CORROSION-INHIBITED SILICONE GREASE

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Notice: The portion of the term of this patent subsequent to Nov. 3, 1987, has been disclaimed.

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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.

5 Claims, No Drawings
3,664,953

1. CORROSION-INHIBITED SILICONE GREASE

This application is a continuation-in-part of my copending application Ser. No. 762,319 filed Sept. 16, 1968 now U.S. Pat. No. 3,537,995 and assigned to the same assignee as the present invention.

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 organopolysiloxane grease compositions which retain all the highly beneficial properties of heretofore 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 about 61 percent to about 98 percent 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:

\[(R)_s (R'CH_2)_{a-b} (RO)_{e-b} \] 

where \( R \) represents a member selected from the class consisting of alkyl radicals having from one to 22 carbon atoms; cycloalkyl radicals having from five to seven 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 hydroxymethyl radical; \( n \) has a value of about 3.5 to 10; \( p \) has a value of about 0 to 0.5, and the sum of \( n+p \) has a value of about 3.5 to 10; 2. from about 2 percent to about 35 percent based upon the weight of the grease of a grease thickening agent; 3. from about 0.01 percent to about 5 percent 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. optionally from about 0.01 percent to about 5 percent 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:

\[ R_2SiO_{(4-m) \over m} \]

where \( R \) represents a member selected from the class consisting of alkyl radicals having from one to 22 carbon atoms; cycloalkyl radicals having from five to seven carbon atoms; mononuclear or binuclear aryl radicals, halogenated derivatives of the aforementioned radicals, cyano lower alkyl radicals, lower alkyl radicals having from two to eight carbon atoms, and hydrogen, and \( m \) has a value of about 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 five to seven 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 and binuclear aryl radicals having up to 16 carbon atoms in the alkyl group, e.g., benzyl, phenylethyl, phenylethynyl, etc., radicals; lower alkyl radicals having from two to eight 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 from two to five carbon atoms, e.g., cyanomethyl, alpha-cyanoethyl, beta-cyanoethyl, gamma-cyanopropyl, etc., radicals. In the preferred embodiment of my invention, the organopolysiloxane fluid of the scope of formula (1) is those in which at least 50 percent of the organic radicals attached to silicon are alkyl 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 monogorganosiloxane units. The only requirement is that the ratio of the various siloxane units employed be selected so that the average composition of the copolymeric fluid is within the scope of formula (1). These various 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 trimethylsilyl oxide units, methylphenylsilyl oxide units, diphenylsilyl oxide units, triphenylsilyl oxide units, methyl-beta-cyanoethylsilyl oxide units, methylsilyl oxide units, phenylsiloxane units, beta-cyanoethyldimethylsilyl oxide units, etc.
3,664,953

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, an alkaline-earth metal or zinc. 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 consistencies of the greases of the present invention depend on the amount of thickening agent employed, the type of thickening agent employed and the particular polyisoxazolone fluids in the grease. Examples of suitable thickening agents include the metallic soaps of fatty acids of at least eight 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. Pat. Nos. 2,456,642 and 2,599,984. Metalic soaps of shorter chain length fatty acids such as acids containing from two to six carbon atoms as well as hydroxy-substituted fatty acids and hydroxy-substituted fatty acid glycerides such as are disclosed in U.S. Pat. Nos. 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 aerosol 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 U.S. Pat. No. 2,599,553, acyl ureas such as octodecanoyl urea as described in U.S. Pat. No. 2,698,300 and the phenylenediamidines such as N,N-acryloyl-stearoyl-p-phenylenediamides as described in U.S. Pat. No. 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 percent to 25 percent 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 polyisoxazolone grease. For satisfactory corrosion inhibition in a bimetallic 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 percent to 5 percent by weight based on the weight of the polyisoxazolone fluid in the composition. When less than 0.01 percent 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 percent 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 polyisoxazolone 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.

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

\[
(R')_n R''(CH_2)_n SiO
\]

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 hydroxyaryl radical and has the formula:

\[
(3) C(CH_3)_3
\]

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 hydroxyaryl-methylenephenylethers joined to the t-butyl-substituted hydroxyaryl radical through 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 tertiobutyl 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 eight carbon atoms in the alkyl group, e.g., benzy1, phenylethyl, etc. radicals. Among the hydroxyaryl radicals represented by Y of formula (3) are, for example, p-hydroxyphenyl, o, o-di(tert-butyl)p-hydroxyphenyl; o-(tert-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-hydroxyphenylethyl radicals, o-o-di(tert-butyl)-p-hydroxyphenylethyl radicals. Illustrative of the hydroxyarylether radicals are o,o-di(tert-butyl)-p-hydroxyphenylether radicals and o,o-di(tert-butyl)-p-hydroxyphenylethyl ether radicals. Illustrative of the hydroxyarylethioether radicals is o,o-di(tert-butyl)-p-hydroxyphenylethioether radicals, etc.

Illustrative of specific radicals represented by R' of formula (2) are, for example:

\[
\begin{array}{c}
\text{HO-CH}_2\text{-CH}_2\text{-CH}_3 \\
\text{HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 \\
\text{HO-CH}_2\text{-CH}_3 \\
\text{HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3
\end{array}
\]

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 tert-butyl-substituted hydroxyarylpropyl radical. The general method of preparation involves a starting material which contains a carbon-nitrogen-bonded hydroxy-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 tert-butyl radicals is then replaced by an allyl radical to produce an allyl-substituted material having the formula:

\[
R'\text{CH}_2\text{CH-CH}_2
\]

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.

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

\[
\text{HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3
\]

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:

\[
\begin{array}{c}
\text{HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 \\
\text{HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3
\end{array}
\]

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 the addition of one of the allylated radicals, followed by the addition of an alpha-olefin having from six to 12 carbon atoms to some type of methylhydrogenpolysiloxane. For example, the preparation of a trimethylsilylethyl chain-stopped methyl allylpolysiloxane of formula (2) involves the reaction between a trimethylsilyl chain-stopped methylhydrogenpolysiloxane having the formula:

\[
\begin{array}{c}
\text{HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 \\
\text{HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3
\end{array}
\]

where 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 one 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. No. 2,823,218 — Speier et al., the reaction product of chloroplatinic acid with either an alcohol, an ether or an aldehyde as described in U.S. Pat. No. 3,220,972 — Lamoreaux, trimethylplatinum iodide and hexamethyldiplatinum as described in U.S. Pat. No. 3,313,773 — Lamoreaux, the platinum olefin complex catalysts as described in U.S. Pat. No. 3,159,601 of Ashby and the platinum cyclopropane complex catalyst as described in U.S. Pat. No. 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 10⁻⁴ and preferably from 10⁻⁸ 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 methylenhydrogenpolysiloxane is first reacted 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 trimethyl-chained-stopped methylhydrogenpolysiloxane containing an average of 38 methylhydrogenpolysiloxane units per molecule. One mole of this methylhydrogenpolysiloxane is reacted with 1 mole of an allylated 3-butyl-substituted phenol, such as the product shown in the formula:

![Image](C6H5CH3CH3CH2+CH2)OH

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 when the thickening agent is a metal soap and the polysiloxane is composed primarily of dimethyldioxy units, it is preferable that a polyether be present in an amount equal to from 0.01 percent to 5.0 percent by weight based upon the weight of the polysiloxane fluids in the compositions, and preferably from 0.1 to 2.0 percent by weight. When the amount of polyether in the grease composition is in excess of 5.0 percent 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. When less than 0.01 percent by weight of the polyether is present, it is found that it is difficult to disperse a metal soap into an all methyl-substituted polysiloxane grease. A vigorous technique such as ball milling is required in the absence of a polyether. When from about one-half to all of the silicon atoms of the polysiloxanes contain a higher alkyl radical having about six to about 12 carbon atoms or more, a polyether dispersing agent is not needed. In situations where there is no compatibility problem, for example, when thickening agents other than metal soaps are used a polyether is not needed to aid in the dispersion. Thickening agents other than metal soaps include, for example, finely divided inorganic oxides of metallic and quasi-metallic materials carbon black, graphite, polyethylene, and phthalocyanine acyl ureas.

Even though there is no requirement that the polyether be present as a dispersing agent, in some instances it is used as a stabilizing agent. It is not a necessary stabilizing agent, however, as any number of other known stabilizing agents may be used or the stabilizing agent may be omitted entirely. Trimethoxyboroxine is an excellent stabilizing agent. In the following examples, polyethers are added to the oxidation inhibited higher alkyl containing grease compositions to impart a royal purple or brown color to the grease. This is its sole function. Without the polyether in the oxidation inhibited higher alkyl containing greases, they have a lack-luster pinkish tinge.

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:

![Image](A-O-(C(H2)4)2O)-B

wherein A and B represent radicals selected from the class comprising hydrogen, alkyl radicals containing from one to 12 carbon atoms, cycloalkyl radicals containing five to seven 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 five carbon atoms; A and B also represent ester forming groups containing from two 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 two to six hydroxyl groups; x is a number having a value of from 4 to 2,000; n is a number having a value of 2 to 4; y has a value of from 2 to 10; and z has a value 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 five to seven carbon atoms in the ring, e.g., cyclopentyl, cyclohexyl, cycloheptyl, etc. radicals; mononuclear and binuclear aryl radicals, e.g., phenyl, napthyl, biphenyl, etc. radicals; mononuclear aryl lower alkyl radicals wherein the alkyl groups attached to the aromatic nucleus contain a total of from one to seven carbon atoms, e.g., benzyl, phenyl ethyl, phenyl propyl, 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; hydroxyether 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, 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 penta-oxypropylene acetate); hydrogen, forming polyglycols (e.g., polyethylene glycol), etc.

To further exemplify the polyethers which can be used, the polyether oil, that is, the (C6H12O)n, — section of the above formula, can be derived form such basic units as the following oxides:

![Image](CH3)(H2)O—

see-propylene oxide —(OH—CH—O)—

see-butylene oxide —(OH—CH—O)—

CH3
or basic units obtained by the dehydration of alkylene glycols, resulting in the formation of the following:
ethylene oxide \( (CH_2-CH_2-O) \),
propylene oxide \( (CH_2-CH=CH-CH_2-O) \),
butylen oxide \( (CH_2-CH(=CH_2)-CH_2-O) \),
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 propylene glycol with ethylene oxide in the presence of boron trifluoride. This mixed polyalkylene glycol can then be reacted with an alkane such as butanol to form the monobutynoxether of the mixed polyalkylene glycol. A number of these polyalkylene oxide materials are commercially available including the material sold under the tradename 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 500 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:

\[
\begin{align*}
\text{C}(\text{CH}_3)\text{H}_2\text{O}\text{C}(\text{CH}_3)\text{H}_2\text{O}\text{C}(\text{CH}_3)\text{H}_2\text{O} & \quad 1 \\
\text{HO} & \quad 5 \\
\text{C}(\text{CH}_3)\text{H}_2\text{O} & \quad 10 \\
\text{C}(\text{CH}_3)\text{H}_2\text{O} & \quad 15 \\
\text{CH}_2\text{CH} & \quad 20 \\
\end{align*}
\]

was prepared by dissolving 424 g. (1 mole) of 4,4'-methylenebis-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 hydroxy 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 average unit formula:

\[
(\text{CH}_3)\text{H}_2\text{SiO}_n(\text{SiH}_2\text{CH}_3)_{1-n}
\]

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 hours, 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 1-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 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:

\[
\text{C}(\text{CH}_3)\text{H}_2\text{O}\text{C}(\text{CH}_3)\text{H}_2\text{O}(\text{SiH}_2\text{CH}_3)
\]

and 0.01 grams 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 grams of N-phenyl-alpha-naphthylamine, 0.1 grams 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 mls 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 galvanic attack. The grease containing zinc chromate continued operating for over 6 months with no indications of pitting or unevenness.

**EXAMPLE 2**

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

\[
(\text{CH}_3)\text{H}_2\text{SiO}_n(\text{SiH}_2\text{CH}_3)_{1-n}
\]

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 hours, 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 temperature at 110°C for an additional 30 minutes to insure that all 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:
applied to the flask to maintain the temperature at 110° C. for an additional 30 minutes to insure that all 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:

\[\text{CH}_3\text{OH} \quad \text{CH}_2\text{OH} \quad \text{CH}_3\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]

\[\text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH} \quad \text{C}(\text{CH}_3)\text{OH}\]
3,664,953

HO—(C₆H₄O)ₓ₋₁(C₆H₄O)ₓ₊₁—H was added with the original base oil. The results are as follows:

<table>
<thead>
<tr>
<th>Grease</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration (150°F/24 hours)</td>
<td>337</td>
<td>319</td>
</tr>
<tr>
<td>bleed (150°F/24 hours)</td>
<td>15.5</td>
<td>19.1</td>
</tr>
<tr>
<td>Evaporation (150°F/24 hours)</td>
<td>1.6</td>
<td>2.1</td>
</tr>
</tbody>
</table>

It can be seen that there are no significant differences in the properties of the greases containing the polyether as opposed to those not containing the polyether.

**EXAMPLE 6**

A grease was prepared from 89 parts of trimethylsilyl stopped polydimethylsiloxane fluid having a viscosity of 500 centistokes, 5.5 parts of a finely divided precipitated silica, 2.5 parts of fumed silica, 2.1 parts of tetramer treated fumed silica, 0.6 parts of pentaerythritol, 0.2 parts of boron and 2 grams of zinc chromate. The mixture was heated and mixed to get a uniform composition; then mixed three times through a Morehouse colloid mill set at 3 mile clearance and deaerated.

This grease in the table below is grease A. A similar grease was prepared except that 0.5 grams of a polyether of the formula HO—[(C₆H₄O)ₓ₋₁(C₆H₄O)ₓ₊₁)—ₙH was added to the above mixture. This is grease B in the following table. The test results, physical properties of Grease A and Grease B, are as follows:

<table>
<thead>
<tr>
<th>Grease</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration (200°F/24 hours)</td>
<td>230</td>
<td>211</td>
</tr>
<tr>
<td>bleed (200°F/24 hours)</td>
<td>4.86</td>
<td>2.3</td>
</tr>
<tr>
<td>Evaporation (200°F/24 hours)</td>
<td>2.06</td>
<td>1.8</td>
</tr>
<tr>
<td>Penetration, after heating 200°F</td>
<td>230</td>
<td>223</td>
</tr>
</tbody>
</table>

Again it is shown by the properties of the greases produced that the polyethers are not an essential component.

While the foregoing examples and discussions 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 retards electrolytic corrosion and oxidation, comprising on a weight basis:
   1. from about 61 percent to about 98 percent based upon the weight of the grease of a polylsiloxane fluid having a viscosity of about 10 centistokes to about 100,000 centistokes of the formula:
   \[
   (R)₄Cl\left(R'\left(CH₂\right)ₙ\right)ₚ\left(SiO\right)ₚ, \]
   where \( R \) represents a member selected from the class consisting of alkyl radicals having from one to 22 carbon atoms; cyanoalkyl radicals having from five to seven carbon atoms; mononuclear and binuclear aryl radicals; mononuclear lower alkyl radicals; halogenated derivatives of the aforementioned radicals; cyano lower alkyl radicals and hydrogen; \( R' \) is a \( t \)-butyl-substituted hydroxylaryl radical of the formula,

2. from about 2 percent to about 35 percent based upon the weight of the grease of a grease thickening agent;
   3. from about 0.01 percent to about 5 percent based upon the weight of the polylsiloxane 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.

where \( y \) is a member selected from the class consisting of hydrogen, monovalent hydrocarbon radicals, hydroxyaryl radicals, hydroxyaryl-substituted monovalent hydrocarbon radicals, hydroxyl ethers joined to the \( t \)-butyl-substituted hydroxylaryl radical through the ether linkage, hydroxylthioethers joined to the \( t \)-butyl-substituted hydroxylaryl radical through the thioether linkage and hydroxylmethylen ethers joined to the \( t \)-butyl-substituted hydroxylaryl radical through the methylene ether linkage; \( n \) 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 percent to about 35 percent based upon the weight of the grease of a grease thickening agent;

3. from about 0.01 percent to about 5 percent based upon the weight of the polylsiloxane 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.

2. A grease composition within the scope of claim 1 in which:
   1. the \( R \) radical is selected 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. A grease composition within the scope of claim 1 in which the metal salt is zinc chromate.

4. A composition within the scope of claim 1 in which:
   1. the \( R \) radical is selected from the class consisting of alkyl radicals containing from eight to 12 carbon atoms; mononuclear aryl radicals and methyl radicals;
   2. the grease thickening agent is selected from the class consisting of lithium myristate and lithium stearate;
   3. the metal salt is zinc chromate.

5. A silicone grease which prevents electrolytic corrosion, comprising on a weight basis, from about 61 percent to about 98 percent based upon the weight of the grease of a polylsiloxane fluid having a viscosity of about 10 centistokes to about 100,000 centistokes of the formula,

\[
Rₙ\left(SiO\right)ₚ, \]

where \( R \) represents a member selected from the class consisting of alkyl radicals having from one to 22 carbon atoms; cyanoalkyl radicals having from five to seven carbon atoms; mononuclear lower alkyl radicals; halogenated derivatives of the aforementioned radicals; cyano lower alkyl radicals and hydrogen; \( R' \) is a \( t \)-butyl-substituted hydroxylaryl radical of the formula,