated, the alkyl substituent of the mono-alkylated phenols employed in preparing the addition agents for use in accordance with our invention have from 4 to 12 carbon atoms. It is preferred to prepare these alkylated phenols by alkylation of phenol with an olefin having from 4 to 12 carbon atoms in the presence of a concentrated sulfuric acid catalyst. Thus, representative olefins or olefin-containing materials which are employed for the alkylation of phenol are butene-1, isobutylene, the amylenes, refinery gas, diisobutylene and triisobutylene. The use of diisobutylene is preferred since the alkylated phenol obtained is primarily para-(alpha, alpha, gamma, gamma) tetramethylbutyl phenol, which is particularly useful in preparing grease additives. However, the n-alkyl phenols having 4 to 12 carbon atoms in the alkyl substituent, prepared by alkylating phenol with an n-alkyl halide in the presence of a Friedel-Crafts catalyst, such as aluminum chloride, can also be employed. Accordingly, any mono-alkylated phenol having from 4 to 12 carbon atoms in the alkyl substituent is useful. Among these alkylated phenols are n-butyl phenol, sec-butyl phenol, tert-butyl phenol, n-amyl phenol, sec-amyl phenol, tert-amyl phenol, n-hexyl phenol, n-octyl phenol, (alpha, alpha, gamma, gamma) tetramethylbutyl phenol, triisobutyl phenol, and mixtures thereof.

The use of alkylated phenols having an alkyl substituent of less than 4 carbon atoms is not satisfactory because the resulting esterified condensation products prepared from such phenols are not sufficiently soluble in mineral lubricating oils and mineral oil lubricant compositions to serve the functions of an efficient additive. Similarly, if the alkyl substituent of the alkylated phenol exceeds 12 carbon atoms, the resulting esterified condensation products tend to be unstable and to become insoluble in mineral oils.

As stated above, suitable fatty mono-carboxylic acids which are esterified with the alkylated phenol before condensation with formaldehyde are the saturated and the mono-olefinic fatty acids having at least 8 carbon atoms. A preferred group of fatty acids are the fatty acids of from 8 to 32 carbon atoms. The saturated fatty acids include caprylic, pelargonic, capric, undecylic, lauric, myristic, palmitic, stearic,

arachidic, behenic, carnaubic, cerotic, melissic and psyllaic acids. The mono-olefinic fatty acids include nonylenic, decylenic, undecylenic, oleic, ricinoleic, erucic and brassidic acids. Mixtures of fatty acids having at least 8 carbon atoms, as obtained from the saponification of fats and fatty oils for example, may also be employed. Naphthenic acids and Hydrofol acids (hydrogenated fish oil fatty acids) are also suitable saturated fatty acids. The fatty acids are generally employed in substantially equimolar amounts with the mono-alkylated phenols. Conventional esterification catalysts, such as sulfuric acid and p-toluene sulfonic acid, can be employed for the esterification.

When the fatty acid has less than 8 carbon atoms, the condensation products of formaldehyde and the fatty acid esters of the mono-alkylated phenols tend to become hard and brittle and of poor solubility in mineral oils. These effects increase as the length of the fatty acid chain decreases. Accordingly, the fatty acid must have at least 8 carbon atoms.

In the condensation of the esterified mono-alkylated phenol with formaldehyde to yield the additives of this invention, the condensation takes place at a mildly elevated temperature of about 210° F. by refluxing the reactants until all of the formaldehyde is consumed. Either acid or alkaline condensing agents may be employed. The condensation product of the mono-alkylated phenol ester and formaldehyde is then dehydrated in the usual manner.

The following example illustrates the preparation of the additives which are employed in accordance with our invention.

Example I

Into a suitable reaction vessel equipped with a stirrer and means for heating and cooling, there were charged 112 pounds (1 pound mol) of octylene (commercial diisobutylene) and 94 pounds (1 pound mol) of phenol. Agitation was begun and 10 pounds of 96% sulfuric acid were gradually added. The temperature of the reaction was so controlled that it did not exceed 220° F. The resulting product was primarily para-(alpha, alpha, gamma, gamma) tetramethylbutyl phenol.

One pound mol of the octyl phenol prepared as described hereinabove and still containing the sulfuric acid catalyst, and 1 pound mol of lauric acid were charged into a suitable closed reaction vessel equipped with a stirrer, a reflux condenser and means for heating and cooling. Agitation was begun and the charge heated while controlling the temperature so that it did not exceed 220° F. Upon completion of the esterification reaction, 1 pound mol of formaldehyde (in a 37% by weight aqueous solution) was added and the mixture refluxed at a temperature of 205–210° F.

for two hours. The charge was then transferred to an open reaction vessel and the temperature increased to 500° F. to complete the reaction and dehydrate the product. The resulting dehydrated product had the following properties:

Penetration, ASTM D5-25:

77° F., 100 grams, 5 sec. ----- 60

Penetration, ASTM D217-44T:

77° F., 150 grams, 5 sec., unworked ---- 43

Neutralization No. ----- 12.2

We have found that the above described condensation products may be compounded with a wide variety of greases to impart advantageous properties thereto. Such greases may be described as mineral lubricating oils thickened to the consistency of a grease by suitable soaps. These greases themselves are well known in the art and may be manufactured by conventional methods. For example, the mineral lubricating oil bases include paraffinic, naphthenic and mixed base mineral lubricating oils, representative examples of which are shown in the following table. As known in the art, the soaps used in thickening the mineral oil base to a grease are fatty acid soaps derived from fatty materials such as tallow, lard, cottonseed oil, stearic acid, soy bean fatty acids and various other fats and fatty acids. The metal of the soap can be an alkali metal, an alkaline earth metal, and various other metals such as lead, zinc, chromium, tin, aluminum, iron, cobalt, nickel, cadmium, mercury, etc. As will be understood by those skilled in the art, the soap and mineral oil base will be selected in accordance with the specific properties of the grease it is desired to manufacture.

In accordance with our invention, small proportions of the herein-described condensation products in a grease will substantially stabilize the grease against bleeding and structural breakdown at high and low temperatures, and will improve the resistance of the grease to oxidation. The amount of condensation product used is sufficient to retard separation of oil from the grease or inhibit oxidation of the grease, the same amount of condensation product conferring both effects, and in general, small amounts, from 0.1 to 5 per cent by weight on the grease, will suffice. The condensation product may be dispersed in an already formed grease by simple mixing, or it may be introduced during the manufacture of the grease, for example by dissolving it in the mineral lubricating oil base used in the manufacture of the grease.

As has been stated, the grease compositions of the present invention may be compounded from a variety of lubricating oil base stocks. The table below is illustrative of mineral lubricating oils which may advantageously be used as a base for the greases referred to; it sets forth the inspection data of such oils.

Table

Base Oil Stock.....	200 MC Neutral Oil	300 Vis. Texas Oil	100/2 Paraf- fin Oil	150 MC Oil	500/3 Texas Oil	1900/5 Texas Oil
Gravity, °API.....	26.2	22.9	27.0	25.4	21.4	21.5
Viscosity, SUV:						
100° F.....	210	304	102.2	2,607	510	1,950
210° F.....	45.4	47.9	38.8	156	53.9	97
Viscosity Index.....	70	62	62	97	39	39
Flash, O.C., °F.....	415	365	355	585	385	475
Fire, O.C., °F.....	475	405	410	650	440	555
Pour, °F.....	+15	-15	+10	+8	-10	+5
Color, NPA.....	2.0	4.75	1.75	4.75	3.0	4.75
Carbon Residue, Per Cent.....	0.02	0.08	0.01	1.10	0.09	0.27
Neutralization No.....	0.02	0.02	0.06	0.05	0.05	0.08

5

The following example is illustrative of a preferred method of preparing a lubricating grease composition according to our invention:

Example II

Into a closed pressure type steam heated kettle, equipped with double motion stirring paddles, were charged 15.65 parts by weight of Hydrofol acids, 1.2 parts by weight of a condensation product prepared in accordance with Example I, 2.05 parts by weight of hydrated lime in a slurry of 4 parts water, and 17 parts by weight of mineral lubricating oils having the following characteristics and blended in the following proportions:

Texas oil (500 SUV/100° F.)	74.5
Mid-Continent Bright Stock	
(150 SUV/210° F.)	6.5

The kettle was closed, saturated steam applied to the heating jacket and the stirring mechanism started. After two hours an internal temperature of 290° F. and a pressure of 39 p. s. i. were attained. The supply of steam to the steam heating jacket was then cut off and the internal pressure of the kettle was reduced to atmospheric pressure by bleeding steam therefrom for a period of ¾ hour. Thereafter, the kettle was opened to the atmosphere and the temperature of the contents was gradually raised to 240° F. over a ½ hour period and further gradually raised to 275° F. over another ½ hour period while adding 13 parts by weight of the blended oil. Steam to the heating jacket was again cut off and 0.94 part by weight of stearic acid was introduced to the mixture. Following this, 51 parts by weight of the blended oil were added over a period of ½ hour while cooling to 250° F. at which time 0.025 part by weight of water was added. The contents of the kettle were then cooled to 175° F. in the course of ¾ hour. Hydrated lime in the amount of 0.21 part by weight was then sprinkled slowly into the kettle over ¼ hour period. The 0.015 part by weight of water was added and the kettle closed and stirred under 20 inches of vacuum for 2 hours while maintaining an internal temperature of 175° F. to 180° F. Grease was then drawn out of the kettle through a 60 mesh screen.

The grease thus prepared had the following make-up and properties as compared to an otherwise identical grease not containing the condensation product.

	Unimproved Grease	Improved Grease
Make-up, percent by Wt.:		
500/2.5 Texas Oil (500 SUV/100° F.)	75.6	74.5
150 MC Bright Stock (150 SUV/210° F.)	6.6	6.5
Calcium Soap of Hydrofol Acids	16.7	16.7
Calcium Soap of Stearic Acid	1.0	1.0
Excess Alkali calculated as Ca(OH) ₂	0.1	0.1
Ester of Example I	trace	1.2
Water by Distillation	trace	trace
Inspection:		
Dropping Point, °F.—		
ASTM D566-42	267	268
Flow Point, °F.—		
Navy Dept. Spec. 14-G-1d	274	272
Penetration, ASTM D217-44T—		
77° F., 150 G., 5 Sec.:		
Unworked	164	166
Worked	270	270
Free Alkalinity as CaO, percent	trace	trace
Oil Separation, 175° F., 7 days, percent—		
AAR M-914-42	8.0	nil
Freezing Point, °F.—		
AAR M-914-42		-50
Oxidation Test, 176° F., Hrs.	18	500+
Pressure Drop, Lbs.	20	3

6

This composition was found to be extremely stable against oil separation or structural breakdown at temperatures up to approximately 200° F. As shown, the grease is further characterized by its high resistance to oxidation.

Further grease compositions compounded in a manner similar to that set forth in Example II and embodying the type of esters prepared as in Example I are illustrated by the following examples:

Example III

	Unimproved Grease	Improved Grease
Make-up, percent by Wt.:		
500/2.5 Texas Oil (500 SUV/100° F.)	75.7	74.4
150 MC Bright Stock (150 SUV/210° F.)	6.6	6.5
Calcium Soap of Hydrofol Acids	13.2	13.2
Sodium Soap of Hydrofol Acids	1.8	1.8
Calcium Soap of Oleic Acid	2.7	2.7
Ester of Example I using Oleic Acid instead of Lauric Acid		1.4
Inspection:		
Dropping Point, °F.—		
ASTM D566-42	225	225
Flow Point, °F.—		
Navy Dept. Spec. 14-G-1d	254	255
Penetration, ASTM D217-44T—		
77° F., 150 G., 5 Sec.:		
Unworked	168	168
Worked	289	289
Free Acidity as Oleic Acid, percent	1.0	0.9
Oil Separation, 175° F., percent—		
AAR M-914-42	15.0	nil
Freezing Point, °F.—		
AAR M-914-42		-50
Mineral Oil Content, percent by Wt.	82.3	80.9
Oxidation Test, 176° F., Hrs.	70	500+
Pressure Drop, Lbs.	20	3

Example IV

	Unimproved Grease	Improved Grease
Make-up, percent by Wt.:		
500/2.5 Texas Oil (500 SUV/100° F.)	76.3	74.9
150 MC Bright Stock (150 SUV/210° F.)	6.6	6.5
Calcium Soap of Stearic Acid	14.3	14.3
Sodium Soap of Oleic Acid	1.9	1.9
Calcium Soap of Oleic Acid	0.9	0.9
Excess Alkali calculated as Ca(OH) ₂	trace	0.03
Ester of Example I using Naphthenic Acids instead of Lauric Acid		1.5
Inspection:		
Dropping Point, °F.—		
ASTM D566-42	232	234
Penetration, ASTM D217-44T—		
77° F., 150 G., 5 Sec.:		
Unworked	219	217
Worked	320	315
Free Acidity as Oleic Acid, percent	0.01	0.02
Mineral Oil Content, percent by Wt.	82.9	81.4
Oxidation Test, 176° F., Hrs.	50	500+
Pressure Drop, Lbs.	20	2

The remarkable stability of grease compositions containing the condensation products employed in our invention is readily apparent from the inspection data shown in the foregoing examples. The oil separation test indicates that the grease compositions of our invention exhibit exceptional structural stability and reduced tendency toward bleeding. The oxidation test also indicates that the compositions of our invention exhibit an excellent stability against oxidation. The oxidation test referred to hereinabove is a modification of the Norma-Hoffman test method. Briefly, the test comprises weighing a total of 20 grams of the grease to be tested equally into five stainless steel sample trays, and placing the trays into a pressure bomb equipped with a valve and pressure gauge and adjusted to a volume of 173 cc. ± 2 cc. The bomb is then closed and flushed five times by filling it with oxygen to about 100 lb./sq. in. pressure, and then allowing the oxygen

to escape. The bomb is then filled with oxygen to 105 lb./sq. in. pressure and immersed in an oil bath held at $176^{\circ}\text{F.} \pm 0.5^{\circ}\text{F.}$ After two hours, oxygen is released from the bomb so as to adjust the pressure to exactly 110 lb./sq. in. The pressure is read and recorded every two hours until the pressure drops 20 lb./sq. in., or for 500 hours if the pressure does not drop as much as 20 lb./sq. in. in that length of time. The oxidation stability of the grease is reported as the number of hours required for the pressure in the bomb to drop 20 lbs., unless this does not occur in 500 hours. In the latter event, the result is reported as 500+.

The grease compositions of our invention may include additional modifying agents, as will be apparent to those skilled in the art, provided they contain the condensation products disclosed herein. Resort may be had to such modifications and variations as fall within the spirit of the invention and the scope of the appended claims.

We claim:

1. A grease composition comprising a mineral lubricating oil thickened to a grease by a soap, and a small amount of a substantially neutral condensation product of formaldehyde and a higher fatty mono-carboxylic acid ester of a mono-alkylated phenol, the higher fatty acid being selected from the class consisting of saturated and mono-olefinic fatty acids having at least 8 carbon atoms and the alkyl substituent of the alkylated phenol having from 4 to 12 carbon atoms, said condensation product being present in an amount sufficient to retard oxidation of the grease.

2. The composition of claim 1, wherein the higher fatty acid is a saturated fatty acid.

3. The composition of claim 1, wherein the higher fatty acid is a mono-olefinic fatty acid.

4. A grease composition comprising a mineral lubricating oil thickened to a grease by a soap, and a small amount of a substantially neutral condensation product of formaldehyde and a higher fatty mono-carboxylic acid ester of a mono-alkylated phenol, the higher fatty acid being selected from the class consisting of saturated and mono-olefinic fatty acids having from 8 to 32 carbon atoms and the alkyl substituent of the alkylated phenol having from 4 to 12 carbon atoms; the molar ratio of alkylated phenol ester to formaldehyde in the condensation product varying from 1:1 to 1:2, said condensation product being present in an amount sufficient to retard oxidation of the grease.

5. The composition of claim 4, wherein the said condensation product is present in an amount of from 0.1 to 5 per cent by weight on the grease.

6. A grease composition comprising a mineral lubricating oil thickened to a grease by a soap, and a small amount of a substantially neutral condensation product of formaldehyde and a higher fatty mono-carboxylic acid ester of a mono-alkylated phenol, the higher fatty acid being selected from the class consisting of saturated and mono-olefinic fatty acids having from 8 to 32 carbon atoms, and the alkylated phenol being (alpha, alpha, gamma, gamma) tetramethylbutyl phenol, said condensation product being present in an amount sufficient to retard oxidation of the grease.

7. A grease composition comprising a mineral lubricating oil thickened to a grease by a soap, and a small amount of a substantially neutral condensation product of formaldehyde and the lauric acid ester of (alpha, alpha, gamma, gamma) tetramethylbutyl phenol, said condensation product being present in an amount sufficient to retard oxidation of the grease.

8. A grease composition comprising a mineral lubricating oil thickened to a grease by a soap, and a small amount of a substantially neutral condensation product of formaldehyde and the oleic acid ester of (alpha, alpha, gamma, gamma) tetramethylbutyl phenol, said condensation product being present in an amount sufficient to retard oxidation of the grease.

9. A grease composition comprising a mineral lubricating oil thickened to a grease by a soap, and a small amount of a substantially neutral condensation product of formaldehyde and the naphthenic acid ester of (alpha, alpha, gamma, gamma) tetramethylbutyl phenol, said condensation product being present in an amount sufficient to retard oxidation of the grease.

10. The composition of claim 6 wherein the said condensation product is present in an amount of from 0.1 to 5 per cent by weight on the grease.

HERSCHEL G. SMITH.
TROY L. CANTRELL.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,487,378	Roehner et al.	Nov. 8, 1949