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LUBRICATING GREASE COMPOSITION

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This invention relates to lubricating grease compositions, and more particularly, to grease compositions which find advantageous applications in the lubrication of light mechanisms, such as small motors, air motors and the like, exemplified by the type of motor used to operate windshield wipers.

In general, when such motors as referred to hereinabove have been operated without a change of lubricant over a prolonged period, the lubricating composition becomes oxidized, resulting in the formation of gummy substances, which prevent satisfactory motor operation. This gum formation is particularly detrimental in the case of light mechanisms, since rather light greases are almost inevitably used for such devices. In fact, these light greases may aptly be termed semi-fluid oils. However, the problem of oxidative deterioration is not uniquely confined to light greases, but is encountered in the heavier types of greases as well.

Another serious problem encountered by users 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 break-down of the grease involved, to the detriment of any mechanism lubricated thereby.

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 suitable fluid consistency to be used in the operation of small motors without undue energy loss, and of such a nature that a single application of the lubricant will be sufficient for the life of the motor.

A still further object of this invention is the provision of stable lubricating grease compositions of improved homogeneity, such that the tendency for the separation of oil from the grease, i. e. "bleeding" is substantially reduced.

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Other objects will be apparent from the following description.

These 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 a metallo compound obtained by reacting an aqueous slurry of a metal hydroxide selected from the group consisting of barium, strontium, magnesium and calcium hydroxides with formaldehyde at a mildly elevated temperature and condensing the resulting product with aniline and a mono-alkyl phenol having from 4 to 12 carbon atoms in the alkyl substituent, said metallo compound being present in an amount sufficient to stabilize the grease against oxidative deterioration.

The metallo compound, which is added to a grease in accordance with our invention, is described and claimed in the copending application of Smith, Cantrell and Peters, Serial No. 790,440, filed December 8, 1947. As shown therein, the metallo compound is prepared by first reacting an aqueous slurry of the metal hydroxide and formaldehyde at a mildly elevated temperature, say 160° F., but not exceeding 200° F. The exact nature of this reaction product is unknown, but the reaction product contains combined therein the metal of the metal hydroxides. This product is then condensed with aniline and a mono-alkyl phenol having from 4 to 12 carbon atoms in the alkyl substituent. The condensation between the reaction product of the metal hydroxide and formaldehyde, and the aniline and phenol proceeds spontantously upon mixing the reactants. Since the reaction is exothermic, care should be taken not to allow the temperature to exceed about 200° F., otherwise dark colored, highly resinous, insoluble products may result. After the condensation is completed, the temperature is raised to distill off all water, both that formed in the condensation and added with the ractants. The reactants are preferably employed in the proportions of 1 mol of metal hydroxide, 2 to 4 mols of formaldehyde, 0.5 to 1.0 mol of aniline and 2 to 4 mols of the mono-alkyl phenol.

The mono-alkyl phenols used in preparing the metallo compound have from 4 to 12 carbon atoms in the alkyl substituent. Thus, the alkyl substituent may include normal or branched chain butyl, amyl, hexyl, heptyl, octyl, decyl and dodecyl radicals. A preferred alkyl substituent is the tetramethylbutyl radical. The mono-alkyl phenols are preferably obtained by alkylating in known manner, in the presence of concentrated sulfuric acid, phenol with olefins having from 4 to 12 carbon atoms. Olefins, such as butene-1, isobutylene, the amylenes, di-isobutylene and tri-isobutylene may conveniently be employed. It is preferred to conduct the alkylation with di-isobutylene since the resulting product is primarily para tetramethylbutyl phenol.

In view of the multiple points of the respective molecules at which the reactants may react, it is believed that a mixture of compounds is obtained. The designation of the reaction product as a "metallo compound" is intended to cover all the compounds present therein.

The following example illustrates a preparation of the metallo compound used in our greases.

EXAMPLE I

Into a jacketed iron reaction vessel (No. 1) were charged 12.9 parts by weight of phenol and 16.5 parts by weight of di-isobutylene. The vessel was closed and the mixture agitated. Then 0.6 part by weight of 94–98% sulfuric acid was added. Cold water was run through the jacket of the reaction vessel in order to maintain a reaction temperature below 220° F. When all of the materials had been added, the temperature was permitted to attain 220° F. and held at that temperature for four hours. The resulting para tetramethylbutyl phenol was dissolved in 73 parts by weight of a mineral lubricating oil.

Into an enamel lined reaction vessel (No. 2) were charged 4.6 parts by weight of calcium hydroxide with sufficient water to make a slurry, to which was added 14.9 parts by weight of a 37% by weight aqueous solution of formaldehyde. The reactants were heated to a temperature of 160° F. for two hours. Thereafter, the reaction product of the calcium hydroxide and formaldehyde was added to the mineral oil solution of para tetramethylbutyl phenol in reactor vessel No. 1 with agitation for 15 minutes. Then 4.3 parts by weight of aniline were added and the temperature maintained below 200° F. The condensation product was then dried by increasing the temperature to 280° F., distilling off the water, following which the product was filtered. The additive thus prepared had the following properties:

Gravity, °API	20.3
Viscosity, SUV, 210° F.	111.4
Color, NPA	4.75
Neutralization No.	0.92 alk.
Ash as sulfate, per cent	4.513

The reactants in the above example were in the relative molar proportions of 1.0 mol of calcium hydroxide, 3 mols of formaldehyde, 2.3 mols of para tetramethylbutyl phenol and 0.7 mol of aniline.

We have found that the above described metallo compounds 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 a suitable soap. These greases themselves are well known in the art and may be manufactured by conventional methods. For example, the mineral lubricating oil bases may 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 may 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. For the soft greases (semi-fluid oils) disclosed herein, it is preferred to employ the calcium soaps of fatty materials such as tallow, soy bean fatty acids, tallow-soy bean fatty acid mixtures, lard, cottonseed oil, and cottonseed oil-degras mixtures.

In acordance with our invention, small proportions of the hereindescribed metallo compound in a grease will substantially reduce the oxidative deterioration of the grease, as well as reduce any bleeding tendency. The amount of metallo compound used is sufficient to stabilize the grease against oxidative deterioration, and in general, small amounts, from 0.1 to 5.0 per cent by weight on the grease, will suffice. The metallo compound 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.

Considerable success has been obtained with the greases described as applied to the lubrication of small air and electric type motors, such as those used to operate windshield wipers and the like. It has been found that lubricating grease compositions prepared in accordance with this invention and used in such motors remain stable over an extremely long period of time; in fact, a single application of the grease is sufficient for the life of the motor, yet the mechanisms receive sufficient lubrication to prevent undue wear. In such applications, the lubricating grease should be rather light, advantageously approaching what may be termed a semi-fluid oil. The rheological properties of such semi-fluid oils may be specified by the Convis Test, Method 294 Gulf, which is set forth in detail in the copending application of Smith, Serial No. 644,369, filed January 30, 1946 now Patent No. 2,526,832, and entitled "Apparatus for Measuring the Pressure Flow Characteristics of Greases." Briefly stated, the Convis Test reports the time in seconds required for 10 cc. of a grease sample to flow out of a Saybolt Furol viscosimeter tube at a specified temperature, say 77° F., and under a force applied to the grease by a specified weight used to depress a piston which causes the grease to flow. Advantageous semi-fluid oils or soft greases exhibiting a Convis Test of from 125 to 275 seconds at a temperature of 77° F. and a weight on the piston of 300 grams have been prepared and found particularly useful in light mechanisms as described hereinabove. However, this invention is not limited to semi-fluid oils, since a wide variety of grease compositions hav-

ing varied functions and properties are benefited by the compounding therewith of a metallo compound herein described.

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, and sets forth the inspection data of such oils.

Table

Base Oil Stock Inspection	200 M. C. Neutral Oil	300 Vis. Texas Oil	100/2 Paraffine Oil	150 M. C. 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	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

In the following examples, there are shown representative grease compositions prepared in accordance with our invention. Examples II and III are representative of the excellent soft greases useful for lubricating windshield wiper mechanisms.

EXAMPLE II

	Semi-Fluid Oil	Improved Semi-Fluid Oil
Make-up, Per Cent by Weight, Lubricating Grease:		
300 Vis. Texas Oil	91.8	91.3
Calcium Soap of Tallow	6.9	6.9
Glycerine	0.7	0.7
Water	0.6	0.6
Compound of Example I		0.5

In the above example, the grease was prepared in the conventional manner, and the metallo compound dispersed in the grease so prepared.

EXAMPLE III

	Semi-Fluid Oil	Improved Semi-Fluid Oil
Make-up, Per Cent by Weight:		
300 Vis. Texas Oil	91.8	91.3.
Calcium Soap of Tallow	6.9	6.9.
Glycerine	0.7	0.7.
Water	0.6	0.6.
Compound of Example I		0.5.
Inspection: Flow Point, ° F., Navy Dept. Spec. 14-G-1d	133	210.
Consistency, mm.: Braun, 77° F., 2.5 G	60	60.
Convis Test, Furol, Sec.: Method 294, Gulf, 10 cc., 77° F., 300 Grams	156	260.
Color	lt. bluish red	lt. bluish red.
Pour Point, ° F	+152	+160.
Ash, Per Cent As CaO	0.65	0.67.
Reaction	alkaline	alkaline.
Bleeding Test, Per Cent, AN-G-3a Mod., 150° F., 50 Hr.: Separated Oil, Per Cent by Weight	fluid	about 19.
Oxidation Test, ASTM D 942-47T, 210° F., 100 Hr., Pressure Drop, Lb	unstable [1]	29.

[1] 5-lb. pressure drop in 8 hr.; 20 lb. pressure drop in 24 hr.

In the above example, the metallo compound was first dissolved in the base oil, and the base oil then compounded into a grease in conventional manner.

The oxidation test shows beyond doubt that the compositions containing the reaction product of

Example I exhibit a marked superiority against oxidative deterioration over the unimproved composition. The bleeding test indicates that the semi-fluid oil containing this metallo compound was in a more homogeneous state since it exhibited less tendency for the separation of oil from the soap gel.

As stated hereinabove, our invention is not confined to semi-fluid oils but includes a wide variety of other greases of greater consistency.

Examples IV, V and VI below are illustrative of such other grease compositions. Such examples demonstrate the stability against oxidative deterioration and bleeding of the grease compositions containing the metallo compounds as compared to the poorer stability of ordinary grease compositions not containing such metallo compounds.

EXAMPLE IV

	Precision Grease	Improved Precision Grease
Make-up: Per Cent by Weight:		
200 M. C. Neutral Oil	81.6	81.1
150 M. C. Oil	7.1	7.1
Sodium Soap of Tallow	7.0	7.0
Sodium Soap of Stearic Acid	3.5	3.5
Glycerine (Theoretical)	0.7	0.7
Added Excess Compounding Alkali as NaOH	0.1	0.1
Compound of Example I		0.5
Inspection:		
Gravity, °API	22.6	22.6
Melting Point, °F., Hawxhurst	263	263
Dropping Point, °F., ASTM D 566-42	344	344
Flow Point, °F., Navy Dept. Spec. 14-G-1d	245	246
Penetration, ASTM D 217-38T, 77° F., 150 G., 5 Sec.:		
Unworked	312	314
Worked	325	328
Oxygen Stability, 176° F., Hr., Method 272, Gulf [1]	100	500+
Bleeding Test, Per Cent, AN-G-3a Mod., 150° F., 50 Hr., Separated Oil, Per Cent by Weight	7	1

[1] Method 272 Gulf, is a modification of ASTM D 942-47T. In the modification, instead of measuring the pressure drop after 100 hours, the time required to give a 10 pound pressure drop is measured.

EXAMPLE V

	Cup Grease	Improved Cup Grease
Make-up: Per Cent by Weight:		
300 Vis. Texas Oil	83.2	82.7
Calcium Soap of Tallow	14.4	14.4
Glycerine (Theoretical)	1.4	1.4
Water	1.0	1.0
Compound of Example I		0.5
Inspection:		
Gravity, °API	18.5	18.5
Melting Point, °F., Hawxhurst	189	190
Flow Point, °F., Navy Dept. Spec. 14-G-1d	207	207
Consistency: mm., Braun, 77° F., 2.50 G	30	30
Penetration, ASTM D 217-38T, 77° F., 150 G., 5 Sec.:		
Unworked	230	232
Worked	280	282
Oxygen Stability, 176° F., Hr., Method 272, Gulf	50	500+
Bleeding Test, Per Cent, AN-G-3a Mod., 150° F., 50 Hr., Separated Oil, Per Cent by Weight	6.5	0.5

EXAMPLE VI

	Chassis Lubricant	Improved Chassis Lubricant
Make-up: Per Cent by Weight:		
100/2 Paraffine Oil	15.7	15.6
500/3 Texas Oil	4.0	4.0
1900/5.0 Texas Oil	33.2	33.0
150 M. C. Oil	37.1	36.9
Sodium Soap of Tallow	5.8	5.8
Calcium Soap of Tallow	2.3	2.3
Glycerine (Theoretical)	0.8	0.8
Added Excess Compounding Alkali as NaOH	0.1	0.1
Sulfurized Lard Oil	1.0	1.0
Compound of Example I		0.5
Inspection:		
Gravity, °API	21.5	21.5
Dropping Point, °F,. ASTM D 566-42	258	258
Flow Point, °F., Navy Dept. Spec. 14-G-1d	150	150
Consistency, mm.: Braun, 77° F., 2.50 G	17	17
Penetration, ASTM D 217-47T: 32° F., 150 G., 5 Sec.:		
Unworked	303	303
Worked	375	375
77° F., 150 G., 5 Sec.:		
Unworked	363	363
Worked	380	380
Convis Test, Furol, Sec., Method 294, Gulf:		
32° F., 5,200 Grams	[1] 498	[1] 498
77° F., 1,200 Grams	[1] 156	[1] 156
Oxygen Stability, 176° F., Hr., Method 272, Gulf	45	500+
Bleeding Test, Per Cent, AN-G-3a Mod., 150° F., 50 Hr. Separated Oil, Per Cent by Weight	12	2

[1] On freshly prepared sample before aging.

The grease compositions of our invention may include additional modifying agents, as will be apparent to those skilled in the art, provided they contain a metallo compound 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.

We claim:

1. A grease composition comprising a mineral lubricating oil thickened to a grease by a soap, and a small amount of the reaction product prepared by reacting an aqueous slurry of 1 mol of a metal hydroxide selected from the group consisting of barium, strontium, magnesium and calcium hydroxides with from 2 to 4 mols of formaldehyde at a mildly elevated temperature and condensing the resulting product with from 0.5 to 1 mol of aniline and from 2 to 4 mols of a mono-alkyl phenol having from 4 to 12 carbon atoms in the alkyl substituent, said product being present in an amount sufficient to stabilize the grease against oxidative deterioration.

2. A grease composition comprising a mineral lubricating oil thickened to a grease by a soap, and a small amount of the reaction product prepared by reacting an aqueous slurry of 1 mol of a metal hydroxide selected from the group consisting of barium, strontium, magnesium and calcium hydroxides with from 2 to 4 mols of formaldehyde at a temperature not exceeding 200° F. and condensing the resulting product with from 0.5 to 1 mol of aniline and from 2 to 4 mols of a mono-alkyl phenol having from 4 to 12 carbon atoms in the alkyl substituent, said product being present in an amount sufficient to stabilize the grease against oxidative deterioration.

3. The composition of claim 2, wherein the said reaction product is present in an amount of from 0.1 to 5.0 per cent by weight on the grease.

4. A grease composition comprising a mineral lubricating oil thickened to a grease by a soap, and a small amount of the reaction product prepared by reacting an aqueous slurry of 1 mol of a metal hydroxide selected from the group consisting of barium, strontium, magnesium and calcium hydroxides with from 2 to 4 mols of formaldehyde at a temperature not exceeding 200° F. and condensing the resulting product at a temperature not exceeding 200° F. with from 0.5 to 1 mol of aniline and from 2 to 4 mols of a mono-alkyl phenol having from 4 to 12 carbon atoms in the alkyl substituent, said reaction product being present in an amount sufficient to stabilize the grease against oxidative deterioration.

5. A grease composition comprising a mineral lubricating oil thickened to a grease by a soap, and a small amount of the reaction product prepared by reacting an aqueous slurry of 1 mol of calcium hydroxide with about 3 mols of formaldehyde at a temperature of about 160° F., and condensing the resulting product with about 0.7 mol of aniline and 2.3 mols of para tetramethylbutyl phenol at a temperature not exceeding 200° F., said reaction product being present in an amount sufficient to stabilize the grease against oxidative deterioration.

6. A semi-fluid oil suitable for the lubrication of light mechanisms comprising a mineral lubricating oil thickened to a semi-fluid oil by a soap, and a small amount of the reaction product prepared by reacting an aqueous slurry of 1 mol of a metal hydroxide selected from the group consisting of barium, strontium, magnesium and calcium hydroxide with from 2 to 4 mols of formaldehyde at a temperature not exceeding 200° F. and condensing the resulting product at a temperature not exceeding 200° F. with from 0.5 to 1 mol of aniline and from 2 to 4 mols of a mono-alkyl phenol having from 4 to 12 carbon atoms in the alkyl substituent, said reaction product being present in an amount sufficient to stabilize the semi-fluid oil against oxidative deterioration.

7. A semi-fluid oil suitable for the lubrication of light mechanisms comprising a mineral lubricating oil thickened to a semi-fluid oil by the calcium soap of tallow, and a small amount of the reaction product prepared by reacting an aqueous slurry of 1 mol of calcium hydroxide with about 3 mols of formaldehyde at a temperature of about 160° F. and condensing the resulting product with about 0.7 mol of aniline and 2.3 mols of para tetramethylbutyl phenol at a temperature not exceeding 200° F., said reaction product being present in an amount sufficient to stabilize the semi-fluid oil against oxidative deterioration.

8. The semi-fluid oil of claim 7, wherein the said reaction product is present in an amount of from 0.1 to 5.0 per cent by weight on the semi-fluid oil.

9. A semi-fluid oil suitable for the lubrication of light mechanisms comprising a soft grease having the following approximate composition in parts by weight:

Mineral lubricating oil, 300 S. U. S. at 100° F	91.3
Calcium soap of tallow	6.9
Glycerine	0.7
Water	0.6

and 0.5 part by weight of the reaction product prepared by reacting an aqueous slurry of 1 mol of calcium hydroxide with about 3 mols of formaldehyde at a temperature of about 160° F. and condensing the resulting product with about 0.7 mol of aniline and 2.3 mols of para tetramethyl-

butyl phenol at a temperature not exceeding 200° F.

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