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STABILIZED LUBRICATING GREASE COMPOSITIONS

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9 Claims. (Cl. 252—42.4)

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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. 44,577, 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 a substantially neutral higher fatty mono-carboxylic acid ester of a fusible, soluble mono-alkylated phenol-formaldehyde condensation product, 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.

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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 esters are prepared by esterification of a fusible, soluble mono-alkylated phenol-formaldehyde condensation product with a higher fatty saturated or mono-olefinic mono-carboxylic acid containing at least 8 carbon atoms at a temperature not in excess of 500° F. The fatty acid is employed in substantially equimolar amounts with the alkylated phenol used in making the alkylated phenol-formaldehyde condensation product, whereby the free hydroxyl groups of the alkylated phenol-formaldehyde condensation product are esterified by the higher fatty acid to produce substantially neutral waxy esters. Conventional esterification catalysts, such as sulfuric acid and p-toluene sulfonic acid can be employed.

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 phe-

nol, 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 (1) the resulting esterified condensation products prepared from such phenols are insufficiently soluble in mineral lubricating oils and mineral oil lubricant compositions to serve the functions of an efficient additive and (2) it is difficult to secure substantially neutral, oil-soluble products by simple esterification of the phenol-formaldehyde condensation product and the higher fatty acid. 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.

The above described mono-alkylated phenols, before the esterification reaction, are first condensed in conventional manner with formaldehyde to produce a fusible, soluble alkylated phenol - formaldehyde condensation product. The mol ratio of alkylated phenol to formaldehyde may vary from 1:1 to 1:2. Either alkaline or acid condensing agents are employed, as will be understood in the art. The resulting condensation product is then dehydrated in the usual manner.

As stated above, suitable fatty mono-carboxylic acids which are esterified with the phenol-formaldehyde condensation product 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.

When the fatty acid has less than 8 carbon atoms, the esterified condensation products 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.

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

EXAMPLE I

a. Preparation of alkylated phenol.—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 per cent 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.

b. Preparation of alkylated phenol-formaldehyde condensation product.—To the alkylated phenol in the same reaction vessel and still containing the sulfuric acid, there were added 160 pounds of a 37 per cent by weight aqueous formaldehyde solution, (2 pound mols of anhydrous formaldehyde). The mixture was agitated and heated at 160° F., and the temperature gradually increased to 220° F. until all of the formaldehyde was consumed. The temperature was then raised to 300° F. to dehydrate the condensation product.

c. Esterification of alkylated phenol-formaldehyde condensation product.—To the dehydrated alkylated phenol - formaldehyde condensation product, there were then added 284 pounds (1 pound mol) of stearic acid and the mixture was agitated and heated to 400° F. until esterification was substantially complete as evidenced by the formation of no more water. The product was then permitted to cool. The product was a light-brownish waxy material, resembling beeswax in odor and appearance. It had the following properties:

Specific gravity, solid state	1.11
Melting point: °F., capillary tube	108–120
Neutralization No.	8.6

We have found that the above described esters 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 esters 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 ester used is sufficient to retard separation of oil from the grease or inhibit oxidation of the grease, the same amount of ester conferring both effects, and in general, small amounts, from 0.1 to 5 per cent by weight on the grease, will suffice. The ester 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. Table I, 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 I

Base Oil Stock / Inspection	200 MC Neutral Oil	300 Vis. Texas Oil	100/2 Paraffine Oil	150 MC Oil	500/3 Texas Oil	1900/5 Texas Oil
Gravity, °API	26.2	22.9	27.0	26.4	21.4	21.5
Viscosity, SUV:						
100° F.	210	305	102.2	2,607	510	1,950
210° F.	45.4	47.9	38.8	156	53.9	97
Viscosity Index	70		62	97		39
Flash, OC, °F.	415	365	355	585	385	475
Fire, OC, °F.	475	405	410	650	440	555
Pour, °F.	+15	−15	+10	+5	−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	0.03

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 an ester prepared in accordance with Example I except that Hydrofol acids were used instead of stearic acid, 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:

	Parts
Texas oil (500 SUV/100° F.)	74.5
Mid-Continental 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. Then 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° 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 ester.

	Improved Grease	Unimproved Grease
Make-up, Percent by Wt.		
500/2.5 Texas Oil (500 SUV/100° F.)	74.5	75.6
150 MC Bright Stock (150 SUV/210° F.)	6.5	6.6
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 (except Hydrofol acids substituted for stearic acid)	1.2	
Water by Distillation	trace	trace
Inspection:		
Dropping Point, ° F.— ASTM D566-42	262	262
Flow Point, ° F.— Navy Dept. Spec. 14-G-1d	270	270
Penetration, ASTM D217-44 T— 77° F., 150 G., 5 Sec.:		
Unworked	170	170
Worked	273	282
Free Alkalinity as CaO, percent	0.05	0.05
Oil Separation, 175° F., 7 days, percent— AAR M-914-42	nil	5.0
Freezing Point, ° F.— AAR M-914-42	−50	−50
Oxidation Test, 176° F., Hrs.	500+	25
Pressure Drop: Lbs.	3	20

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 comparative examples:

EXAMPLE III

	Improved Grease	Unimproved Grease
Make-up, percent by Wt.:		
500/2.5 Texas Oil (500 SUV/100° F.)	74.4	75.7
150 MC Bright Stock (150 SUV/210° F.)	6.5	6.6
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	1.4	
Inspection:		
Dropping Point, ° F.— ASTM D566-42	227	227
Flow Point, ° F.— Navy Dept. Spec. 14-G-1d	258	258
Penetration, ASTM D217-44T— 77° F., 150 G., 5 Sec.:		
Unworked	166	165
Worked	287	286
Free Acidity as Oleic Acid, percent	1.11	1.0
Oil Separation, 175° F., percent— AAR M-914-42	0.4	15.0
Freezing Point, ° F.— AAR M-914-42	−55	−50
Mineral Oil Content, percent by Wt.	80.9	82.3
Oxidation Test, 176° F., Hrs.	500+	60
Pressure Drop, Lbs.	2	20

EXAMPLE IV

	Improved Grease	Unimproved Grease
Make-up, percent by Wt.:		
500/2.5 Texas Oil (500 SUV/100° F.)	74.9	76.3
150 MC Bright Stock (150 SUV/210° F.)	6.5	6.6
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 $Ca(OH)_2$	0.03	0.03
Ester of Example I	1.5	----------
Inspection:		
Dropping Point, ° F. ASTM D566-42	236	234
Penetration, ASTM D217-44T— 77° F., 150 G., 5 Sec.:		
Unworked	219	221
Worked	319	321
Free Acidity as Oleic Acid, percent	0.55	0.6
Mineral Oil Content, percent by Wt.	81.4	82.9
Oil Separation, 175° F., percent AAR M-914-42	0.2	12.0
Oxidation Test, 176° F., Hrs.	500+	45
Pressure Drop, Lbs.	2	20

EXAMPLE V

	Improved Grease	Unimproved Grease
Make-up, Per Cent by Wt.:		
500/2.5 Texas Oil (500 SUV/100° F.)	74.2	75.3
150 MC Bright Stock (150 SUV/210° F.)	6.5	6.6
Calcium Soap of Hydrofol Acids	17.0	17.0
Calcium Soap of Stearic Acid	0.8	0.8
Excess Alkali calculated as $Ca(OH)_2$	0.3	0.3
Ester of Example I	1.2	----------
Inspection:		
Dropping Point, °F.— ASTM D566-42	282	282
Penetration, ASTM D217-44T— 77° F., 150 G., 5 Sec.:		
Unworked	228	228
Worked	328	328
Free Acidity as Oleic Acid, Per Cent	0.15	0.1
Oil Separation, 175° F., Per Cent— AAR M-914-42	nil	4.0
Mineral Oil Content, Per Cent by Wt.	80.7	81.9
Oxidation Test, 176° F., Hrs.	500+	70
Pressure Drop, Lbs.	4	20

EXAMPLE VI

	Improved Grease	Unimproved Grease
Make-up, Per Cent by Wt.:		
500/2.5 Texas Oil (500 SUV/100° F.)	73.8	74.9
150 MC Bright stock (150 SUV/210° F.)	6.4	6.5
Calcium Soap of Hydrofol Acids	18.5	18.5
Excess Alkali calculated as $Ca(OH)_2$	0.1	0.1
Ester of Example I	1.2	----------
Inspection:		
Dropping Point, °F.— ASTM D566-42	246	244
Flow Point, °F.— Navy Dept. Spec. 14-G-1d	295	295
Penetration, ASTM D217-44 T— 77° F., 150 G., 5 Sec.:		
Unworked	177	177
Worked	254	253
Free Acidity as Oleic Acid, Per Cent	0.09	1.0
Oil Separation, 175° F., Per Cent— AAR M-914-42	nil	7.0
Freezing Point, °F.— AAR M-914-42	−50	−50
Mineral Oil Content, Per Cent by Wt.	80.2	81.4
Oxidation Test, 176° F., Hrs.	500+	35
Pressure Drop, Lbs.	3	20

The remarkable stability of grease compositions containing the esters 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 grease 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° F.±0.5° 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 an ester as 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.

What is claimed is:

1. A grease composition comprising a mineral lubricating oil thickened to a grease by a soap, and a small amount of a substantially neutral higher fatty mono-carboxylic acid ester of a fusible, soluble mono-alkylated phenol-formaldehyde condensation product, 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 ester 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 higher fatty mono-carboxylic acid ester of a fusible, soluble mono-alkylated phenol-formaldehyde condensation product, 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 to formaldehyde in the alkylated phenol-formaldehyde condensation product varying from 1:1 to 1:2, said ester being present in an amount sufficient to retard oxidation of the grease.

5. The composition of claim 4, wherein the said ester 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 higher fatty mono-carboxylic acid ester of a fusible, soluble mono-alkylated phenol-formaldehyde condensation product, 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 be-

ing (alpha, alpha, gamma, gamma) tetramethylbutyl phenol, said ester 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 stearic acid ester of a fusible, soluble (alpha, alpha, gamma, gamma) tetramethylbutyl phenol-formaldehyde condensation product, said ester being present in an amount sufficient to retard oxidation of the grease.

8. The composition of claim 7, wherein the said ester is present in an amount of from 0.1 to 5 per cent by weight on 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 stearic acid ester of a fusible, soluble tertiary-butyl phenol-formaldehyde condensation product, said ester being present in an amount sufficient to retard oxidation of the grease.

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REFERENCES CITED

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

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

Certificate of Correction

Patent No. 2,506,905 May 9, 1950

HERSCHEL G. SMITH ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 5, Table I, third column thereof, for "205" read *305*;

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 25th day of July, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.