Patented July 11, 1950 2,514,982

UNITED STATES PATENT OFFICE

2,514,982

STABILIZED LUBRICANT

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No Drawing. Application October 18, 1946, Serial No. 704,300

4 Claims. (Cl. 252—52)

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This invention relates to the stabilization of lubricating compositions against the deleterious effects of oxidation by the addition thereto of certain outstanding oxidation inhibitors. More particularly, this invention relates to the stabilization of certain non-hydrocarbon lubricants with specified polynuclear phenol derivatives.

The use of certain polymeric materials, such as polymers of propylene oxide, as lubricants has been suggested. While such polymers have found a limited use as substitutes for mineral oil lubricants, their utility has been limited by their relatively great susceptibility to oxidize, and the poor response which they show toward standard antioxidants, such as those employed with petroleum base lubricants.

These polymeric lubricants and the other non-mineral oil lubricants defined hereinafter, are especially distinguished from mineral oil lubricants by the volatility of their oxidation products. Petroleum oils have a tendency to form sludge and gummy or resinous products upon oxidation. Presumably they polymerize under the influence of certain oxygen containing intermediates, probably peroxides, aldehydes, etc.

Contrary to this phenomenon, the non-hydrocarbon lubricants defined hereinafter do not form appreciable amounts of sludge or thicken to any great extent upon oxidation. Instead, the oxidation products are of such a volatile nature that they escape from the lubrication system, thus causing high lubricant losses. While this escape of volatile oxidation products prevents undue formation of lacquer and carbon on engine parts, nevertheless the high lubricant consumption is a factor which has limited utilization of the non-hydrocarbon lubricants except under mild operating condition.

The other point which distinguishes the subject lubricants from mineral oils is their unaccountable insensitivity toward anti-oxidants normally employed with mineral oils. Actually, many of the standard anti-oxidants appear to promote the oxidation of the subject oxidants rather than retard it.

One class of anti-oxidants generally useful for the stabilization of mineral oils is the group comprising substituted phenols. While many of these are good mineral oil anti-oxidants, and have inhibiting properties in other organic compositions, they are not, as a group, effective anti-oxidants for the non-hydrocarbon substances described more particularly hereinafter. However, a restricted number of substituted phenols, also described fully hereinafter, have been found to

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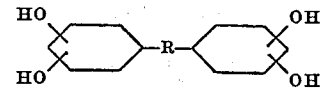
have an outstanding stabilizing effect in the compositions of this invention.

It is an object of the present invention to provide new lubricating compositions. It is another object of this invention to provide improved non-hydrocarbon lubricating compositions. It is a third object of this invention to provide a superior antioxidant for polymeric alkylene oxides and alkylene glycols, and for certain thioethers and polysulfides as more particularly defined hereinafter. It is a further object to provide improved non-mineral oil lubricants having a reduced tendency to oxidize and polymerize. Other objects will appear hereinafter.

Now, in accordance with this invention, it has been found that non-hydrocarbon lubricants comprising units of the general configuration:

$$-\left\{[O-R]_{m-1}-[O-R-(S)_p-R]_{n-1}\right\}_r-$$

wherein m, n, p and r are integers and each R is an organic radical, are effectively protected against oxidation by the presence of a minor amount of a polynuclear phenol derivative having the general formula



wherein R is an aliphatic hydrocarbon radical having from 2 to 20 carbon atoms.

Lubricants having the first general configuration include, among others, polyalkylene oxides and glycols having units of the general formula

$$-O-R-$$

Also included are the monomeric and polymeric thioethers having units of the general configuration

$$-O-R-S-R-$$

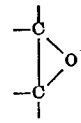
wherein the R's are organic radicals; monomeric or polymeric polysulfides having units of the general configuration

$$-O-R-\left(S\right)_p-R-$$

wherein p is an integer and the R's are organic radicals; and copolymers of individual members of each group with other members of the same or different groups.

Alkylene oxides. and particularly the alkylene oxides having the oxygen bound to adjacent carbon atoms, form polymers of the above configura-

tion. These monomeric oxides have the general configuration

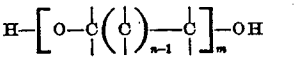


wherein the free valences are satisfied with hydrogens or organic radicals.

Alkylene oxides which form such polymers include ethylene oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide, isobutylene oxide, tetramethylethylene oxide, methylphenylethylene oxide, cyclohexene oxide, methylcyclohexene oxide, 1,2-cetene oxide; and other substances containing the epoxide linkage such as epichlorohydrin, epibromohydrin, and glycides such as glycidol and 1,2-epoxy-2-butanol, as well as derivatives and polymerizable homologs and analogs of the aforementioned substances.

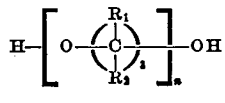
Copolymers of the alkylene oxides useful in compositions of the present invention include for example the copolymers of ethylene oxide and propylene oxide; and copolymers of ethylene oxide and isobutylene oxide; the copolymers of propylene oxide and epichlorohydrin; the copolymers of propylene oxide and 1,2-butylene oxide; the copolymers of propylene oxide and glycidol; and the copolymers of propylene oxide and isobutylene oxide.

Polymers similar to those above are formed from the alkylene glycols, including the polymethylene glycols and the ethylene glycols. The monomeric and lower polymeric glycols have the general configuration



wherein m and n are integers and the free valences are satisfied with hydrogen atoms or organic radicals. When n is 1, the general formula is that of an ethylene glycol, wherein the glycollic hydroxyls are on adjacent carbon atoms.

Glycols having three carbon atoms separating the glycollic hydroxyls are derived from propanediol-1,3 (trimethylene glycol) and have the general formula:



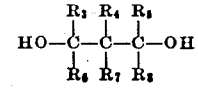
wherein n is an integer and R_1 and R_2 are hydrogens or organic radicals.

If R_1 and/or R_2 are not hydrogen atoms, they may be organic radicals such as alkyl, aralkyl, aryl, etc. Preferably, if they are not hydrogens, they are aliphatic radicals, especially saturated lower aliphatic radicals, but may also be groups which contain olefinic or acetylenic links. Typical of the trimethylene alkyl substituted glycols are the methylated trimethylene glycols, including 1-methyl-1,3-propanediol; 2-methyl-1,3-propanediol; 1,1-dimethyl-1,3-propanediol; 1,2-dimethyl-1,3-propanediol; 1,3-dimethyl-1,3-propanediol; 2,2-dimethyl-1,3-propanediol; 1,1,2-trimethyl-1,3-propanediol; 1,1,3-trimethyl-1,3-propanediol; 1,2,2-trimethyl-1,3-propanediol; 1,2,3-trimethyl-1,3-propanediol; 1,1,2,2-tetramethyl-1,3-propanediol; 1,1,3,3-tetramethyl-1,3-propanediol; 1,2,3,3-tetramethyl-1,3-propanediol; 1,1,2,2,3-pentamethyl-1,3-propanediol; 1,1,2,3,3-pentamethyl-1,3-propanediol; and hexamethyl-1,3-propanediol.

In place of the methyl groups other alkyl

groups may be utilized such as ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, etc., radicals, as well as their isomers. Preferably, when alkyl groups are the substituents R_1 and R_2, they have from 1 to 10 carbon atoms, and still more preferably from 1 to 5.

It will be understood that R_1 and R_2 may be similar or dissimilar groups. Thus, when expanding the general formula given hereinbefore to its indicated number of carbon atoms, it then becomes



wherein R_3 through R_8 are either hydrogen atoms or similar or dissimilar organic radicals. Those derivatives of trimethylene glycol, other than trimethylene glycol itself, which gives the most satisfactory polymers for general use have either one or two of the R's as lower alkyl groups. Thus, 2-methyl-1,3-propanediol and 2,2-dimethyl-1,3-propanediol form excellent polymers when treated according to the method of the present invention.

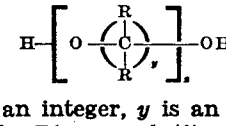
Other lower alkyl substituted trimethylene glycols which polymerize readily are 1-methyl-2-ethyl-1,3-propanediol; 2-methyl-2-ethyl-1,3-propanediol; 1-methyl-3-ethyl-1,3-propanediol; 2-methyl-2-propyl-1,3-propanediol; 1-methyl-2-isopropyl-1,3-propanediol; 2-methyl-2-butyl-1,3-propanediol; 2-methyl-3-butyl-1,3-propanediol; and the homologs, analogs and derivatives of the same.

Cycloaliphatic radicals may be one or more of the substituents represented by R_3 to R_8 in the above general formula. Thus R_3 through R_8 may be such radicals as cyclohexyl, methylcyclohexyl, dimethylcyclohexyl, ethylcyclohexyl, etc. However, open chain alkyl substituents form polymers having preferred properties.

The polymers have modified properties if the trimethylene glycol derivative contains other active groups, such as additional hydroxyls, carboxyls, carbonyls, halogens, sulfur, phosphorus, nitrogen, etc.

Polymethylene glycols having 6 or more carbon atoms separating the glycollic hydroxyls also form polymers and copolymers which are readily stabilized with the subject polynuclear phenol derivatives.

The polymethylene glycols from which such polymers are prepared have the general formula



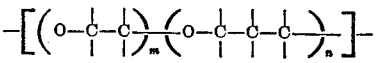
wherein z is an integer, y is an integer greater than 5 and the R's are substituents attached to each carbon atom, such as hydrogen atoms or organic radicals, especially hydrocarbon radicals. Preferably z is an integer less than 10, and more preferably is an integer than 1 to 4. Actually, when z is more than 1, the glycol is a dimer, trimer, etc., of the corresponding monomeric glycol. The polymethylene glycols polymerizing most readily are those in which y is an integer than 6 to 20.

Monomeric, unsubstituted polymethylene glycols falling within the above formula include 1,6-hexanediol; 1,7-heptanediol; 1,8-octanediol; 1,9-nonanediol; 1,10-decanediol; 1,12-dodecanediol; and polymerizable homologs, analogs and derivatives of the same.

The above glycols are those in which all of the R substituents attached to the carbon atoms are hydrogen atoms. When one or more of the R's are substituents other than hydrogen atoms they may be hydrocarbon radicals, such as aliphatic, aromatic, or alicyclic hydrocarbon radicals, or radicals containing non-hydrocarbon members, such as hydroxyl, carboxyl, or carbonyl groups, or sulfur, selenium tellerium, phosphorus or nitrogen atoms. Preferably, however, any organic radicals attached to the polymethylene glycol are hydrocarbon radicals. Of these, the aliphatic hydrocarbons are preferred, and the saturated lower aliphatic radicals give the most stable polymers and have the widest utility. Hence, the preferred R's, other than hydrogen, are the lower alkyls, such as methyl, ethyl, propyl, iso-propyl, butyl, sec-butyl, tert-butyl, amyl, iso-amyl, hexyl, etc. groups. Again even when R's other than hydrogen are present, it is preferred that the monomeric glycol contain a preponderance of hydrogen substituent R's. The most reactive glycols are those in which less than 4 R's are other than hydrogen, and the greatest reactivity is possessed by those having 2 or less R's which are organic radicals.

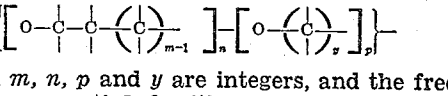
Glycols which fall within the above classification include 1,6-heptanediol; 1,6-octanediol; 1,6-nonanediol; 1,6-dodecanediol; 1,6-decanediol; 1,7-octanediol; 1,7-nonanediol; 1,7-decanediol; 1,7-dodecanediol; 1,8-nonanediol; 1,8-decanediol; 1,9-decanediol; 1,9-dodecanediol; 1,10-dodecanediol; 2,7-octanediol; 2,7-nonanediol; 2,7-decanediol; 2,7-dodecanediol; 2,8-nonanediol; 2,8-decanediol; 2,8-dodecanediol; 2,9-decanediol; 2,9-dodecanediol; 2,3-dimethyl-1,6-hexanediol; 2,4-dimethyl-1,6-hexanediol; 2,5 - dimethyl-1,6-hexanediol; 4,4-dimethyl-1,6-hexanediol; 5,5-dimethyl-1,6-hexanediol; 2 - methyl - 3 - ethyl-1,7-heptanediol; 2-ethyl-3-methyl-1,7 - heptanediol; 3,3-diethyl-1,7-heptanediol; 3,4 - diisopropyl-1,8-octanediol; etc. and their polymerizable homologs, analogs and derivatives.

The polymers described hereinbefore may be homopolymers or may be copolymers. For example an ethylene glycol may be copolymerized with a trimethylene glycol to give copolymers having units of the general configuration:



wherein m and n are integers and the free valences within the brackets are satisfied with hydrogen atoms or organic radicals. These include copolymers of ethylene glycol and trimethylene glycol; ethylene glycol and 1-methyl-1,3-propanediol; ethylene glycol and 2-methyl-1,3-propanediol; ethylene glycol and 2,2-dimethyl-1,3-propanediol; ethylene glycol and 1,3-diethyl-1,3-propanediol; 1,2-dimethylethylene glycol and trimethylene glycol; 1,2-dimethylethylene glycol and 1,3-dibutyl-1,3-propanediol, etc.

Other copolymers falling within the general formula of substances stabilized according to the present invention include the copolymers of an ethylene glycol or a trimethylene glycol with a polymethylene glycol having more than 5 carbon atoms separating the glycollic hydroxyls. These copolymers have units of the general configuration:

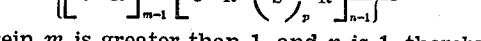


wherein m, n, p and y are integers, and the free valences are satisfied with hydrogen atoms or

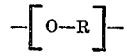
organic radicals. These include for example, copolymers of ethylene glycol and hexamethylene glycol; trimethylene glycol and hexamethylene glycol, etc.

The alkylene oxides usually are polymerized at temperatures from about −60° C. to about 100° C. in the presence of alkalies, acids amines or salts. The glycols are polymerized at higher temperatures (150–300° C.) in the presence of dehydration catalysts, such as iodine, mineral acids, such as nitric acid or sulfuric acid, hydrogen halides such as hydrogen iodide or hydrogen chloride; or organic sulfonic acids such as para-toluene sulfonic acid.

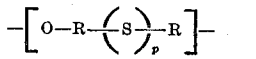
All of the polymers and copolymers described hereinbefore are those having units of the general formula



wherein m is greater than 1, and n is 1, thereby giving polymers having units of the general configuration

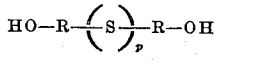


On the other hand, when m is 1 and n is greater than 1, the non-hydrocarbons have units of the general configuration:



wherein p is an integer. These substances may be monomeric or polymeric thio-ethers or polysulfides.

The hydroxy thio-ethers and polysulfides from which the present lubricating compositions may be prepared are represented by the general formula



wherein the R's are organic radicals and p is an integer. When p is 1, the general formula is that of a dihydroxy thio-ether, whereas when p is more than 1 the general formula is that of a dihydroxypolysulfide. Preferably, p is an integer from 1 to 6, the polymers of greatest utility are those in which p is an integer between 1 and 3, inclusive.

The dihydroxythioethers having the general formula:

HO—R—S—R—OH

have organic radicals which are either similar or dissimilar. Preferably they are similar hydrocarbon radicals. The aliphatic hydrocarbon radicals, and especially the saturated aliphatic hydrocarbon radicals form polymers with the subject alkylene glycols having high stability against oxidation.

When the R's are saturated aliphatic hydrocarbon radicals, they may be of primary, secondary or tertiary character with relation to the thio-ether sulfur atom, dependent upon their method of formation. For example, the primary dihydroxy thio-ethers have the general formula:

HO—R—CH_2—S—CH_2—R—OH

wherein the R's are saturated aliphatic radicals. Thio-ethers of this configuration are conveniently prepared by the "abnormal" condensation of unsaturated alcohols with hydrogen sulfide. Thus, when allyl alcohol and hydrogen sulfide are condensed in the presence of ultra-violet light at

moderate temperatures, one of the products is bis (gamma hydroxypropyl) sulfide.

A typical preparation of this character is that of the condensation of hydrogen sulfide with allyl alcohol, as follows:

Allyl alcohol (500 cc.) and hydrogen sulfide (124 g.) were mixed in a quartz tube and irradiated near a 250 watt mercury arc lamp for two hours. During the first hour the pressure rose from 140 p. s. i. to 190 p. s. i., after which it fell to 160 p. s. i. In this time the temperature increased from 100° C. to 150° C., due in part to the exothermic character of the reaction, but mainly due to the heat from the mercury arc lamp. The product was subjected to fractional distillation, that part remaining in the still above 134° C. at 0.3 cm. Hg pressure being bis (gamma-hydroxypropyl) sulfide.

Suitable alcohols for the preparation of primary dihydroxythioethers include isopropenyl alcohol, allyl alcohol, crotenyl alcohol, methallyl alcohol, and their homologs, analogs and substitution products. Dihydroxy thioethers formed by the above method include bis (beta-hydroxyethyl) sulfide and bis (gamma-hydroxypropyl) sulfide.

If the thioether has hydroxyl groups on other than terminal carbons, the dihydroxy thioethers include bis (alpha-hydroxyethyl) sulfide, bis (alpha- and beta-hydroxypropyl) sulfide.

Mixed hydroxythioethers are useful in forming the copolymers of the present invention. These include beta-hydroxyethyl-gamma-hydroxy-propyl sulfide, hydroxy-methyl-beta-hydroxyethyl sulfide, alpha-hydroxyethyl-alpha-hydroxypropyl sulfide, as well as their homologs, analogs and derivatives. Higher thioethers of this class may be prepared having hydroxybutyl, hydroxyamyl, hydroxyethyl, etc., groups.

Those hydroxythioethers having the general formula

$$HO—R—CH_2—S—CH_2—R—OH$$

in which the R's are similar saturated aliphatic radicals having from 1 to 6 carbon atoms are preferred in preparing the copolymers of the present invention.

When the monomeric sulfur compound is a polysulfide having the general formula

$$HO—R—\left(S\right)_p—R—OH$$

it is preferred that p be a number between 2 and 6, and that the R's be similar or dissimilar saturated aliphatic hydrocarbons. The latter may have, however, functional groups attached thereto, such as carboxyl, carbonyl, hydroxyl, etc. Preferably the R's are similar saturated aliphatic radicals having from 2 to 20 carbon atoms. While these latter may be of primary, secondary or tertiary nature, with respect to the sulfur atom, those forming polymers of the greatest utility have the general formula

$$HO—R—CH_2—\left(S\right)_p—CH_2—R—OH$$

wherein the R's are similar saturated aliphatic hydrocarbons having 1 to 19 carbons (preferably 1 to 6) and p is an integer from 2 to 6 (preferably 2 or 3). Such polysulfides may be prepared, for example, by the condensation of two molecules of a mercaptoalkyl alcohol, as follows:

One of the by-products of the reaction of allyl alcohol and hydrogen sulfide, described above, is gamma-mercaptopropyl alcohol. It is isolated by distillation of the irradiated condensation mixture, the fraction distilling of 132–134° C. (16 cm. Hg pressure) being gamma-mercaptopropyl alcohol, in a yield of 18.0% based on the charge.

One mol of the mercaptopropyl alcohol was mixed with an aqueous solution in the presence of one mol of potassium hydroxide. Starting at room temperature, the calculated quantity of iodine was added slowly. The product was distilled, yielding bis (gamma-hydroxypropyl) disulfide as the fraction boiling above about 180° C. under 0.2 cm. Hg pressure.

Polysulfides having the preferred structure include bis (gamma-hydroxypropyl) disulfide, bis (beta-hydroxyethyl) disulfide, bis (hydroxymethyl) disulfide, hydroxymethyl-gamma-hydroxypropyl disulfide, hydroxymethyl-beta-hydroxyethyl disulfide, beta-hydroxyethyl-gamma-hydroxypropyl disulfide, etc., and their homologs and analogs.

The various substances described above are chain-like monomers or polymers containing one or two terminal hydroxyl groups. These hydroxyls may be acted upon by the usual methods with such materials as etherifying or esterifying agents in order to obtain products having altered properties, such as solubility or improved action as lubricants.

Various etherifying agents may be used for etherifying the terminal hydroxyl groups. These include alkyl halides, such as methyl iodide, methyl bromide, ethyl chloride, propyl iodide; aralkyl halides such as benzyl chloride and methylbenzyl chloride; hydroxyalkyl chlorides such as hydroxyethyl chloride; carboxyalkylating agents such as sodium monochloracetate; and alkylene halides such as allyl chloride. Ordinarily, the etherification is carried out in strongly basic environment; sodium hydroxide, liquid ammonia and quaternary ammonium bases and salts being the usual basic substances present.

Esterification of the terminal hydroxyls may be accomplished with various inorganic groups such as nitrates, phosphates or sulfates. However, preferred esterifying agents are the organic acids, anhydrides or acid chlorides, and especially fatty acid anhydrides and their chlorides, including for example those of formic, acetic, propionic, butyric, hexoic, 2-ethylhexoic, and higher fatty acids, such as lauric, stearic, myristic, palmitic and capric acids. Usually, the esters are formed by treatment of the hydroxylated polymer with the anhydride of the acid in the presence of a catalyst such as sulfuric or phosphoric acid. The saturated fatty acids form the most stable esters with the glycol polymers.

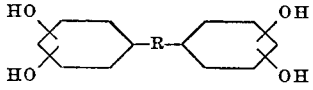
At times it is preferable to allow only partial esterification or etherification, thus forming half-esters or half-ethers instead of the di-esters or diethers theoretically possible. For other purposes the end group hydroxyls may not only be partially or completely esterified or etherified, but also may be so treated as to result in the formation of mixed ethers, mixed esters or ether-esters.

Etherification or esterification of the end-groups may take place simultaneously with or subsequent to polymerization, and may be effected prior to or subsequent to any decolorizing or purifying processes. Preferably, the end-group modification is carried out immediately after polymerization and before purification or decolorizing, but a secondary preferred time for

modification is during the polymerization step itself.

In employing this latter alternative, the exact mechanism by which substitution of the end-groups occurs is obscure. However, it has been discovered, in accordance with this invention, that by using an active modifying agent, such as an alcohol, as the diluent during the polymerization, reaction occurs to give polymers having at least one substituted end group, such as on ether group or ester group. For example, if alcohols such as n-octyl alcohol, n-decyl alcohol, n-dodecyl alcohol, etc., or their isomers, are used as diluents during the polymerization, the corresponding ethers of the polymers are formed. Since this provides a convenient method for modifying the properties of the polymer, it is preferred that the alcoholic diluent, or other modifying agent, have from 6 to 20 carbon atoms. The reactive diluent may be the only diluent present, or may be mixed with one or more inert diluents.

The preferred group of stabilizers have the general configuration



wherein R is an aliphatic hydrocarbon radical having from 2 to 20 carbon atoms. The substances giving the most satisfactory results are those in which the pair of hydroxyl groups attached to each phenyl radical are on adjacent carbon atoms. This preferred group includes 1, 4-bis (3,4-dihydroxphenyl) butane; 2,3-dimethyl-1,4-bis (3,4-dihydroxyphenyl) butane; 1,6-bis (2,3-dihydroxyphenyl) hexane; 3,5-diethyl-1,7-bis (3,4-dihydroxyphenyl) heptane; 2-methyl-3-propyl-1,4-bis (3,4-dihydroxyphenyl) butane; and their homologs and analogs.

The amount of polynuclear phenols required to stabilize the substances defined hereinbefore varies somewhat with the conditions to which the composition will be subjected, with the secondary additives in the composition and with the exact identity of the monomer or polymer to be stabilized. Ordinarily, the inhibitor gives optimum stabilization when present in amount between about 0.05% and about 5% by weight, preferably from 1% to 2.5%.

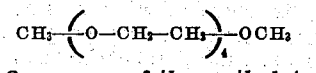
Polynuclear substituted phenols may be used in combination with secondary additives such as corrosion inhibitors (including organic acidic materials forming water-insoluble soaps), E. P. agents, etc., as well as gelling agents, such as calcium, barium, sodium, potassium, lithium or strontium soaps, for the preparation of non-hydrocarbon greases which are stable towards oxidizing influences.

The stabilized compositions comprising the present invention are useful for general lubrication purposes, such as automotive lubrication, Diesel engine lubrication, cutting oils, aircraft lubrication, instrument lubrication, etc. The subject compositions are superior to mineral oils in that relatively little engine deposits are formed during use, and are superior to the uninhibited bases from which the compositions are prepared in that lubricant consumption of the stabilized compositions is relatively low.

The polynuclear substituted phenols may be dissolved in the other components of the composition, or may be dispersed uniformly throughout in a finely divided form, held in suspension by colloidal action. The polymeric alkylene oxides and glycols, for example, exhibit certain colloidal properties, but in the absence of, or in addition to, such inherent properties, other colloidal materials or mutual solvents may be added to aid in creating a uniform dispersion of a relatively permanent character.

The following example illustrates the present invention:

A lower polymer of ethylene glycol was methylated with methyl chloride in the presence of concentrated sodium hydroxide, as described hereinbefore. The methylated polymer had a molecular weight and methoxyl content corresponding to the formula

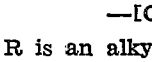


Seventy-five grams of the methylated polymer was heated at 140° C. in a closed bomb under an initial oxygen pressure of 50 pounds per square inch, in the presence of 1 square centimeter copper per gram of polymer. The oxygen pressure dropped 10 pounds in one-half hour and 20 pounds in less than 1 hour.

A sample of the polymer was oxidized under conditions identical with those above, except that 1% of 2,3-dimethyl-1,4-bis (3,4-dihydroxyphenyl) butane was dissolved therein. It required 35 hours for the oxygen pressure to drop 10 p. s. i., and 101 hours for the oxygen pressure to drop 20 p. s. i. The rate of oxidation was constant throughout the test period.

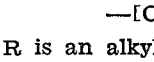
We claim as our invention:

1. A lubricating composition comprising as the major lubricating ingredient thereof, an oleaginous polymer having recurring units of the general configuration

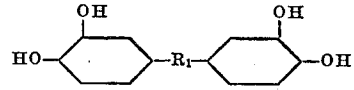


wherein R is an alkylene hydrocarbon radical, and from about 0.05% to about 5% by weight of 2,3 - dimethyl - 1,4 - bis (3,4-dihydroxyphenyl) butane.

2. A lubricating composition comprising as the major lubricating ingredient thereof an oleaginous polymer having recurring units of the general configuration

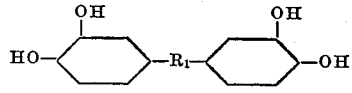


wherein R is an alkylene hydrocarbon radical, and from about 0.05% to about 5% by weight of a polynuclear phenol having the general configuration



wherein R_1 is an alkylene hydrocarbon radical containing up to 20 carbon atoms and the two dihydroxy phenyl groups are separated by at least a four carbon atom chain of said R_1.

3. A lubricating composition comprising as the major lubricating ingredient thereof an oleaginous polyalkylene glycol and from about 0.05% to about 5% by weight of a polynuclear phenol having the general configuration:



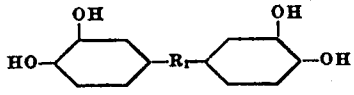
wherein R_1 is an alkylene hydrocarbon radical containing up to twenty carbon atoms and the two dihydroxyphenyl groups are separated by at least a four-carbon-atom chain of said R_1.

4. A lubricating composition comprising as the

major lubricating ingredient thereof an oleaginous polymer having recurring units of the general configuration:

—[O—R]—

wherein R is an alkylene hydrocarbon radical and from about 0.05% to about 5% by weight of a polynuclear phenol having the general configuration:



wherein R_1 is an alkylene hydrocarbon radical containing up to twenty carbon atoms, the two dihydroxyphenyl groups being separated by a four-carbon-atom chain, said carbon atoms being a part of the group R_1.

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