This invention relates to improved mineral oil compositions and more particularly to the addition of certain alkyl phenol polysulfides and paraffinic oils in order to improve their properties, particularly with respect to stability when used at elevated temperatures such as in use as lubricants in internal combustion engines.

The organic sulfur compounds to which this invention relates are alkyl phenol polysulfides and are represented as follows:

\[
\begin{align*}
&\text{Organic sulfur compounds:} \\
&R \text{ is an alkyl group of preferably 2 to 8 carbon atoms, although larger and smaller alkyl groups are not excluded; } R' \text{ is preferably the same as } R, \text{ but may also be any other alkyl group or } H; \text{ and } n \text{ is an integer, from 2 to about 4 and is preferably 2. Either or both of the aromatic nuclei may be replaced by naphthyl, anthracyl or other condensed aromatic radicals. The formulas illustrated are purely diagrammatic and the substituent radicals, such as hydroxy and alkyl, are not limited to the positions shown therein. These radicals may be connected to any position in the benzene ring, but those compounds in which the alkyl radicals are in ortho or para position to the hydroxy group are preferred. Derivatives of these compounds containing other groups connected to either the alkyl groups, the aromatic nuclei, and/or the sulfur group, are also included. For example, the alkyl groups may be aryl-alkyl groups, such as benzylic. Likewise, the sulfur may be wholly or partially replaced by selenium or tellurium. It has now been found that the addition of these compounds to mineral lubricating oils results in blends which are highly resistant to oxidation and which show a decreased tendency to corrosion of bearings and to form sludge, particularly in service in lubricating internal combustion engines. Other and further objects of this invention will be apparent from the following description and the claims.}

The following examples illustrate the use of the compounds described herein as stabilizing agents in lubricating oils:

**Example 1**

Di-tertiary amyl di-phenol disulfide was dissolved, in 0.2% concentration, in a highly refined S. A. E. 20 petroleum lubricating oil having a Viscosity Index of 90. A similar solution was prepared with the same oil and di-tertiary butyl dl-phenol disulfide. These solutions are indicated by the Blends A and B, respectively, in the following table. The improvement in the stability of the blend is indicated by the following results of tests on the original oil and the blend.

<table>
<thead>
<tr>
<th></th>
<th>Original oil</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion</td>
<td>Passes</td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>Slight number</td>
<td>24.0</td>
<td>11.0</td>
<td>10.3</td>
</tr>
<tr>
<td>Cone number</td>
<td>0.45</td>
<td>0.29</td>
<td>0.17</td>
</tr>
<tr>
<td>Load resistance</td>
<td>0.005</td>
<td>0.025</td>
<td>0.010</td>
</tr>
<tr>
<td>Oxidation rate</td>
<td>200</td>
<td>4-7-13-18</td>
<td>15-19-16-18</td>
</tr>
</tbody>
</table>

The methods of testing used in the above example are as follows:

**Cone test**

This method is a means for determining the tendency of an oil to deposit solid matter upon heated metallic surfaces. It consists in slowly dropping the oil to be tested over a heated metal (generally steel) cone, having a circumferential groove milled out in a screw fashion on the periphery so as to allow a time of contact of about one minute between the heated steel surface and the oil. A total volume of 60 cc. of oil is dropped from a dropping funnel during a period of 2 hours to obtain this time of contact. The temperature of the cone may be any desired value, but for lubricating oils 250° F. is preferable since it represents approximately the extreme temperature to which oils are exposed in ordinary engine use. The cone is weighed before the test. After all the oil is run over the metal surface, the cone is washed with naphtha to remove adhering oil and the total deposit left is obtained by difference in weight. This value is generally reported in grams. The test does not appear to have any relation to the oxygen absorption test, since it is possible to have two compounds giving the same cone deposit in lubricating oils, but having widely varying oxygen absorption rates, and vice versa.

**Slight test**

This test of the tendency of an oil to sludge under oxidizing conditions is described in Proc. A. S. T. M. 24, 964, II (1924), except that the oxidation is conducted for 24 hours.

**Oxygen absorption test**

This test is used for the most part in judging the susceptibility to oxidation and acid formation of a lubricating oil at elevated temperatures.
The results are generally given as the number of cc.'s of oxygen absorbed by 10 cc. of an oil per 15 minute interval at 200° C.

**Corrosion Test**

This consists in immersing a bright copper strip for three hours in the oil maintained at 212° F. It is used to determine the presence of "corrosive" sulfur in oil, which is indicated by discoloration or pitting of the copper strip.

**Lead Tolerance Test**

This test is used to determine the tendency of an oil to corrode bearings. It is also known as the Underwood Test. 1500 cc. of the oil is maintained at 328° F, and is sprayed for 5 hours against two each of copper-lead and cadmium-silver alloy bearings. The oil dripping from the bearing is recirculated. The bearings are weighted before and after the test to determine any loss in weight. The test is then repeated with addition of a soluble lead compound, preferably lead olate, in increments of 0.005% by weight of lead. A loss in weight of 50 mg. indicates the "lead tolerance" of the oil has been exceeded, and the amount of lead added in the previous test is recorded as the "lead tolerance." A lead tolerance below 0.020 is considered unsatisfactory.

**Example 2**

Runs under closely comparable conditions were made in a C. F. R. (Cooperative Fuel Research) engine with a highly refined Mid-Con-55ent lubricating oil of 72 seconds Saybolt viscosity at 210° F, and with blends of the same oil and di-tertiary amyl di-phenol disulfide. After each run the engine was taken down, inspected and rated by demerits according to the condition of the piston parts, valves and cylinder. On this scale the demerit rating is higher as the engine condition is worse. The runs were each made for 14 hours at a jacket temperature of 375° F. The results are given below:

<table>
<thead>
<tr>
<th>C. F. R. engine tests</th>
<th>Blank</th>
<th>Blend with amyl phenol disulfide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Demerit rating</td>
<td>5.54</td>
<td>3.93</td>
</tr>
</tbody>
</table>

Other alkyl phenol polysulfides may also be used for preparing improved lubricating oil compositions of high stability in the manner described in the above examples. Such compounds preferably have at least one alkyl groups of about 2 to 8 carbon atoms. Compounds containing two alkyl phenol groups in which the alkyl radicals contain about 4 to 6 carbon atoms are preferred. The alkyl groups may be normal, iso, secondary or tertiary. They may also be cyclo but the open chain alkyl groups are preferred. The polysulfide compounds may be either symmetrical or unsymmetrical, i.e., containing different alkyl and/or aryl radicals. The aryl radicals may be polyhydroxy including such groups as those derived from resorcinol, hydroquinone and their alkylated and arylated derivatives. They may also contain condensed aromatic nuclei such as those derived from naphthol and its corresponding derivatives.

One suitable method for preparing the alkyl phenol polysulfides which are used in this invention is to react alkyl phenols with sulfur monochloride. This reaction is preferably conducted in the presence of an inert diluent, preferably in 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.

Suitable alkyl phenols for use in this reaction may be prepared by condensing phenols with olefins of preferably 2 to 8 carbon atoms or with mixtures thereof. Such olefins are readily obtained in the cracking of petroleum oils and waxes.

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 their 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. Lubricating oil blends containing this mixed product exhibit less corrosion tendencies than those containing only the alkyl phenol disulfide.

The use according to this invention of other derivatives of the alkyl phenol polysulfides which contain other substituent groups in addition to the hydroxy and alkyl groups, is not precluded. Such additional substituent groups should not, however, offset the solubilizing effect of the alkyl groups to an extent sufficient to render the compound insoluble in lubricating oil. Examples of suitable groups or radicals which may be attached to either the aryl or the alkyl group, are radicals containing oxygen such as ether, aldehyde, ketone, acid and ester radicals, those containing nitrogen such as amines and aromatic and CN and those containing sulfur, selenium, tellurium and the like.

The sulfur atoms present in the polysulfide linkage of the alkyl phenol polysulfides may also be wholly or partly replaced by the heavier nonmetallic elements of group 6, such as selenium and tellurium.

While these compounds, or mixtures thereof with other members of the same class, with polymers thereof, and with the alkyl phenol monosulfides, may be added in any desired concentration within their solubility limits to lubricating oils, they are preferably used in concentrations of about 0.1 to 2.0%; a concentration...
of about 0.5% will be found sufficient to stabilize the majority of petroleum lubricating oils. These compounds greatly stabilize mineral lubricating oils at elevated temperatures, especially the highly refined oils such as synthetic oils, solvent extracted oils obtained by treatment of mineral lubricating oils with single solvents such as phenol, dichloroethy ether, furfural, propene, 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 particularly effective with such oils having viscosity indices above 60, 80, 100 or more. Lubricating oils also stabilized 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, volatilization, chemical reagents, and adsorptive agents, as well as coal tar or shale distillates, pale oils, neutrals, bright stocks and residual stocks, cracking coals tar fractions, condensed or polymerized fractions, and the like, either waxy, dewaxed, or non-waxy. The lubricants to which these stabilizing agents are added may also contain dyes, metallic or other soap, pour inhibitors, sludge dispersing, oxidation inhibitors, and the like. Lubricants or compounds, such as linear low molecular weight oils, resins, rubber, fatty oils, heat thickened fatty oils, sulfurized fatty oils, extreme pressure lubricating agents, organo-metallic compounds, bright stocks, such as refined petroleum lubricating oil residues, volatilized fats, mineral oils and/or waxes, colloidal solids such as graphite, zinc oxide, etc., and the like.

Especially desirable lubricating compositions may be prepared by adding to lubricating oil both an alkyl phenol polysulfide and an oiliness agent, such as a suitable organic ester. Examples of such esters are esters of fatty acids of about 10 carbon atoms with alcohols. Esters of the acids obtained by limited oxidation of paraffin wax may be used, for example, the isopropyl esters of oxidized wax acids which are substantially monobasic. The hydroxyl groups of the alkyl phenol polysulfides may also be partially or completely esterified with an organic acid, preferably a fatty acid. These esterified compounds may be mixed with other non-esterified alkyl phenol polysulfides. The oiliness agent may be used in any suitable concentration. The amount used is usually between 0.1 and 5.0% of the total composition, and 0.5, 1.0 to 2.0% is generally sufficient.

A preferred method for preparing compounds suitable for use in this invention is as follows:

**EXAMPLE 1**

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 polysulfide. 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 adsorptive materials such as clay.

Higher polysulfides suitable for use in the present invention may be prepared by condensings 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. \( R(C_6H_5)OH.S_2.(C_6H_5)OH.R'\rightarrow R(C_6H_5)OH.SH+H_2O\rightarrow 2R(C_6H_5)OH.SH\)

2. \( 2R(C_6H_5)OH.SHL+6Cl_2\rightarrow R(C_6H_5)OH.SL.(C_6H_5)OH.R'\)

3. \( 2R(C_6H_5)OH.SHL+6Cl_2\rightarrow R(C_6H_5)OH.SL.(C_6H_5)OH.R'\)

4. \( \text{R} \) and \( \text{R}' \) 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 molar 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 for the disulfides.

This invention is not to be limited to any specific examples or explanation, all of which are presented herein solely for the purpose of illustration, but is limited only by the following claims, in which it is desired to claim all novelty in so far as the prior art permits.

**We claim:**

1. An improved lubricating composition comprising a mineral lubricating oil having dissolved therein a small amount sufficient to increase the stability of said oil of an alkyl phenol polysulfide of the formula

   \[
   \text{R} \begin{array}{c}
   \text{OH} \\
   \text{S}_2 \\
   \text{OH} \\
   \text{R}'
   \end{array}
   \]

   in which \( \text{R} \) and \( \text{R}' \) are alkyl groups having at least 2 carbon atoms each and \( n \) is an integer, from 2 to 4.

2. Composition according to claim 1 in which \( n=2 \).

3. Composition according to claim 1 in which \( n=2 \), and \( \text{R} \) and \( \text{R}' \) are alkyl groups of 2 to 3 carbon atoms each.

4. Composition according to claim 1 in which \( n=2 \) and \( \text{R} \) and \( \text{R}' \) are branched alkyl groups.

5. Composition according to claim 1 in which said mineral lubricating oil is a highly refined petroleum lubricating oil having a Viscosity Index above 90.
6. A mineral lubricating oil containing about 0.01 to 1% of a dialkyl diphenol disulfide, in which the alkyl groups contain about 4 to 6 carbon atoms each.

5. An improved lubricating composition comprising a mineral lubricating oil having dissolved therein a small amount of diamyl diphenol disulfide.

3. An improved lubricating composition comprising a highly refined petroleum lubricating oil having dissolved therein a small amount of ditertiary amyly diphenol disulfide.


10. An alkyl polysulfide having the formula

\[ \text{R} \cdot (\text{C}_n \text{H}_{2n+1}) \cdot \text{OH} \cdot \text{S}_n \cdot (\text{C}_n \text{H}_{2n+1}) \cdot \text{OH} \cdot \text{R'} \]

in which R and R' are alkyl radicals of about 2 to 8 carbon atoms each and n is 2 to 4.

11. A composition of matter comprising a mineral lubricating oil containing dissolved therein, in an amount sufficient to increase the stability of said oil, an alkyl phenol polysulfide in which pairs of alkyl phenol groups are interlinked by a plurality of sulfur atoms, said alkyl phenol groups being composed of an aromatic nucleus containing a hydroxyl substituent group and an alkyl substituent group having at least 2 carbon atoms.

12. A composition of matter as described in claim 11 in which about 0.01 to 1% of the alkyl phenol polysulfide is contained in the lubricating oil.

13. A composition of matter comprising a mineral lubricating oil containing dissolved therein about 0.01 to 1% of an alkyl phenol disulfide in which pairs of alkyl phenol groups are interlinked by two sulfur atoms, each alkyl phenol group being composed of an aromatic nucleus containing a hydroxyl substituent group and an alkyl substituent group having at least two carbon atoms.

14. An alkyl phenol disulfide which is composed of a pair of aromatic nuclei interlinked through 2 sulfur atoms, each aromatic nucleus containing a hydroxyl substituent group and an alkyl substituent group containing 2 to 8 carbon atoms.

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