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3,537,995

CORROSION-INHIBITED SILICONE GREASE

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4 Claims

ABSTRACT OF THE DISCLOSURE

The addition of a metal chromate or dichromate to a silicone lubricating grease reduces galvanic corrosion during the lubrication of dissimilar metal surfaces which are separated by a lubricating film of the grease.

This invention relates to improved organopolysiloxane grease compositions. More particularly, the present invention is concerned with organopolysiloxane grease compositions which provide improved resistance to corrosion of dissimilar metals which are separated by a lubricating film of the grease.

Organopolysiloxane greases and grease compositions are well known in the art and have been used as lubricants, dielectric compounds, sealing compounds and high vacuum greases. These organopolysiloxane greases have been particularly valuable because of their high degree of heat stability, their water repellency, their high and low temperature viscosity characteristics, and dielectric properties. In many of their applications these greases are employed in contact with parts made of dissimilar metals. While the greases themselves are not corrosive to parts made of dissimilar metals, it has been found that where the grease has been employed in contact with parts made of dissimilar metals that corrosion develops because a galvanic action is set up between the dissimilar metals. This has been particularly true when one of the metals lubricated was sintered iron and the second metal part was made of aluminum.

In an attempt to solve the problem of corrosion, it has been suggested in the art to employ additives in the grease composition. While many of these additives have served their purpose so far as corrosion inhibition is concerned in systems which did not contain dissimilar metals, they failed completely to prevent corrosion caused by galvanic action set up by dissimilar metals in a lubricated system.

It is an object of the present invention to provide improved organo-polysiloxane grease compositions which retain all the highly beneficial properties of theretofore known organopolysiloxane grease compositions and which, in addition, may be employed in the lubrication of bearing surfaces otherwise corroded by galvanic action. The grease compositions of the present invention contain a metal salt of a chromate or dichromate as an additive to provide improved corrosion resistance when the grease composition is applied to lubricated surfaces of dissimilar metals in close proximity to each other. For example, the surfaces of sintered iron and aluminum, which surfaces are only separated from each other by a thin film of grease. It has been found that the presence of a minor amount of a metal salt of a chromate or dichromate in an organopolysiloxane grease composition provides markedly improved corrosion resistance to dissimilar metal parts which are in close proximity to each other and are separated from each other only by a thin film of the organopolysiloxane grease composition.

The grease compositions of the present invention comprise, on a weight basis:

- (1) from 61% to 98% of a polysiloxane fluid containing silicon-bonded organo groups selected from the class consisting of alkyl radicals having from one to 22 carbon atoms, cycloalkyl radicals having from 5 to 7 carbon atoms in the ring, mononuclear and binuclear aryl radicals, mononuclear aryl lower alkyl radicals, halogenated derivatives of the aforementioned radicals and cyano lower alkyl radicals;

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(2) from 2% to 35% of a grease thickening agent;

- (3) from 0.01% to 5% of a metal salt selected from the class consisting of metal salts of chromates and metal salts of dichromates;

- (4) optionally from 0.01% to 5% of a polyether;

- (5) optionally a sufficient amount of base to maintain the grease on the alkaline side.

The fluid organopolysiloxanes employed in the practice of the present invention except for those containing higher alkyl radicals, are well known in the art. The preparation of the fluid organopolysiloxanes containing higher alkyl radicals is described later in this specification. The organopolysiloxane fluids may be characterized as organopolysiloxane fluids in which all of the valences of silicon other than those satisfied by oxygen atoms are satisfied by monovalent organic radicals attached to silicon through a silicon carbon linkage. This type of organopolysiloxane can be characterized as having the average formula:



where R represents a member selected from the class consisting of alkyl radicals having from one to 22 carbon atoms, cycloalkyl radicals having from 5 to 7 carbon atoms in the ring, mononuclear and binuclear aryl radicals, mononuclear aryl lower alkyl radicals, halogenated derivatives of the aforementioned radicals, cyano lower alkyl radicals, lower alkenyl radicals having from 2 to 8 carbon atoms, and hydrogen; and m has a value of from 2.002 to 3.0. Among the specific radicals represented by R in Formula 1 are alkyl radicals, e.g., methyl, ethyl, propyl, octyl, decyl, dodecyl, tetradecyl, etc. radicals; cycloalkyl radicals having 5 to 7 carbon atoms in the ring, e.g., cyclopentyl, cyclohexyl, cycloheptyl, etc. radicals; mononuclear and binuclear aryl radicals, e.g., phenyl, naphthyl, biphenyl, tolyl, xylyl, etc. radicals; mononuclear aralkyl radicals having up to 16 carbon atoms in the alkyl group, e.g., benzyl, phenylethyl, phenyloctyl, etc. radicals; lower alkenyl radicals having from 2 to 8 carbon atoms, e.g., vinyl, allyl, pentenyl, etc. radicals; halogenated derivatives of the above radicals; e.g., chlorophenyl, dichlorophenyl, tetrachlorophenyl, dibromophenyl, chloronaphthyl, chlorobutyl, etc. radicals; cyano lower alkyl radicals having 2 to 5 carbon atoms, e.g., cyanomethyl, alpha-cyanoethyl, beta-cyanoethyl, gamma-cyanopropyl, etc. radicals. In the preferred embodiment of my invention, the organopolysiloxane fluids within the scope of Formula 1 are those in which at least 50% of the organic radicals attached to silicon are methyl radicals.

It should be understood that the viscosity of the organopolysiloxane fluid within the scope of Formula 1 will vary with the molecular weight of the fluid and with the nature of the silicon-bonded organic groups in the fluid. Although any organopolysiloxane fluid within the scope of Formula 1 is applicable, in the practice of the present invention it is preferred that the fluid have a viscosity of from about 10 centistokes to 100,000 centistokes when measured at 25° C.

It should also be understood that the organopolysiloxane fluids of Formula 1 can include siloxane units of every type and formulation such as triorganosiloxane units and diorganosiloxane units alone or in combination with monoorganosiloxane units. The only requirement is that the ratio of the various siloxane units employed be selected so that the average compositions of the copolymeric fluid is within the scope of Formula 1. These vari-

ous siloxane units may contain the same or different silicon-bonded organic radicals. For example, the siloxane units employed in preparing the fluid of Formula 1 can contain trimethylsiloxane units, methylphenylsiloxane units, diphenylsiloxane units, triphenylsiloxane units, methyl-beta-cyanoethylsiloxane units, methylsiloxane units, phenylsiloxane units, betacyanoethylsiloxane units, etc.

The metal salts of chromates and dichromates employed in the practice of the invention can be selected from the class consisting of the chromate and dichromate salts of any known metal above hydrogen in the electromotive series and is preferably a salt of a metal such as an alkali metal or an alkaline-earth metal. Chromate and dichromate salts of metals lower in the electromotive series than hydrogen such as lead and silver, while usable in low concentrations, are expensive and have a tendency to plate out upon the bearing surfaces replacing the original bearing metal which is oxidized by the exchange and is carried into the grease as a contaminant. Examples of metal salts of chromates and dichromates which are useful in the practice of the present invention are barium chromate, sodium dichromate, magnesium chromate, potassium chromate, calcium dichromate, zinc chromate, lithium chromate, etc. The preferred salts are those formed from the alkali metals and the alkaline-earth metals.

The third component of the grease composition of the present invention are the grease thickening agents, which are well known in the art. This invention contemplates the use of any of these well known thickening agents to form a grease composition of the desired consistency. The term "grease" as employed in the present application is intended to refer to grease-like materials which may have consistencies varying from readily flowable materials to materials which exhibit almost no flow. The consistency of the greases of the present invention depend on the amount of thickening agent employed, the type of thickening agent employed and the particular polysiloxane fluids in the grease. Examples of suitable thickening agents include the metallic soaps of fatty acids of at least 8 carbon atoms where the metals in such soaps include aluminum, lead, zinc, manganese, lithium, sodium, potassium, calcium, barium, strontium, copper, mercury, bismuth, chromium, iron, cobalt, nickel, etc. The use of many of such metal soaps are disclosed in U.S. Pats. 2,456,642 and 2,599,984. Metallic soaps of shorter chain length fatty acids such as acids containing from 2 to 6 carbon atoms as well as hydroxy-substituted fatty acids and hydroxy-substituted fatty acid glycerides such as are disclosed in Pats. 2,551,931 and 2,508,741 may also be employed as thickening agents.

Other specific metallic soaps which can be used as thickening agents in the practice of the present invention include lithium-2-ethylhexoate, lithium hydroxy stearate, lithium myristate and lithium caprate.

In addition to metal soaps, the compositions of the present invention may employ as grease thickening agents finely divided inert oxides of metallic and quasi-metallic materials such as silica, alumina, iron oxide, titania, zinc oxides, glass fibers and clays. Silica, when used as a thickening agent, is preferably employed as an aerogel, but may also be employed as fumed silica, precipitated silica, or natural deposits such as diatomaceous earth.

In addition to the relatively simple thickening agents described above, the invention of the present application contemplates the use of complex metal soaps such as aluminum benzoate stearate as described in Pat. 2,599,553, acyl ureas such as octadecanoyl urea as described in Pat. 2,698,300 and the phenylenediamides such as N,N-acetyl-stearoyl-p-phenylenediamides as described in Pat. 2,709,157. In addition, a particularly useful group of thickening agents are the aromatic substituted ureas which are commonly referred to as ASU thickeners. Another suitable thickening agent is phthalocyanine. Other thickeners include carbon black, graphites and polyethylene.

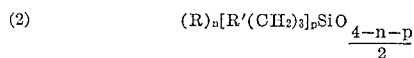
While the amounts of thickening agent employed in the grease compositions of the present invention are not critical and may vary within wide limits depending on the particular consistency desired in the final product, it has been found that the amount of thickening agent usually varies from about 2% to 35% and preferably from about 5% to 25% by weight based on the weight of the grease composition.

One critical feature, however, of the grease composition of the present invention is the amount of the metal salt of the chromate or dichromate present in the polysiloxane grease. For satisfactory corrosion inhibition in a bi-metallic system, it has been found that the metal salt of the chromate or dichromate must be present in an amount equal to from about 0.01% to 5% by weight based on the weight of the polysiloxane fluid in the composition. When less than 0.01% by weight of the metal salt of the chromate or dichromate is present, it is found that the resulting grease composition is ineffective to prevent corrosion when in contact with dissimilar metals. When the amount of the metal salt of the chromate or dichromate in the grease composition is in excess of 5% by weight, it is found that there is no significant improvement in properties of the grease and the excess may have a deleterious effect on the grease composition, e.g., higher bleeds, poorer lubricity due to the presence of a coarse powder, etc.

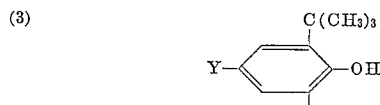
The grease composition of the present invention can be prepared in conventional fashion by merely mixing polysiloxane fluid and the thickening agent and the metal salt of the chromate or dichromate in conventional mixing and/or milling equipment. Especially satisfactory results have been obtained when the composition has been mixed on a conventional paint mill or on a conventional colloid mill.

Other additives can be present in the composition of this invention if desired. For example, the incorporation of pigments, additives for improving the lubricity or stability of greases, other corrosion inhibitors, acids or bases to control pH, and antioxidants is within the scope of this invention. The addition of many of such materials is described in the art.

For example, the polysiloxane used to make the greases of the present invention may optionally and preferably, contain a t-butyl-substituted hindered hydroxaryl radical attached to a silicon atom of the polysiloxane through a propylene radical. This antioxidant is represented by the R' radical of the formula:



where R is as above described, n has a value of 1.502 to 3.0, p has a value of from 0 to 0.5 and preferably from 0.01 to 0.1, the sum of $n+p$ has a value of 2.002 to 3.0 and R' is a t-butyl-substituted hindered hydroxaryl radical and has the formula:



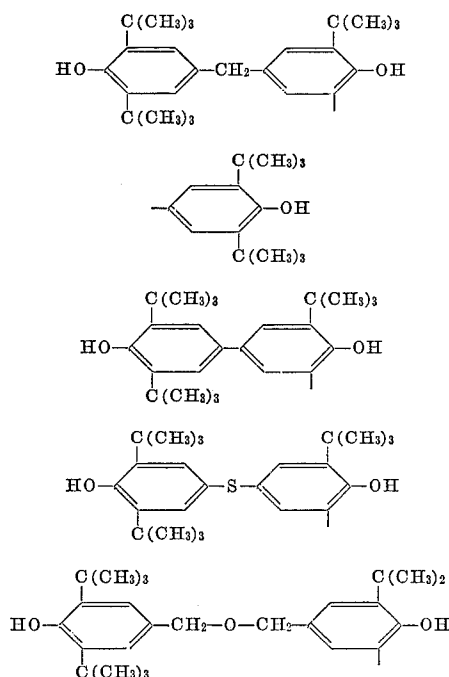
where Y is a member selected from the class consisting of hydrogen, monovalent hydrocarbon radicals, hydroxyaryl radicals, hydroxyaryl-substituted monovalent hydrocarbon radicals, hydroxyaryl ethers joined to the t-butyl-substituted hydroxyaryl radical through the ether linkage, hydroxyarylthioethers joined to the t-butyl-substituted hydroxyaryl radical through the thioether linkage and hydroxyarylmethylene ethers joined to the t-butyl-substituted hydroxyaryl radical through the methylene ether linkage. As is seen from Formulas 2 and 3, the R' radical has a valence bond joining the aromatic nucleus to a divalent propylene radical which in turn is attached to silicon. In the ortho position with respect to this valence bond is a hydroxy radical and in the meta position is a

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tertiary butyl radical. In the other meta position is the Y radical previously described. The t-butyl group is adjacent to the hydroxyl group and hinders its reactivity. Thus, the hydroxyaryl radical is a hindered hydroxyaryl radical.

Among the monovalent hydrocarbon radicals free of aliphatic unsaturation represented by Y in Formula 3 are, for example, alkyl radicals having from one to 22 carbon atoms, e.g., methyl, ethyl, propyl, butyl, octyl, etc. radicals; aryl radicals, e.g., phenyl, naphthyl, etc. radicals; aryl lower alkyl radicals having from one to 8 carbon atoms in the alkyl group, e.g., benzyl, phenylethyl, etc. radicals. Among the hydroxyaryl radicals represented by Y of Formula 3 are, for example, p-hydroxyphenyl, o,o-di(t-butyl)-p-hydroxyphenyl; o - (t-butyl)-o-allyl-p-hydroxyphenyl, etc. radicals. Illustrative of the hydroxyaryl-substituted monovalent hydrocarbon radicals within the definition of Y of Formula 3 are, for example, p-hydroxyphenylmethyl radicals, o,o - di(t-butyl)-p-hydroxyphenyl-ethyl radicals. Illustrative of the hydroxyarylether radicals are o,o-di(t-butyl)-p-hydroxyphenylether radicals and o,o-di(t-butyl)-p-hydroxy-phenylmethylether radicals. Illustrative of the hydroxyarylthioether radicals is o,o-di(t-butyl)-p-hydroxyphenylthioether radicals, etc.

Illustrative of specific radicals represented by R' of Formula 2 are, for example:



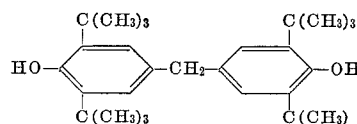
The nature of the compositions within the scope of the present invention is best understood by reference to the preparation of the composition which contain the silicon-bonded t-butyl-substituted hydroxyarylpropyl radical. The general method of preparation involves a starting material which contains a nuclear carbon-bonded hydroxyl-substituted phenyl nucleus containing tertiary butyl radicals in both of the meta positions with respect to the Y group of such phenolic compound. One or more of the nuclear-bonded t-butyl radicals is then replaced by an allyl radical to produce an allyl-substituted material having the formula:



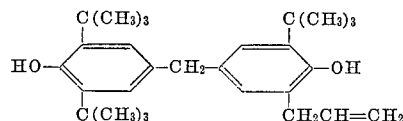
where R' is as previously defined. The allyl radical of this material is then reacted with an organopolysiloxane containing silicon-hydrogen linkages so as to attach the phenyl nucleus to the silicon atom through the propylene radical.

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As a general illustration of this method, a commercial phenolic compound having the formula:

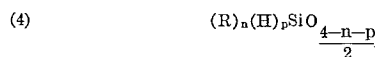


is dissolved in a mixture of toluene and ethanol and then an ethanol solution of potassium hydroxide is added to the solution. This results in the conversion of the phenol to the potassium phenylate. An amount of allyl chloride in ethanol sufficient to replace one tertiary butyl radical from each molecule is slowly added, the mixture is refluxed, salts are filtered, the product is washed and stripped to produce the allylated product having the formula:



The allylated product is then reacted with the silicon hydrogen containing polysiloxane in the presence of a platinum compound catalyst to produce the desired product.

The preparation of the polysiloxanes within the scope of Formula 2 involves an SiH-olefin addition reaction. This reaction simply involves first the addition of one of the allylated R' radicals, followed by the addition of an alpha-olefin having from 6 to 12 carbon atoms to some type of methylhydrogenpolysiloxane. For example, the preparation of a trimethylsilyl chain-stopped methyl higher alkyl polysiloxane of Formula 2 involves the reaction between a trimethylsilyl chain-stopped methylhydrogenpolysiloxane having the formula:



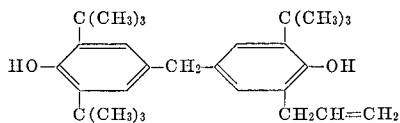
where R, n and p are as above defined, an allylated R' radical and an alpha-olefin. The reaction of the allylated R' radical and the alpha-olefin with the polysiloxane of Formula 4 can take place in the presence of the elemental platinum or platinum compound catalysts. The platinum compound catalyst can be selected from that group of platinum compound catalysts which are operative to catalyze the addition of silicon-hydrogen bonds across olefinic bonds. The polysiloxanes within the scope of Formula 1 are prepared in the same manner except that the step of adding the allylated R' radical is omitted.

Among the many useful catalysts for this addition reaction are chloroplatinic acid as described in U.S. Pat. 2,823,218—Spier et al., the reaction product of chloroplatinic acid with either an alcohol, an ether or an aldehyde as described in U.S. Pat. 3,220,972—Lamoreaux, trimethylplatinum iodide and hexamethyldiplatinum as described in U.S. Pat. 3,313,773—Lamoreaux, the platinum olefin complex catalysts as described in U.S. Pat. 3,159,601 of Ashby and the platinum cyclopropane complex catalyst as described in U.S. Pat. 3,159,662 of Ashby.

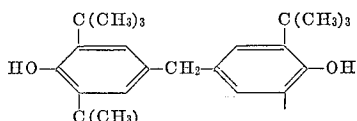
The SiH-olefin addition reaction may be run at room temperature or at temperatures up to 200° C., depending upon catalyst concentration. The catalyst concentration can vary from 10⁻⁷ to 10⁻³ and preferably from 10⁻⁵ to 10⁻⁴ moles of platinum as metal per mole of olefin containing molecules present. Generally, the methylhydrogenpolysiloxane is first mixed with the allylated R' radical, all of the catalyst is added and the reaction takes place. The reaction product is mixed with a portion of the alpha-olefin, then the remaining alpha-olefin is added at a rate sufficient to maintain the reaction temperature in the neighborhood of from about 50 to 120° C. and, at the end of the addition of the alpha-olefin, the reaction is completed.

When preparing a copolymer of the type described in Formula 2, the methylhydrogenpolysiloxane is first re-

acted with the appropriate amount of the allylated material and then the appropriate amount of alpha-olefin is added. For example, when it is desired to produce a product within the scope of Formula 2 in which n is 2.025 and p is 0.025, the starting material can be a trimethylsilyl chain-stopped methylhydrogenpolysiloxane containing an average of 38 methylhydrogensiloxane units per molecule. One mole of this methylhydrogenpolysiloxane is reacted with 1 mole of an allylated *t*-butyl-substituted phenol, such as the product shown in the formula:



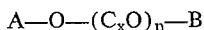
to produce a trimethylsilyl chain-stopped copolymer in which the average molecule contains 37 methylhydrogensiloxane units and 1 unit in which the R' is the radical shown in the formula:



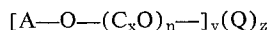
Then one mole of the resulting copolymer is reacted with 37 moles of an appropriate alpha-olefin, such as decene-1, according to the method previously described, to produce a copolymer within the scope of Formula 2 in which n is 2.025 and p is 0.025.

For improved ease of dispersion of the thickening agent in the polysiloxane, it is preferable that a polyether be present in an amount equal to from about 0.01% to 5.0% by weight based upon the weight of the polysiloxane fluids in the compositions, and preferably from 0.1 to 2.0% by weight. When less than 0.01% by weight of the polyether is present, it is found that it is difficult to disperse the thickening agent into an all methyl-substituted polysiloxane grease. When a substantial number of substituents of the polysiloxane are higher alkyl radicals, the polyether is not needed. When the amount of polyether in the grease composition is in excess of 5.0% by weight, it is found that the weight loss of the grease at temperatures in excess of 300° F. is so excessive that the grease is unsuitable for use in many high temperature applications.

The polyethers which are used herein in combination with the polysiloxane oils according to this invention are polymeric alkylene oxides and/or polymeric alkylene glycols, and may be represented by the following formulas:



and



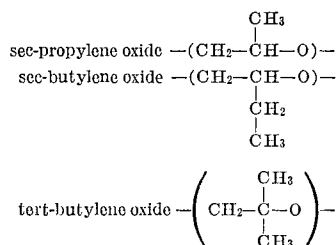
wherein A and B represent radicals selected from the class comprising hydrogen, alkyl radicals containing from 1 to 12 carbon atoms, cycloalkyl radicals containing 5 to 7 carbon atoms in the ring, mononuclear and binuclear aryl radicals and mononuclear aryl lower alkyl radicals wherein the alkyl groups attached to the aromatic nucleus contain a total of no more than 5 carbon atoms; A and B also represent ester forming groups containing from 2 to 12 carbon atoms; A and B may or may not be alike. When there is more than one A radical per molecule, the A radicals may or may not be the same. Q is a residue of a polyhydric initiator radical containing at least two hydroxyl radicals such as ethylene glycol, glycerol, trimethylolpropane, and other polyhydric alcohols having from 2 to 6 hydroxyl groups; n is a number having a value of from 4 to 2000; x is a number having a value of 2 to 4; y has a value of from 2 to 10; and z has a value of from 1 to 5.

More specifically, A and B represent radicals selected from the class comprising hydrogen; alkyl radicals having from one to 12 carbon atoms, e.g., methyl, ethyl, propyl,

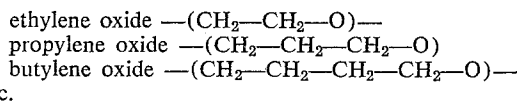
butyl, octyl, etc. radicals; cycloalkyl radicals having 5 to 7 carbon atoms in the ring, e.g., cyclopentyl, cyclohexyl, cycloheptyl, etc. radicals; mononuclear and binuclear aryl radicals, e.g., phenyl, naphthyl, biphenyl, etc. radicals; mononuclear aryl lower alkyl radicals wherein the alkyl groups attached to the aromatic nucleus contain a total of from one to 7 carbon atoms, e.g., benzyl, phenylethyl, phenylpropyl, etc.; and ester groups having from one to 12 carbon atoms such as the residues formed by the removal of a carboxyl hydrogen from a fatty acid, e.g., acetate, propionate, octoate, etc. residues; hydroxy-ether groups derived from glycols such as butylene glycol, octylene glycol, etc.; and groups formed by esterification with a hydroxyl group of a non-fatty acid, e.g., propyl phosphate, octyl sulfonate, butyl sulfate, etc.

The polyethers may be prepared from the various alkylene oxides (e.g., ethylene oxide), the higher 1,2-epoxides (such as 1,2-propylene oxide), the alkylene glycols (e.g., ethylene glycol) and mixtures of these. The resulting products may be polyoxyalkylene diols or polyalkylene glycol derivatives; that is, the terminal hydroxyl groups can remain as such, or one or both of the terminal hydroxyl groups can be removed during the polymerization reaction or subsequent thereto, as by etherification or esterification to yield mono- or di-ether or mono- or di-ester groups or a combination of such terminal groups whereby certain desirable properties are imparted to the final polymeric mixtures. For example, in the above formula, A and/or B may be: alkyl radicals, forming a di-alkyl polyether (e.g., dibutyl heptaoxypropylene diether); ester forming radicals, forming alkyl oxyalkylene esters (e.g., butyl pentaoxypropylene acetate); hydrogen, forming polyglycols (e.g., polyethylene glycol), etc.

To further exemplify the polyethers which can be used, the polyether oil, that is, the $-(C_xO)_n-$ section of the above formula, can be derived from such basic units as the following oxides:



etc. or basic units obtained by the dehydration of alkylene glycols, resulting in the formation of the following:



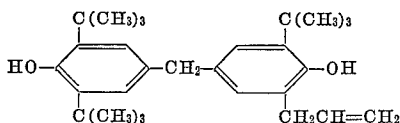
etc. Polyethers containing combinations of the above described basic units have been found to be quite useful in the practice of the present invention. A composition containing two different alkylene oxide groups can be prepared, for example, by reacting a polypropylene glycol with ethylene oxide in the presence of boron trifluoride. This mixed polyalkylene glycol, if desired, can then be reacted with an alkanol such as butanol to form the monobutoxyether of the mixed polyalkylene glycol. A number of these polyalkylene oxide materials are commercially available including the material sold under the trade name "Ucon" by Union Carbide Corporation, and the materials sold under the name of "Pluracol" by the Wyandotte Chemicals Corporation.

The molecular weight of the polyether oils used according to this invention can range from 300 to 200,000, from 400 to 20,000 being preferred.

The following examples are illustrative of the practice of my invention and are not intended for purposes of limitation. All parts are by weight unless otherwise indicated.

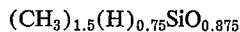
EXAMPLE 1

An allylated product of the formula:

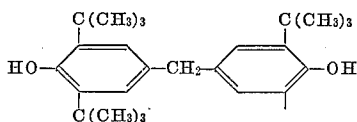


was prepared by dissolving 424 g. (1 mole) of 4,4'-methylene-bis-2,6-ditertiarybutylphenol in an equal weight of toluene and an equal weight of ethyl alcohol. One thousand grams of a solution containing 112 g. of potassium hydroxide in ethyl alcohol was made and slowly added to the phenol to provide the stoichiometric equivalent of the phenolic hydroxyl groups. A brilliant purple solution resulted which, when dried, showed no evidence of phenol and tested completely for complete conversion to the potassium phenylate. An additional equivalent amount of ethyl alcohol was added and 1.5 moles of allyl chloride was slowly introduced to the reaction mixture, which was refluxed for 2 hours at 70° C. All solids were filtered from the reaction mixture and the product was washed and stripped. Infrared analysis showed that the phenolate had been converted to phenol and that the allyl group was in place. Nuclear magnetic resonance evidence pointed to a replacement of one tertiary butyl group on one of the two aryl radicals by an allyl radical.

To a reaction vessel was added 300 g. of a liquid trimethylsilyl chain-stopped methylhydrogenpolysiloxane of the formula:

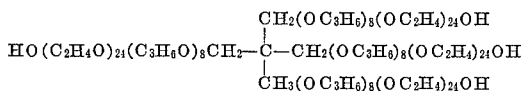


To this mixture was added 0.00125 gram of chloroplatinic acid hexahydrate and 28.8 grams of the allylated product over a period of 0.5 hour, while the temperature of the reaction mixture was maintained at 110° C. External heating was discontinued. Then 500 grams of decene-1 was added slowly to the reaction mixture over a one hour period, during which time the temperature was maintained at 110° C. by the exothermic reaction resulting from the addition. After complete addition of the decene-1, heat was applied to the flask to maintain temperature at 110° C. for an additional 30 minutes to insure that all $\equiv\text{SiH}$ is totally reacted and then the reaction product was vacuum stripped at 282° C. and 10 mm. Hg using a nitrogen purge. This resulted in a base oil within the scope of Formula 1 in which R is decyl, R' is a radical of the formula:



n has a value of 2.234, and p has a value of 0.016. Since there are fewer than one of the t-butylhydroxyarylpropyl-substituted silicon atoms per 8 silicon atoms and the polysiloxane contains 8 silicon atoms per molecule, it is apparent that the compositions of the present invention comprise a blend of products within the scope of Formula 2, some of which contain the internal antioxidant radical and some of which do not.

To 36 grams of the base oil and 18 grams of lithium myristate in a grease kettle were added 0.75 gram of a polyether of the formula:



and 0.01 gram of finely divided lithium hydroxide. The mixture was stirred and heated to 240° C. The mixture was maintained at 240° C. for 10 minutes with stirring. The mixture was then slowly cooled at a rate of 1.4° C. per minute to 150° C. at which temperature 0.45 gram of N-phenyl-alpha-naphthylamine, 0.1 gram of finely divided lithium hydroxide, 36 grams of the base oil, 7

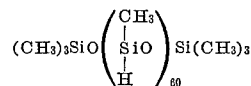
grams of lithium myristate, and 2 grams of zinc chromate were added. The slow cooling was continued to room temperature. The mixture was then milled three times through a Morehouse colloid mill set at 3 mils clearance. The resulting material was a light grade (290-330 penetration) grease with the following properties:

Penetration (worked 60X) -----	296.
Bleed (24 hours at 150° C.) -----	7.8%.
Evaporation (24 hours at 150° C.) ..	1.4%.
Appearance -----	Smooth paste, yellow-purple in color.

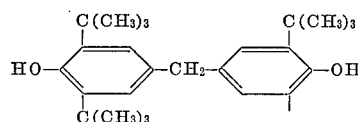
A similar grease was also made without using zinc chromate. Each grease was applied to a bearing with dissimilar metals as wearing surfaces. One wearing surface was made of aluminum and the second wearing surface was made of sintered iron. After running for about 200 hours, the bearing without the zinc chromate showed signs of pitting and unevenness due to the galvanic attack. The grease containing zinc chromate continued operating for over 6 months with no indication of pitting or unevenness.

EXAMPLE 2

To a reaction vessel was added 300 g. of a liquid trimethylsilyl chain-stopped methylhydrogenpolysiloxane of the formula:

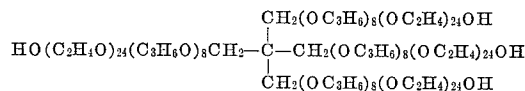


To this mixture was added 0.00125 gram of chloroplatinic acid hexahydrate and 28.8 grams of the allylated product described in Example 1 over a period of 0.5 hour, while the temperature of the reaction mixture was maintained at 110° C. Heating was discontinued. Then 683 grams of decene-1 was added slowly to the reaction mixture over a one hour period, during which time the temperature was maintained at 110° C. by the exothermic reaction resulting from the addition. After complete addition of the decene-1, heat was applied to the flask to maintain the temperature at 110° C. for an additional 30 minutes to insure that all $\equiv\text{SiH}$ was totally reacted and then the reaction product was vacuum stripped at 282° C. and 10 mm. Hg using a nitrogen purge. This resulted in a base oil within the scope of Formula 2 where R is decyl and methyl, and R' is a radical of the formula:



n has a value of 2.018, and p has a value of 0.0148. Since p , the ratio of the t-butylhydroxyaryl radicals to silicon atoms is less than one in 62, and there are 62 silicon atoms per siloxane molecule, it is apparent that the compositions of the present invention comprise a blend of products within the scope of Formula 2 in which the majority of the polysiloxane molecules contain one R' radical and a minor amount of the polysiloxane molecules which do not contain an R' radical.

To 36 grams of the base oil and 18 grams of lithium myristate in a grease kettle were added 0.75 gram of a polyether of the formula:



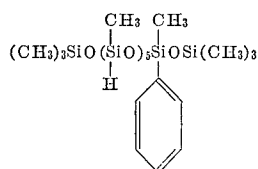
and 0.01 gram of finely divided lithium hydroxide. The mixture was stirred and heated to 240° C. The mixture was maintained at 240° C. for 10 minutes with stirring. The mixture was then slowly cooled at a rate of 1.4° C. per minute to 150° C. at which temperature 0.45 gram of N-phenyl-alpha-naphthylamine, 0.1 gram of finely divided lithium hydroxide, 36 grams of the base oil and 7 grams of lithium myristate and 2 grams of zinc chromate

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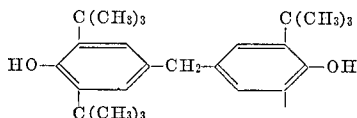
were added. The slow cooling was continued to room temperature. The mixture was then milled three times through a Morehouse colloid mill set at 3 mils clearance. The resulting material was a light grade (290–330 penetration) grease.

EXAMPLE 3

To a reaction vessel was added 300 g. of a liquid trimethylsilyl chain-stopped methylhydrogenpolysiloxane of the formula

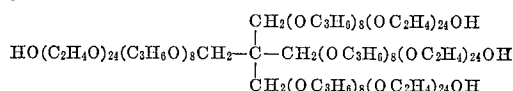


Over a period of 0.5 hour to this mixture was added 0.00125 gram of chloroplatinic acid hexahydrate and 28.8 grams of the allylated product described in Example 1 while the temperature of the reaction mixture was maintained at 110° C. Heating was discontinued and 440.0 grams of dodecene-1 was added slowly to the reaction mixture over a one hour period, during which time the temperature was maintained at 110° C. by the exothermic reaction resulting from the addition. After complete addition of the dodecene-1, heat was applied to the flask to maintain temperature at 110° C. for an additional 30 minutes to insure that all $\equiv\text{SiH}$ is totally reacted. The reaction product was then vacuum stripped at 282° C. and 10 mm. Hg using a nitrogen purge. This resulted in a base oil within the scope of Formula 2 where R is dodecyl, methyl and phenyl, R' is a radical of the formula:



n has a value of 2.225 and p has a value of 0.0186. Since there is an average of only 0.146 inhibitor radicals per polysiloxane molecule it is apparent that the compositions of the present invention comprise a blend of products within the scope of Formula 1, some of which contain one inhibitor radical but the majority of which do not.

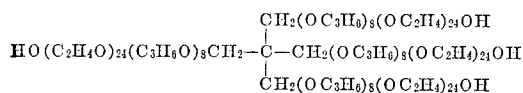
To 36 grams of the base oil and 18 grams of lithium myristate in a grease kettle were added 0.75 gram of a polyether of the formula:



and 0.01 gram of finely divided lithium hydroxide. The mixture was stirred and heated to 240° C. The mixture was maintained at 240° C. for 10 minutes with stirring. The mixture was then slowly cooled at a rate of 1.4° C. per minute to 150° C. at which temperature 0.45 gram of N-phenyl-alphanaphthylamine, 0.1 gram of finely divided lithium hydroxide, 36 grams of the base oil and 7 grams of lithium myristate and 2 grams of zinc chromate were added. The slow cooling was continued to room temperature. The mixture was then milled three times through a Morehouse colloid mill set at 3 mils clearance. The resulting material was a light grade (290–330 penetration) grease.

EXAMPLE 4

To 880 grams of the base oil of Example 1 in a grease kettle were added 20 grams of zinc chromate, 0.2 gram of a polyether of the formula:



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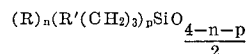
10.5 grams of a finely divided fumed silica, 0.5 gram of pentaerythritol and 0.8 gram of trimethoxyboroxine. The mixture was heated to 125° C. and maintained at 125° C. for 60 minutes with stirring. The mixture was cooled to room temperature. The mixture was then milled three times through a Morehouse colloid mill set at 3 mils clearance. The resulting material was a smooth semi-transparent, yellow-brown grease.

While the foregoing examples and discussion have illustrated many of the variations and compositions possible within the scope of the present invention, it should be understood that this invention relates broadly to a silicone grease which contains a metal salt of a chromate or of a dichromate, which metal salt prevents corrosion of dissimilar metal surfaces separated by a film of the grease.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A silicone grease which is used to lubricate dissimilar metal surfaces, comprising

- (1) from about 61% to about 98% based upon the weight of the grease of a polysiloxane fluid having a viscosity of about 10 centistokes to about 100,000 centistokes of the formula:

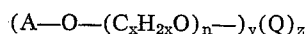


where R represents a member selected from the class consisting of alkyl radicals having from one to 22 carbon atoms; cycloalkyl radicals having from 5 to 7 carbon atoms; mononuclear and binuclear aryl radicals; mononuclear aryl lower alkyl radicals; halogenated derivatives of the aforementioned radicals; cyano lower alkyl radicals and hydrogen; R' is a t-butyl hydroxyaryl radical; n has a value of from 2.002 to 3.0; p has a value of 0 to 0.5; and the sum of $n+p$ has a value of 2.002 to 3.0;

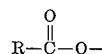
- (2) from about 2% to about 35% based upon the weight of the grease of a grease thickening agent;
- (3) from about 0.01% to about 5% based upon the weight of the polysiloxane fluid of a metal salt being at least one selected from the class consisting of alkali metal, alkaline earth metal and zinc salts of chromates and dichromates;
- (4) from about 0.01% to about 5% by weight based upon the weight of the polysiloxane fluid of a polyether selected from the formulas consisting of



and



wherein A and B represent radicals selected from the class consisting of hydrogen, alkyl radicals containing from 1 to 12 carbon atoms, cycloalkyl radicals containing 5 to 7 carbon atoms in the ring, mononuclear and binuclear aryl radicals and mononuclear aryl lower alkyl radicals wherein the alkyl groups attached to the aromatic nucleus contain a total of no more than 5 carbons atoms;



wherein R is alkyl containing from 1 to 11 carbon atoms; Q is a residue of a polyhydric initiator radical containing at least two hydroxyl radicals selected from the class consisting of ethylene glycol, glycerol, trimethylolpropane, and other polyhydric alcohols having from 2 to 6 hydroxyl groups; n is a number having a value of from 4 to 2000; x is a number having a value of 2 to 4; y has a value of from 2 to 10; and z has a value of from 1 to 5; the polyether having a molecular weight of from about 300 to about 200,000;

- (5) a sufficient amount of a metal base to maintain the grease in an alkaline condition.

2. The grease composition of claim 1, wherein:

- (1) the R radical of the polysiloxane fluid is selected

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- from the class consisting of alkyl radicals containing 10 carbon atoms and methyl radicals;
- (2) the grease thickening agent is a lithium soap of a higher fatty acid having from 12 to 22 carbon atoms;
- (3) the metal salt is present in an amount of about 0.1% to about 2%;
- (4) from about 0.1% to about 2% of the polyether is employed.
3. The grease composition of claim 1, wherein the metal salt is zinc chromate.
4. A grease composition of claim 1, wherein:
- (1) the R radical of the polysiloxane fluid is selected from the group consisting of alkyl radicals containing from 8 to 12 carbon atoms; mononuclear aryl radicals and methyl radicals;
- (2) the grease thickening agent is selected from the group consisting of lithium myristate and lithium stearate;
- (3) the metal salt is zinc chromate.

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U.S. Cl. X.R.

252—25, 28, 49.6, 387