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GREASE COMPOSITIONS CONTAINING COMPLEX ALKALINE EARTH METAL SALTS

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The present invention is concerned with grease compositions. More specifically, the invention is concerned with grease compositions containing novel gelling agents, namely, complex alkaline earth metal salts of acetic acid and of partial esters of phosphoric acid.

This application is a continuation-in-part of application Serial No. 354,406, filed May 11, 1953, now abandoned.

Recently developed for use as mineral lubricating oil detergents are oil-soluble, complex metal salts of organic acids such as formic, acetic and caproic acids and of partial esters of phosphoric acid. These salts and lubricating oil compositions containing the same are described by Ferdinand P. Otto in applications Serial Nos. 246,501, filed September 13, 1951 (now abandoned) and 541,849, filed October 22, 1955; and related zinc salts are described by Ferdinand P. Otto and Edmund W. Flynn in applications Serial Nos. 246,502, filed September 13, 1951 (now abandoned), and 541,848, filed October 22, 1955.

I have now found that, while the complex metal salts described in the aforesaid applications are excellent additives for lubricating oils, they are not suitable for use as gelling agents for greases. This is particularly so for greases subjected to high temperatures during use. However, I have now discovered a related class of novel complex metal salts which are gelling agents of excellent character and particularly effective for high temperature greases. It is with such agents that this invention is concerned.

It is well known that greases lose some or all of their effectiveness when subjected to high temperature operations. In lubricating machine parts, for example, it is essential that a grease retain its gel structure during use; failure to do so results in high consumption of the grease and frequent servicing. In general, available greases suffer from a marked tendency to change in character when used over a wide range of temperature, particularly at high temperatures of the order of 300–500° F. and higher. Some conventional greases are characterized by excessive softening when exposed to such high temperature operation, thereby extruded too rapidly from the area being lubricated to provide efficient lubrication.

It is an object of this invention, therefore, to provide a grease effective for high temperature use, such as 200–500° F. and higher. A further object is to provide a grease which retains its original character over a wide range of operating conditions. Another object is to provide a novel group or class of gelling agents. Other objects of the invention will be apparent from the following description.

The gelling agents of this invention can be designated broadly as complex metal salts of partial esters of phosphoric acid and of acetic acid. The nature of these salts is unknown at this time and, therefore, no exact chemical formula can be ascribed to them. They can best be described by the process for producing them.

The complex metal salts are prepared by first preparing a partial ester of phosphoric acid by the reaction of phosphorus pentoxide with an alkyl-substituted hydroxy-

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aromatic compound in which the alkyl portion contains from eight to fourteen carbon atoms, preferably nine to twelve carbon atoms. The ester is then reacted by either of three methods, viz.,

- (1) Reacting a mixture of the ester and acetic acid with an alkaline earth metal hydroxide or oxide,
- (2) Reacting the ester with a salt of an alkaline earth metal to form the normal metal salt of the partial ester and then further reacting the normal metal salt with an alkaline earth metal acetate, or
- (3) Reacting the ester with a sufficient amount of alkaline earth metal acetate to provide the complex salt (i. e., without intermediary formation of the normal salt).

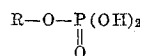
In accordance with method (2), the metal salt reagent used to form the normal salt need not be a carboxylate salt, but can be a hydroxide, carbonate or an alcoholate. However, the metal constituent of both salt reagents, i. e., the one utilized in forming the normal salt and the complex salt is preferably the same metal, and the latter salt reagent is preferably an acetate.

In each of the aforesaid methods, (1) through (3), a temperature of at least about 400° F., and preferably 400–500° F., is employed. The heating period is generally from about 0.1 to about 2 hours. However, a preferred procedure involves preparation of the desired complex metal salts in oil. In the preferred procedure, the partial esters and acetic acid are blended with sufficient mineral oil to give 15 to 25 percent of the desired complex salt in the finished grease. An alkaline earth hydroxide, in an amount sufficient to at least neutralize all the acids employed, is then added and the resulting mixture is heated to 400–500° F. to form the grease. The grease is cooled statically or with stirring, and is milled to a smooth consistency.

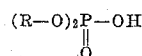
As indicated above, in view of the complex nature of the reactions involved in the formation of the complex metal salts, their exact structure is not yet known. The complexity of these salts is indicated by the complexity of the esters from which they are prepared.

When an alkylated hydroxyaromatic compound, such as an alkyl phenol is reacted with phosphorous pentoxide in a 3:1 mol ratio, indications are that the product consists essentially of a mixture of:

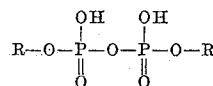
- (1) Mono-alkaryl phosphoric acids



- (2) Di-alkaryl phosphoric acid



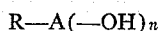
- and (3) pyrophosphoric acids such as di-alkaryl pyrophosphoric acid



wherein R is an alkyl-substituted aromatic hydrocarbon group such as nonyl phenyl.

The relative proportions of the foregoing compounds present in the product are governed to some extent by the proportions of hydroxyaromatic compound and phosphorus pentoxide used in the reaction. For example, when the mol ratio of the hydroxyaromatic compound to P_2O_5 is 3:1, the major components of the reaction product are considered to be most probably the mono- and di-esters of phosphoric acid with minor amounts of esters of pyrophosphoric acid. When a mol ratio of 2:1 is used, the proportion of alkaryl pyrophosphoric acid in the mixture is increased.

Alkyl hydroxyaromatic compounds suitable for preparing the partial esters contemplated herein can be represented by the general formula:



wherein A is an aromatic nucleus or group such as phenyl, naphthyl, etc.; R is an alkyl group containing from eight to fourteen carbon atoms, and is preferably of branched-chain configuration; and n is a small whole number from one to two, preferably one. Preferred of such compounds are alkyl phenols having from nine to twelve carbon atoms in the alkyl group. Nonylphenol is especially preferred.

As is well known in the art, such alkylhydroxyaromatic compounds can be prepared by alkylation of a hydroxyaromatic compound, such as phenol. Alkylation of the aryl hydroxide can be accomplished by methods such as a Friedel-Crafts synthesis using a halogenated compound. Alkylation can also be effected by reaction of the aryl hydroxide with unsaturated hydrocarbons, or alcohols, in the presence of a suitable catalyst, such as H_2SO_4 , $ZnCl_2$, BF_3 , HF , etc.

Typical aryl hydroxides or phenols which may be used as the starting material for the alkylation reaction are: phenol, resorcinol, hydroquinone, catechol, cresol, xylenol, hydroxydiphenol, benzylphenol, phenyl-ethyl-phenol, phenol resins, methyl-hydroxydiphenyl, guaiacol, alpha and beta naphthol, alpha and beta methyl naphthol, tolyl naphthol, xylyl naphthol, benzyl naphthol, anthranol, phenyl methyl naphthol, phenanthrol, chlorphenol and the like. Preference is given to phenol.

In preparing the alkaryl phosphoric acid ester, the alkyl hydroxyaromatic compound and P_2O_5 are heated together at a temperature of from about $50^\circ C.$ ($122^\circ F.$) to about $150^\circ C.$ ($302^\circ F.$) for a period of time to insure substantially complete reaction, usually from about five to fifteen hours. An inert solvent, such as toluene, xylene or the like, can be used to facilitate the reaction. A mineral oil can also be used as the solvent, in which case the product is an oil concentrate which can be used directly in the preparation of the complex metal salt and ultimately in the preparation of the desired gelling agent. In this way the ultimate gelling agent is obtained in the form of an oil concentrate and can be conveniently utilized as such for preparation of greases. When a solvent other than mineral oil is used, the P_2O_5 reaction mixture is filtered and topped at elevated temperature and reduced pressure to remove the solvent.

The proportions of alkyl hydroxyaromatic compound and P_2O_5 used in the reaction can be varied between from about one to about three mols of the alkyl hydroxyaromatic compound to one mol of P_2O_5 . In general, the use of a 2:1 ratio yields a complex salt with acetic acid which has greater gelling power.

As indicated previously, in preparing the complex metal salt of the phosphoric acid ester, the normal salt can be prepared first by reaction of the ester with a suitable metal salt, such as a hydroxide, carbonate, alcoholate, etc. The complex salt can then be formed by further reaction of the normal salt with an alkaline earth metal acetate, preferably of the same metal constituent as the metal salt reagent used in the formation of the normal ester salt. Also, the complex salt can be prepared directly by reacting the ester with a sufficient amount of an alkaline earth metal acetate salt to provide twice the amount of metal which would be equivalent to the acid-hydrogen content of the phosphoric acid partial ester. However, the most advantageous method involves reacting a mixture of acetic acid and partial ester product with an alkaline earth metal hydroxide, wherein the hydroxide is used in an amount at least sufficient to neutralize the acetic acid and partial ester product.

The proportions of ester and acetic acid to be used in preparing the gelling agents can be varied over a fairly wide range. In general, it is preferred to use an amount

of acetic acid equivalent to the ester on the basis of neutralization number. The amount of acetic acid can be reduced to about fifty percent of this amount, but increasing it much above the equivalent amount results in the formation of greases which are excessively fluid and which are unsatisfactory for high temperature use.

The reactions required to produce the complex salts by any one of the methods recited above, are within the skill of those familiar with the art. The reactions are accomplished at temperatures of from about $400^\circ F.$ to about $500^\circ F.$, in a relatively short time, generally from about 0.1 hour to 2 hours. A suitable solvent medium, such as benzene, toluene, xylene and the like, or a mineral oil can be used as the solvent. In the latter case, an oil concentrate of the complex salt is obtained.

The preferred method, however, involves preparation of the desired complex metal salts in oil. The partial esters and acetic acid are blended with sufficient mineral oil to give 15 to 25 percent of the desired complex salt in the finished grease. An alkaline earth metal salt reagent in an amount sufficient to at least neutralize all the acids employed, is then added and the resulting mixture is heated to $400-500^\circ F.$ to form the grease. The grease is cooled statically or with stirring, and is milled to a smooth consistency.

Alkaline earth metals are employed in forming the gelling agents of this invention, particularly calcium and barium. Calcium is preferred in view of its lower cost. The hydroxides are preferred for neutralizing the mixture of alkaryl phosphoric and acetic acids to form the gelling agents.

Several illustrative but non-limiting examples of some specific gelling agents and greases containing the same are set forth below. In the examples, all parts are by weight unless otherwise described.

EXAMPLE I

Calcium grease of nonylphenol- P_2O_5 product (3:1 ratio) and acetic acid

A nonylphenol- P_2O_5 product was prepared by adding 0.33 molar proportion of P_2O_5 in small portions to 1.0 molar proportion of nonylphenol at $200^\circ F.$, while mechanically stirring the mixture which formed. After the addition of P_2O_5 was completed, the temperature was raised to $300^\circ F.$ and was so maintained for about three hours. The viscous product was then filtered through a thin layer of filtering clay (Hy-flo clay) on a heated Buchner funnel. The product—the filtrate—had a neutralization number of 195, and contained 7.6 percent of phosphorus.

Five parts of this product, one part of glacial acetic acid, 1.4 parts of $Ca(OH)_2$ and 20 parts of a solvent refined naphthenic oil having a viscosity of 513.5 SUS (Saybolt Universal seconds) at $100^\circ F.$, were mixed and were heated with constant stirring. The resultant mixture began to thicken at $410^\circ F.$ and formed a heavy gel at $420^\circ F.$ The mass was stirred while it was cooled to room temperature, after which the heavy grainy gel which resulted was milled to a smooth consistency.

EXAMPLE II

Calcium grease of nonylphenol- P_2O_5 product (3:1 ratio) and acetic acid

This grease was prepared by the procedure described in Example I above, except that the proportions of reactants were increased twenty-fold. The heavy grease so obtained was blended with additional mineral oil (140 parts) to reduce the soap content to twenty percent (weight). This blend was put through a colloid mill. The final grease had a buttery consistency.

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EXAMPLE III

Calcium grease of nonylphenol-P₂O₅ product (3:1 ratio) and acetic acid

One hundred parts of a nonylphenol-P₂O₅ product similar to that which is described in Example I, above, ten parts of glacial acetic acid (fifty percent of the amount used in Examples I and II), twenty-two parts of Ca(OH)₂ and four hundred parts of a solvent refined naphthenic oil having a viscosity of 513.5 SUS at 100° F., were mixed in a grease kettle and heated. A temperature of about 500° F. was required to form a gel. Heating was continued for about five minutes after the gel had formed. The product was then cooled to room temperature (about 75° F.) while it was stirred. The resulting grease was quite heavy in consistency and dark in color.

EXAMPLE IV

Calcium grease of nonylphenol-P₂O₅ product (3:1 ratio) and acetic acid

This grease was prepared in the same manner as the grease of Example III, except that twenty-five parts of glacial acetic acid and thirty-one parts of Ca(OH)₂ were used. In this case, gelation occurred at about 415° F.

EXAMPLE V

Calcium grease of nonylphenol-P₂O₅ product (2:1 ratio) and acetic acid

A nonylphenol-P₂O₅ product was prepared in the same manner as the corresponding product described above in Example I; however, here, 0.5 molar proportion of P₂O₅ was used per molar proportion of nonylphenol. The product so obtained had a neutralization number of 207 and was considerably more viscous than the product prepared with a 3:1 ratio.

One hundred parts of the 2:1 product, 22.2 parts of glacial acetic acid, 30.0 parts of Ca(OH)₂ and 400.0 parts of a solvent refined naphthenic oil having a viscosity of 513.5 SUS at 100° F., were charged to a grease kettle and were heated. Gelation occurred at about 425° F.

EXAMPLE VI

Barium grease of nonylphenol-P₂O₅ product (3:1 ratio) and acetic acid

One hundred parts of a nonylphenol-P₂O₅ product similar to that described in Example I above, 20.0 parts of glacial acetic acid, 110.0 parts of Ba(OH)₂·8H₂O and 400.0 parts of a solvent refined naphthenic oil having a viscosity of 513.5 SUS at 100° F., were mixed in a grease kettle and were heated. Gelation occurred at about 495° F. The resultant gel was grainy in character. It was cooled to about 75° F. and was put through a colloid mill. The resulting grease was smooth and of heavy consistency.

EXAMPLE VII

Calcium grease of dodecylphenol-P₂O₅ product (3:1 ratio) and acetic acid

A dodecylphenol-P₂O₅ product was prepared in the manner described in Example I, above. The neutralization number of the product so obtained was 170.

One hundred parts of this dodecylphenol-P₂O₅ product, 17.7 parts of glacial acetic acid, 25.0 parts of Ca(OH)₂ and 400.0 parts of solvent refined naphthenic oil having a viscosity of 513.5 SUS at 100° F., were charged to a grease kettle and were heated to 445° F. during a period of 1-2 hours, whereupon gelation occurred. After heating the mixture for about ten minutes at 445° F., the resulting heavy grease was cooled to room temperature (about 75° F.) while it was stirred. The grease was blended with 100 parts of the oil described above, and a rather soft, adhesive grease was formed.

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EXAMPLE VIII

Calcium grease of tetradecylphenol-P₂O₅ product (3:1 ratio) and acetic acid

A tetradecylphenol-P₂O₅ product was prepared by the procedure described in Example I, above. The product so prepared had a neutralization number of 150.

One hundred parts of this tetradecylphenol-P₂O₅ product, 16.1 parts of glacial acetic acid, 22.0 parts of Ca(OH)₂ and 375.0 parts of solvent refined naphthenic oil having a viscosity of 513.5 SUS at 100° F. were charged to a grease kettle and were heated to about 470° F. during a period of 1-2 hours, whereupon gelation occurred. The mixture was heated at about 470° F. for about five minutes, then the grease was cooled to room temperature (about 75° F.) while it was stirred.

EXAMPLE IX

Calcium grease from nonylphenol-P₂O₅ product (2:1 ratio) and excess calcium acetate

A mixture of 10.0 parts of nonylphenol-P₂O₅ product (described in Example V), 6.5 parts of calcium acetate and 40.0 parts of a solvent refined naphthenic oil having a viscosity of 513.5 SUS at 100° F., was heated with stirring. Foaming occurred between 200 and 400° F. Foam subsided at 400° F. and the mixture was very fluid. It became more viscous at 440-450° F. and set to a coarse, grainy gel. It was cooled to room temperature and milled to a fairly smooth grease.

EXAMPLE X

Calcium grease from the calcium salt of nonylphenol-P₂O₅ product (2:1 ratio) and calcium acetate

A mixture of 10.0 parts of nonylphenol-P₂O₅ product (described in Example V), 1.37 parts of Ca(OH)₂ and 40.0 parts of oil (as in Example I), was heated with stirring to 350° F. to form the calcium salt of the partial ester of phosphoric acid. This was cooled to 175° F. and 3.25 parts of calcium acetate were added. The mixture was reheated with stirring. It remained fluid up to 450° F. It began to thicken at this point and form a soft, grainy gel at 450-460° F. On cooling to room temperature, it was milled to a fairly smooth, somewhat softer grease than Example IX.

In general, the greases of this invention are characterized by high dropping points, which fact indicates their use for high temperature applications. The dropping points and penetration values, of the greases described above are listed in Table I below.

TABLE I

Grease	A. S. T. M. ¹ Penetration, mm./10	A. S. T. M. ² Dropping Point, ° F.
Example I.....		450
Example II.....	250	440
Example III.....	285	460
Example IV.....	320	410
Example V.....	195	460
Example VI.....	225	340
Example VII.....	345	485
Example VIII.....	360	135

¹ A. S. T. M. Designation D 217-48.

² A. S. T. M. Designation D 566-42.

The data presented in Table I reveals that the greases illustrative of the invention are suitable for high temperature applications. In contrast, the grease of Example VIII, derived from tetradecylphenol, has an unsatisfactory dropping point value, as low as 135° F., and has a rather high penetration value (360). These unsatisfactory characteristics are ascribed, in part at least, to the excessive length of the alkyl chain, tetradecyl, of the alkylphenol. As indicated above, the maximum number of carbon atoms in said alkyl chain is preferably about twelve.

Illustrative Examples I through VIII are presented in

tabular form in Table II below, together with additional examples, in order to emphasize certain critical relationships. As shown, the examples are arranged in order of the number of carbon atoms of the alkyl group attached to the alkaryl hydroxyaromatic constituent.

paratus employed is described in the Institute Spokesman, 6, No. 12, page 4, March 1943. The procedure followed in this test is given below:

1. Work 99 grams of grease and 1 cc. of distilled water

TABLE II

Greases of alkaline earth metal complexes of alkylphenol-P₂O₅ products and acetic acid

Example No.	Reactants (Parts by Wt.)				Gelation Temp., ° F.	Properties of Grease	
	Alkylphenol-P ₂ O ₅ Product ¹	Acetic Acid	Metal Hydroxide	Oil		A. S. T. M. Penetration, mm./10	A. S. T. M. Dropping Point, ° F.
XVI.....	100 (C ₈).....	23	30 (Ca)....	400	Fluid to 435.....		
III.....	100 (C ₈).....	10	22 (Ca)....	400	500.....	285.....	480
XVII.....	100 (C ₈).....	15	26 (Ca)....	500	435.....	280.....	410
I.....	5 (C ₈).....	1	1.4 (Ca)....	20	420.....	Insufficient Sample.	450
II.....	100 (C ₈).....	20	28 (Ca)....	500	420.....	290.....	440
V.....	100 (C ₈).....	22.2	30 (Ca)....	400	425.....	195.....	460
IV.....	100 (C ₈).....	25	31 (Ca)....	400	415.....	320.....	410
XI.....	100 (C ₈).....	30	35 (Ca)....	400	Fluid to 500.....		
XII.....	100 (C ₈).....	40	40 (Ca)....	400	Fluid to 550.....		
VI.....	100 (C ₈).....	20	110 (Ba)....	400	495.....	225.....	340
XIII.....	100 (C ₁₂ -Diamyl).....	17.7	25 (Ca)....	400	Fluid to 490.....		
VII.....	100 (C ₁₂).....	17.7	25 (Ca)....	500	445.....	345.....	485
VIII.....	100 (C ₁₄).....	16.1	22 (Ca)....	375	470.....	360.....	135
XIV.....	100 (C ₁₅).....	11.0	15 (Ca)....	400	Fluid to 450.....		
XV.....	100 (Wax-5-14).....	13.3	20 (Ca)....	400	Fluid to 500.....		

¹ Ratio of Alkylphenol to P₂O₅ is (3:1) in all cases except No. V which is (2:1). Alkyl group in Alkylphenol is branched in all cases except No. XIV.

The wax phenol (0.5-14) used in Example XV was prepared in the manner described on pages 8 through 10 of said application Serial No. 246,501.

A number of observations can be made from the data set forth in Table II. Examples I-V and XVII involve a nonylphenol-P₂O₅ product, and all greases derived therefrom are of excellent character. Thus, a nonyl alkyl group and the nonylphenol-P₂O₅ product are preferred. In contrast, the octylphenol-P₂O₅ product (Example XVI) failed to form a grease. Diamyl phenol (Example XIII), tetradecylphenol (Example VIII), pentadecyl phenol (Example XIV), and wax phenol (Example XV), either failed to yield a grease or the grease was unsatisfactory in that it was too soft in consistency.

Examples I-V and XI, XII and XVII illustrate the effect of varying the amount of acetic acid on the calcium base grease. The use of 15 to 25 parts of acetic acid to 100 parts of the nonylphenol-P₂O₅ product, is preferred since greases of good consistency and high dropping points are formed at the lower temperatures, 415-435° F. When the amount of acetic acid was reduced to 10 parts (Example III), a temperature of 500° F. was required to form the grease, while 30 to 40 parts of acetic acid (Examples XI and XII) failed to yield a grease.

A comparison of Example V with Example IV, indi-

on a glass plate with a spatula until the droplets of water disappear into grease.

2. Transfer the wet grease to a 3 ounce asphalt tin and cool the sample to 77° F.
3. Scrape off the excess grease from the top of the tin with the blade of the spatula and determine the penetration of the grease, using the micropenetration cone and shaft assembly (weight 58.3 grams).
4. Charge the rolling stability test cylinder with 100 grams of the wet grease and distribute the grease uniformly on the inside walls of the cylinder. Place the weighted roll in the cylinder and screw the cylinder cap on tightly.
5. The grease is worked in the cylinder at room temperature for a period of 2 hours.
6. At the end of the rolling time period, disassemble the apparatus. Remove the rolled grease from the cylinder and roller with a spatula and transfer the grease to a 3 ounce tin for penetration measurement. Cool the rolled grease to 77° F. within 15 minutes and determine the micropenetration.

The description of the equipment used in determining oil separation, subsequent to the rolling stability test, is described in the Institute Spokesman, volume XI, No. 7, pages 4-5, October 1947.

Results of this severe test are shown in Table III below:

Grease	Micro Penetration Before Roll Test	Micro Penetration After Roll Test	Micro Penetration after roll test +1% water	After 16 Hours at 160° F.	After 16 Hours at 160° F. + 1% water	Percent (Wt.) Oil Bled	Percent (Wt.) Oil Bled +1% water
II.....	88	140	115	45	110	0.9	2.7

cates that the use of a 2:1 ratio (Example V) of alkylphenol to P₂O₅ instead of a 3:1 ratio, is responsible for a grease of heavier consistency.

Calcium is the preferred metal, since barium (Example VI) yields a grease of much lower dropping point, although still in the range suitable for a high temperature grease.

To further illustrate the excellent character of the instant gelling agents and greases containing the same, grease II shown above in Table II was subjected to a severe test. The grease was evaluated for shear stability in the presence of water. The rolling stability test ap-

Grease II, therefore, was satisfactory in all respects in this test.

In summary, it can be stated that the preferred gelling agent of this invention is the complex calcium salt of a mixture of nonylphenol-P₂O₅ acid product (2:1 ratio or 3:1 ratio) and acetic acid in which approximately equivalent amounts of the two acids are used based on neutralization number, and in which the acids are reacted with calcium hydroxide in an amount at least sufficient to neutralize the acids, said gelling agent being formed at a temperature of 400-450° F. in the presence

of mineral oil. The amount of gelling agent to be used in forming a grease can vary from about ten percent to about fifty percent. In general, fifteen to twenty-five percent is a suitable concentration.

OIL VEHICLES

The oil vehicles or oleaginous vehicles of the greases of this invention can vary considerably in character. In general, mineral oils used are those characterized by a viscosity (S. U. S.) of greater than about 40 seconds at 100° F., preferably from about 60 to about 6000 seconds at 100° F. In place of all or part of the mineral oil component, other oils of lubricating viscosity can also be used. Such oils include synthetic vehicles comprising polymerized olefins, esters of aliphatic dibasic acids, esters of polyalcohols and monocarboxylic acids, silicones, silicate esters, esters of phosphorus-containing acids, fluorocarbons, etc. Typical of such synthetic oils are: polypropylene, polypropylene glycol, di(-2-ethyl hexyl) sebacate, di(-2-ethyl hexyl) adipate, dibutyl phthalate, polyethylene glycol di(-2-ethyl hexoate), polymethylsiloxane. The synthetic vehicles are most suitable for providing greases for use in aircraft, since many of such greases require lubricating value over a wide temperature range, from about -100° F. to about 500° F.

MODIFYING AGENTS

It is to be understood that the greases of this invention can also contain other characterizing materials and fillers. For example, the greases can contain anti-oxidants such as amines (e. g., phenyl alpha-naphthylamine), phenols (e. g., 2-6-di-tertiary butyl-4-methyl phenol), and the like; lubricity improving agents such as free fat, free fatty acids, esters of alkyl and/or aryl acids, sulfurized fats, lead soaps, etc. Typical fillers include carbon black, silica flour and colloidal clay. Other additives which can be present are: extreme pressure agents, such as a chloronaphtha xanthate; and tackiness agents such as polyisobutylenes.

UTILITY

The greases of this invention are suitable for a wide range of industrial applications. Some, for example, are suitable for use as multi-purpose automotive greases, serving as chassis, wheel-bearing, water-pump grease lubricants. Others are multi-purpose industrial greases serving as plain-bearing and anti-friction greases for normally loaded and heavily loaded equipment. In general, then, greases contemplated herein range from semi-fluid types suitable as textile machinery lubricants, to solid block type greases used in lubrication of machinery in steel mills, paper mills, cement mills, etc.

I claim:

1. A grease comprising an oleaginous lubricant and a gelling agent in an amount sufficient to thicken said vehicle to form a grease, said gelling agent being prepared by the steps of: (1) reacting one molar proportion of phosphorus pentoxide with from about one to about three molar proportions of an alkyl hydroxyaromatic compound of the general formula $R-A-(OH)_n$ wherein R is an alkyl group containing from eight to fourteen carbon atoms, n is a small whole number from one to two, and A is an aromatic nucleus, to form an acidic, partial ester of phosphoric acid, and (2) forming a mixture of the acidic, partial ester obtained by step (1) and a quantity of acetic acid from about fifty percent to about one hundred percent equivalent to said acidic, partial ester on the basis of neutralization number, and (3) reacting the mixture formed in step (2) with an alkaline earth metal compound selected from the group consisting of an oxide and a hydroxide, at a temperature between about 400° F. and about 500° F., the amount of said metal compound being at least sufficient to neutralize the acetic acid and the acidic, partial ester.

2. A grease comprising an oleaginous lubricant and a

gelling agent in an amount sufficient to thicken said vehicle to form a grease, said gelling agent being prepared by the steps of: (1) reacting one molar proportion of phosphorus pentoxide with from about one to about three molar proportions of an alkyl hydroxyaromatic compound of the general formula $R-A-(OH)_n$ wherein R is an alkyl group containing from eight to fourteen carbon atoms, n is a small whole number from one to two, and A is an aromatic nucleus, to form an acidic, partial ester of phosphoric acid, and (2) reacting the acidic, partial ester of step (1) with a quantity of an alkaline earth metal salt to form the corresponding normal metal salt of said acidic, partial ester, and (3) reacting the said normal metal salt with an alkaline earth metal acetate at a temperature between about 400° F. and about 500° F.

3. A grease comprising an oleaginous lubricant and a gelling agent in an amount sufficient to thicken said vehicle to form a grease, said gelling agent being prepared by the steps of: (1) reacting one molar proportion of phosphorus pentoxide with from about one to about three molar proportions of an alkyl hydroxyaromatic compound of the general formula $R-A-(OH)_n$ wherein R is an alkyl group containing from eight to fourteen carbon atoms, n is a small whole number from one to two, and A is an aromatic nucleus, to form an acidic, partial ester of phosphoric acid, and (2) reacting the acidic, partial ester of step (1) with an alkaline earth metal acetate at a temperature between about 400° F. and about 500° F., the amount of said acetate being sufficient to provide twice the amount of alkaline earth metal equivalent to the acid-hydrogen content of said acidic, partial ester.

4. A grease as defined by claim 1 wherein the alkyl hydroxyaromatic compound is nonylphenol.

5. A grease as defined by claim 1 wherein the alkaline earth metal is calcium.

6. A grease as defined by claim 1 wherein the gelling agent comprises from about ten percent by weight to about fifty percent by weight of said grease.

7. A gelling agent prepared by the steps of: (1) reacting one molar proportion of phosphorus pentoxide with from about one to about three molar proportions of an alkyl hydroxyaromatic compound of the general formula $R-A-(OH)_n$ wherein R is an alkyl group containing from eight to fourteen carbon atoms, n is a small whole number from one to two, and A is an aromatic nucleus, to form an acidic partial ester of phosphoric acid, and (2) forming a mixture of the acidic, partial ester obtained by step (1) and a quantity of acetic acid from about fifty percent to about one hundred percent equivalent to said acidic, partial ester on the basis of neutralization number, and (3) reacting the mixture formed in step (2) with an alkaline earth metal compound selected from the group consisting of an oxide and a hydroxide, at a temperature between about 400° F. and about 500° F., the amount of said metal compound being at least sufficient to neutralize the acetic acid and the acidic, partial ester.

8. A gelling agent prepared by the steps of: (1) reacting one molar proportion of phosphorus pentoxide with from about one to about three molar proportions of an alkyl hydroxyaromatic compound of the general formula $R-A-(OH)_n$ wherein R is an alkyl group containing from eight to fourteen carbon atoms, n is a small whole number from one to two, and A is an aromatic nucleus, to form an acidic, partial ester of phosphoric acid, and (2) reacting the acidic, partial ester of step (1) with a quantity of an alkaline earth metal salt to form the corresponding normal metal salt of said acidic, partial ester, and (3) reacting the said normal metal salt with an alkaline earth metal acetate at a temperature between about 400° F. and about 500° F.

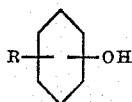
9. A gelling agent prepared by the steps of: (1) reacting one molar proportion of phosphorus pentoxide with from about one to about three molar proportions of an alkyl hydroxyaromatic compound of the general formula $R-A-(OH)_n$ wherein R is an alkyl group containing

from eight to fourteen carbon atoms, n is a small whole number from one to two, and A is an aromatic nucleus, to form an acidic, partial ester of phosphoric acid, and (2) reacting the acidic, partial ester of step (1) with an alkaline earth metal acetate at a temperature between about 400° F. and about 500° F., the amount of said acetate being sufficient to provide twice the amount of alkaline earth metal equivalent to the acid-hydrogen content of said acidic, partial ester.

10. A gelling agent as defined by claim 7 wherein the alkyl hydroxyaromatic compound is nonylphenol.

11. A gelling agent as defined by claim 7 wherein the alkaline earth metal is calcium.

12. A grease comprising a mineral oil having a viscosity from about 100 to about 1000 S. U. S. at 100° F. and a gelling agent in an amount of about fifteen to about twenty-five percent by weight of said grease, said grease being prepared by the steps of (1) reacting P_2O_5 with an alkyl phenol



wherein R is an alkyl group containing from nine to twelve carbon atoms, to form an acidic, partial ester of phosphoric acid, and (2) adding to the partial ester obtained by step (1) a quantity of acetic acid from about fifty percent to about one hundred percent equivalent to said acidic, partial ester on the basis of neutralization number, and a quantity of said mineral oil such that the finished grease contains from about fifteen to about twenty-five percent by weight of said gelling agent, and (3) reacting the mixture formed in step (2) with an alkaline earth metal hydroxide, in an amount sufficient to at least neutralize all of the acids of the mixture formed in step (2), and (4) heating the resulting mixture of step (3) to a temperature from about 400° F. to about 500° F., to form said grease, and (5) cooling said grease and milling said grease to a smooth consistency.

13. A grease comprising a mineral lubricating oil and a gelling agent in an amount sufficient to thicken said oil to form a grease, said gelling agent being prepared by the steps of (1) reacting phosphorus pentoxide with nonylphenol, the molar ratio of said phenol to said pentoxide being about 3:1, to form an acidic, partial ester of phosphoric acid, and (2) forming a mixture of the acidic, partial ester obtained by step (1) and a quantity of acetic acid about fifty percent equivalent to said acidic, partial ester on the basis of neutralization number and a mineral lubricating oil, and (3) reacting the mixture formed in step (2) with calcium hydroxide at a temperature of about 500° F., the amount of said calcium hydroxide being about equivalent to neutralize the acetic acid and the acid, partial ester.

14. A grease comprising a mineral lubricating oil and a gelling agent in an amount sufficient to thicken said oil to form a grease, said gelling agent being prepared by the steps of (1) reacting phosphorus pentoxide with non-

ylphenol, the molar ratio of said phenol to said pentoxide being about 2:1, to form an acidic, partial ester of phosphoric acid, and (2) forming a mixture of the acidic, partial ester obtained by step (1) and a quantity of acetic acid about equivalent to said acidic, partial ester on the basis of neutralization number, and a mineral lubricating oil, and (3) reacting the mixture formed in step (2) with calcium hydroxide at a temperature of about 500° F., the amount of said calcium hydroxide being about equivalent to neutralize the acetic acid and the acid, partial ester.

15. A grease comprising a mineral lubricating oil and a gelling agent in an amount sufficient to thicken said oil to form a grease, said gelling agent being prepared by the steps of (1) reacting phosphorus pentoxide with nonylphenol, the molar ratio of said phenol to said pentoxide being about 3:1, to form an acidic, partial ester of phosphoric acid, and (2) forming a mixture of the acidic, partial ester obtained by step (1) and a quantity of acetic acid about equivalent to said acidic, partial ester on the basis of neutralization number, and a mineral lubricating oil, and (3) reacting the mixture formed in step (2) with barium hydroxide at a temperature of about 500° F., the amount of said barium hydroxide being about equivalent to neutralize the acetic acid and the acid, partial ester.

16. A gelling agent prepared by the steps of (1) reacting phosphorus pentoxide with nonylphenol, the molar ratio of said phenol to said pentoxide being about 3:1, to form an acidic, partial ester of phosphoric acid, and (2) forming a mixture of the acidic, partial ester obtained by step (1) and a quantity of acetic acid about fifty percent equivalent to said acidic, partial ester on the basis of neutralization number, and a mineral lubricating oil, and (3) reacting the mixture formed in step (2) with calcium hydroxide at a temperature of about 500° F., the amount of said calcium hydroxide being about equivalent to neutralize the acetic acid and the acid, partial ester.

17. A gelling agent prepared by the steps of (1) reacting phosphorus pentoxide with nonylphenol, the molar ratio of said phenol to said pentoxide being about 2:1, to form an acidic, partial ester of phosphoric acid, and (2) forming a mixture of the acidic, partial ester obtained by step (1) and a quantity of acetic acid about equivalent to said acidic, partial ester on the basis of neutralization number, and (3) reacting the mixture formed in step (2) with calcium hydroxide at a temperature of about 500° F., the amount of said calcium hydroxide being about equivalent to neutralize the acetic acid and the acid, partial ester.

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