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EXTREME PRESSURE LUBRICATING COMPOSITION

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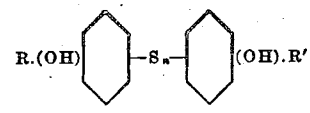
No Drawing. Application December 13, 1938, Serial No. 245,503

16 Claims. (Cl. 252—46)

This invention relates to improved lubricating compositions suitable for lubricating bearing surfaces under "extreme pressure" conditions, involving very heavy loads per unit of bearing area. The lubricating compositions of this invention are especially suited for lubricating steel bearings.

It has already been shown in my copending application, Serial No. 93,764, filed August 1, 1936, jointly with Eugene Lieber, that alkyl phenol polysulfides are improved stabilizing agents for lubricating oils. It has now been found that by the use of larger proportions of the alkyl phenol polysulfides above about 5% and preferably about 8 to 15%, the ability of the lubricating oil blends to carry heavy loads is greatly increased, the resulting lubricants being effective cutting oils, transmission oils, hypoid gear lubricants and the like. They are also suitable for use in the preparation of greases.

The alkyl phenol polysulfides used in preparing the improved lubricating compositions of this invention are represented as follows:



in which R and R' represent alkyl groups of 2 to about 8 or more carbon atoms, preferably of 4 to 8 carbon atoms. R' is preferably the same as R but may also be a different alkyl group from R. These alkyl groups may be normal or iso, and primary, secondary, or tertiary groups. Either or both of the aromatic nuclei may be replaced by naphthyl, anthracyl, or other condensed aromatic radicals. *n* is an integer from 2 to about 4, and is preferably 2. The formula illustrated is purely diagrammatic and the substitutent radicals, hydroxyl, alkyl, and sulfur, may be connected to any position in the benzene ring, but those compounds in which the alkyl radicals are in ortho or para positions to the hydroxyl groups are preferred. Derivatives of these compounds containing additional alkyl, hydroxy and/or sulfur groups, or still other groups such as halogen and CN, which may be connected to either the alkyl groups, the aromatic nucleus, and/or the sulfur group, are also included. For example, the alkyl groups may be aryl-alkyl groups, such as benzyl. Likewise, the sulfur may be wholly or partially replaced by selenium or tellurium.

The use of these compounds in the preparation of extreme pressure lubricants is illustrated by the following example:

EXAMPLE 1

Tertiary amyl phenol disulfide was added to a pale paraffin lubricating oil having a Saybolt viscosity of 100 seconds at 100° F. and derived from petroleum. This straight mineral oil and the blends were then tested under comparable conditions in an Almen machine using a steel pin. The test was conducted according to the method described in the National Petroleum News, November 2, 1932. The results are given in the following table, in which the maximum number of weights carried without failure is indicated for each oil.

Lubricating oil

	Number of weights
Straight mineral oil	3 to 4
Straight mineral oil +6% amyl phenol disulfide	13
Straight mineral oil +8% amyl phenol disulfide	15

Still higher concentrations containing up to about 25% of tertiary amyl phenol disulfide were prepared in similar lubricating oils. All such concentrations were satisfactory extreme pressure lubricants and carried 15 weights (the maximum number used in the Almen test).

A similar blend of the same lubricating oil containing 24% of tertiary amyl phenol thioether carried only 7 weights.

The halogenated alkyl phenol sulfides are effective extreme pressure lubricant aids in even lower concentrations in lubricating oil than the corresponding unhalogenated compounds, and concentrations as low as 1 to 2% of such halogenated compounds may be used. This is shown in the following example:

EXAMPLE 2

A blend of chlorinated amyl phenol sulfide was prepared with a petroleum lubricating oil and tested for extreme pressure lubricating properties, as described in Example 1.

Lubricating oil

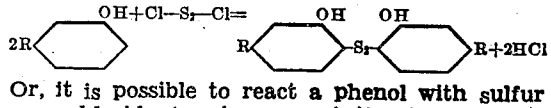
	Number of weights
Straight mineral oil	3 to 4
Straight mineral oil +2% chlorinated amyl phenol disulfide (13.5% chlorine)	15

Similar results are obtained with the corre-

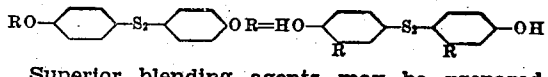
sponding chlorinated alkyl phenol thioethers, although the unchlorinated thioether, as indicated above, is of much less value as an extreme pressure lubricant aid.

The halogenated alkyl phenol sulfides may contain halogen in either the alkyl or the aryl groups or both. They are readily prepared by direct halogenation. For example, the alkyl phenol disulfide is heated to 90 to 100° C. and chlorine is bubbled through the heated compound with rapid stirring. The hydrogen chloride is allowed to escape as it is formed. When the desired amount of chlorine has been absorbed (readily indicated by the increase in weight of the chlorinated product), the mixture is blown with air to remove residual hydrochloric acid. The product is then ready for immediate use, provided the hydrochloric acid has been fully removed. Instead of blowing the reaction product with air, this product may be dissolved in a suitable solvent, such as naphtha, benzol, or ethylene dichloride, and this solution washed with dilute aqueous sodium carbonate or even with water alone. The washed solution is then dried and the solvent removed, the residue being the finished chlorinated product. The chlorination may also be carried out in an inert solvent, such as carbon tetrachloride. In this case the reaction is somewhat slower. By such direct chlorination treatments alkyl phenol sulfides containing chlorine in concentrations up to about 22% by weight and even higher are readily prepared.

The alkyl phenol polysulfides used in this invention may be prepared in a number of ways. For example, the corresponding phenol may be heated with sulfur monochloride, driving off HCl according to the reaction:



Or, it is possible to react a phenol with sulfur monochloride to give, say, 4:4' dihydroxy diphenyl disulfide which may then be alkylated either by reacting with an olefin or an alcohol or alkyl chloride in presence of a condensing agent such as sulfuric acid, boron fluoride, aluminum chloride, etc. Another method of preparation is to first produce 4—4' dihydroxy diphenyl disulfide by reacting phenol with sulfur monochloride, and then prepare ethers by reaction in alkaline media with alkyl chlorides or dialkyl sulfates. These ethers, in turn, may then be isomerized in the presence of anhydrous aluminum chloride to produce dialkyl diphenol polysulfides as in the example:



Superior blending agents may be prepared from alkylated phenols obtained by condensation of phenol with the C_4 and/or C_5 fraction of cracked petroleum hydrocarbons, these being rich in secondary and tertiary olefins of 4 and/or 5 carbon atoms, the alkylated products being converted to the dialkyl phenol polysulfides by any of the above processes. The secondary olefins may be separated from the tertiary, and condensed separately to produce corresponding mixed disecondary-or ditertiary-phenol polysulfides.

The crude compounds formed by the above methods may be further purified by distillation, extraction, treating with clay, acid, etc.

Suitable methods for preparing the blending agents used in this invention are also described in my copending application Serial No. 97,196, filed August 21, 1936, jointly with Eugene Lieber, and involve the reaction of an alkyl phenol with a sulfur halide. This reaction is preferably conducted in the presence of an inert diluent, preferably an alkyl halide such as ethylene chloride, which boils at the reaction temperature and is condensed under reflux while withdrawing the evolved hydrogen halide from the reaction zone. When the reaction is completed, as evidenced by the failure to liberate further hydrogen halide, the solvent and any unreacted phenol are removed by distillation and the polysulfide is obtained as a distillation residue.

The reaction of the alkyl phenol and sulfur monochloride is preferably conducted with a ratio of between about 0.4 and 0.6 mol of sulfur monochloride per mol of alkyl phenol. The use of higher ratios leads to the formation of resins which are insoluble in petroleum lubricating oils. Even with the preferred ratios a small proportion of polymers such as dimers and trimers are obtained along with the desired product. Such relatively low molecular weight polymers are soluble in petroleum lubricating oils and are not objectionable in the product. In fact, it has been found that in some instances their presence is advantageous.

The reaction may also be conducted with a mixture of sulfur monochloride and sulfur dichloride, in which mixture the proportion of the latter is usually less than 0.75 and is preferably about 0.10 to 0.35, based on the total sulfur halide used. In using this mixed reagent there is obtained as a reaction product a mixture of alkyl phenol disulfide with an amount of alkyl phenol monosulfide corresponding to the proportions of the respective sulfur halides used.

The following example illustrates a suitable method for preparing alkyl phenol sulfides used in this invention.

EXAMPLE 3

One molal proportion of tertiary amyl phenol is dissolved in ethylene chloride and the solution is heated to boiling under reflux. A solution of ½ molal proportion of sulfur monochloride in ethylene dichloride is then added slowly with stirring to the boiling solution of amyl phenol. The hydrogen chloride gas evolved during the reaction is withdrawn from the reaction zone through the reflux condenser. When the addition of sulfur monochloride solution is completed, the boiling of the reaction mixture under reflux is continued for about six hours or until no further emission of hydrogen chloride is detectable. By this means all the hydrogen chloride is removed. The time of refluxing can be cut down by blowing an inert gas, such as nitrogen or flue gas through the reaction mixture. This may be done during the reaction or after all the reagents have been added as desired.

The solvent ethylene chloride is then removed from the reaction mixture by distillation and any unreacted amyl phenol is removed by distillation under vacuum at a temperature of preferably not above about 150 to 175° C.

There is thus obtained as distillation residue a product consisting substantially of the desired amyl phenol disulfide. This product is a dark brown to reddish colored viscous liquid, which is soluble in most organic solvents, including petroleum and fractions thereof such as gasoline, kerosene, burning and Diesel oils, and lubricating oils. The crude product may be used directly as

obtained or after any desired purification, as by treatment with selective solvents or adsorbtive materials such as clay.

Higher polysulfides suitable for use in the present invention may be prepared by condensing alkyl hydroxy thiophenols with sulfur monochloride or sulfur dichloride. The alkyl hydroxy thiophenols may be obtained by reduction either of the alkyl phenol disulfides described above or of alkyl phenol chlor sulfonic acids. These reactions may be illustrated as follows:

1. $R(C_6H_3)OH.S_2.(C_6H_3)OH.R' + H_2 = 2[R(C_6H_3)OH.SH]$

2. $2[R(C_6H_3)OH.SH] + S_2Cl_2 = R(C_6H_3)OH.S_4.(C_6H_3)OH.R'$

3. $2[R(C_6H_3)OH.SH] + SCl_2 = R(C_6H_3)OH.S_3.(C_6H_3)OH.R'$

R and R' in the above formulae have the same significance as in the first formula presented herein. Reactions 2 and 3 may be conducted under the same conditions described in Example 1, using half the molal proportion of the sulfur halide. These tri and tetra sulfides may be used as blending agents with lubricating oils in the same manner already described herein for the disulfides.

The alkyl phenol polysulfides described above are blended with lubricating vehicles of any desired viscosity, depending upon the use to which the extreme pressure lubricant is to be put. These lubricants include mineral lubricating oils, especially the highly refined oils such as synthetic oils, solvent extracted oils obtained by treatment of mineral lubricating oils with single solvents such phenol, dichlorethyl ether, furfural, propane, nitrobenzene, crotonaldehyde, etc., or by double or multiple solvents such as propane-cresol, etc., clay or acid treated oils, also aluminum chloride treated oils, white oils, hydrogenated oils, and the like. These compounds are especially effective with such oils having viscosity indices above 60, 80, 100 or more. Lubricating oils also improved by these compounds are other mineral oils of over 35 or 40 viscosity Saybolt at 210° F., and even those having a viscosity of over 100 seconds at 100° F., either in the crude form or partially or highly refined by distillation, voltolization, chemical reagents, and adsorptive agents, as well as coal tar or shale distillates, pale oils, neutrals, bright stocks and other residual stocks, cracking coil tar fractions, condensed or polymerized fractions, and the like, either waxy, dewaxed, or non-waxy. The alkyl phenol polysulfides may also be added to thickly viscous and solid hydrocarbon lubricants, and to greases containing hydrocarbon lubricants and soaps, with or without water and other compounding agents. They are also effective lubricant aids in cutting oils, being preferred for use in the true oil type which contains little or no water and is used without emulsification with water. They may also be added to "miscible" cutting oils intended for emulsification with water before use, but are less effective in such dilute aqueous compositions.

The lubricants to which these improved agents are added may also contain dyes, metallic or other soaps, pour inhibitors, sludge dispersers, oxidation inhibitors, thickeners, V. I. improvers such as soluble linear polymers of isobutylene, oiliness agents, resins, rubber, fatty oils, heat thickened fatty oils, sulfurized fatty oils, extreme pressure lubricating agents, such as lead soaps, organo-metallic compounds, bright stocks (such as refined petroleum lubricating oil residues), voltolized fats, mineral oils and/or waxes, colloidal solids such as graphite, zinc oxide, etc., and the like.

This invention is not to be limited to any specific examples, all of which have been presented solely for the purpose of illustration, but is to be limited only by the following claims, in which it is desired to claim all novelty insofar as the prior art permits.

I claim:

1. An extreme pressure lubricant composition comprising a hydrocarbon lubricant and an alkyl phenol sulfide in an amount between above 5% and 25%.

2. An extreme pressure lubricant composition comprising a hydrocarbon lubricant and an alkyl phenol polysulfide in an amount between above 5% and 25%.

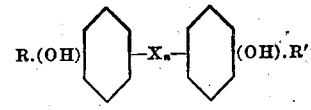
3. An extreme pressure lubricant composition comprising a hydrocarbon lubricant and an alkyl phenol disulfide in an amount between above 5% and 25%.

4. An extreme pressure lubricant composition comprising a hydrocarbon lubricant and a halogenated alkyl phenol sulfide in an amount between above 5% and 25%.

5. An extreme pressure lubricant composition comprising a hydrocarbon lubricant and a chlorinated alkyl phenol sulfide in an amount between above 5% and 25%.

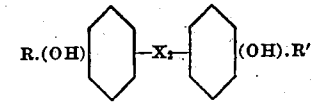
6. An extreme pressure lubricant composition comprising a hydrocarbon lubricant and a chlorinated alkyl phenol disulfide in an amount between above 5% and 25%.

7. Extreme pressure lubricant composition comprising a mineral lubricating oil and about 8 to 25% of a compound having the formula:



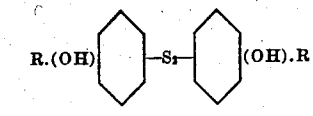
in which R and R' represent alkyl groups having at least two carbon atoms each, X represents an element of the sulfur family, consisting of sulfur, selenium and tellurium, *n* represents an integer 2 to 4, and in which the groups R, R', OH and X are each connected to the aryl nucleus.

8. Extreme pressure lubricant composition comprising a petroleum lubricating oil containing about 8 to 25% of a compound having the formula:



in which R and R' represent alkyl groups having four to eight carbon atoms each, X represents an element of the sulfur family, consisting of sulfur, selenium and tellurium, and in which the groups R, R', OH and X are each connected to the aryl nucleus.

9. Extreme pressure lubricant composition comprising a petroleum lubricating oil containing about 8 to 25% of a di-alkyl diphenol disulfide having the formula:



in which R represents an alkyl group having from four to five carbon atoms, and in which

the groups R, OH and S are each connected to the aryl nucleus.

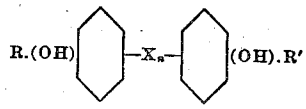
10. Composition according to claim 9 in which the carbon atom in each of the said two alkyl groups attached to the phenol ring is also attached to at least two other carbon atoms of the alkyl group.

11. Composition according to claim 9 in which the radicals represented by R are secondary alkyl groups.

12. Composition according to claim 9 in which the radicals represented by R are tertiary alkyl groups.

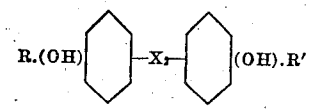
13. Extreme pressure lubricant composition comprising a mineral lubricating oil containing above about 8% of ditertiary amyl diphenol disulfide.

14. An extreme pressure lubricating composition comprising a hydrocarbon lubricant containing above about 5% to 25% of a compound having the formula:



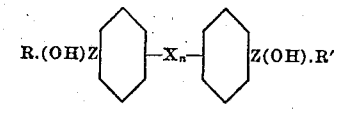
in which R and R' represent alkyl groups having at least two carbon atoms each, X represents an element of the sulfur family consisting of sulfur, selenium and tellurium, n represents an integer 2 to 4, and in which the groups R, R', OH and X are each connected to the aryl nucleus.

15. An extreme pressure lubricating composition comprising a petroleum lubricating oil containing above about 5% to 25% of a compound having the formula:



in which R and R' represent alkyl groups having four to eight carbon atoms each, X represents an element of the sulfur family, consisting of sulfur, selenium and tellurium, and in which the groups R, R', OH and X are each connected to the aryl nucleus.

16. An extreme pressure lubricating composition comprising a mineral lubricating oil and above about 5% to 25% of a compound having the formula:



in which R and R' represent alkyl groups having at least two carbon atoms each, X represents an element of the sulfur family, consisting of sulfur, selenium and tellurium, n represents an integer 2 to 4, Z represents a halogen element, and in which the groups R, R', Z, OH and X are each connected to the aryl nucleus.

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