

## UNITED STATES PATENT OFFICE

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## PROCESS FOR PREPARING IMPROVED OXIDATION INHIBITORS AND PRODUCTS THEREOF

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This invention relates to the improvement of oxidation inhibitors of the aryl sulfide type, particularly those prepared by reaction of aromatic compounds with a sulfur halide.

It has already been proposed to prepare blending agents, especially suitable as oxidation inhibitors in petroleum lubricating oils, by reacting an alkyl phenol with a sulfur halide. When using sulfur chlorides, the resulting products are alkyl phenol monosulfides, or disulfides, depending respectively upon whether sulfur dichloride  $\text{SCl}_2$ , or sulfur monochloride  $\text{S}_2\text{Cl}_2$ , are used. The products also may contain some of the lower polymers of the simple reaction products. These polymers are also soluble in petroleum lubricating oils, are effective as oxidation inhibitors therefor, and the total reaction product or the separate monomer and polymer fractions, may each be used as an oxidation inhibitor in lubricating oils. These products are represented by the following formula:



where  $x$  represents 1 or 2, and  $\text{R}$  and  $\text{R}'$  represent alkyl groups which may be the same or different. Polymers such as those formed by linking one or more  $\text{R}(\text{C}_6\text{H}_5)_x\text{OH.S}_2\text{.OH}$  groups to an aromatic nucleus of the products represented by the above formula are also included.

These compounds are effective for inhibiting the oxidation of lubricating oils and the oils containing them are in general entirely satisfactory for use and do not corrode bearings in actual operation. However, it has been observed that the lubricating oil blends of these compounds often fail to pass the "copper strip corrosion test," a laboratory test which is accepted as a standard for indicating corrosion tendencies.

An object of this invention is to prepare improved oxidation inhibitors of the types described above which have, among other advantages, a greatly lessened tendency to corrode copper. The use of these improved products as blending agents in lubricating oils, and the resulting oil compositions, represent other objects of this invention.

Still other and further objects of this invention will be apparent from the following description and the claims. It has now been found that the tendency of these aryl sulfide oxidation inhibitors to corrode copper can be greatly decreased by heating the inhibitor with an oil capable of reacting with sulfur, to a temperature sufficient to cause sulfurization of the oil. Suitable oils for this purpose include the hydrocarbon oils, both

paraffinic and unsaturated, such as the petroleum oils and synthetic hydrocarbon oils, also fatty oils of animal, vegetable, and marine origin, and the like. The use of viscous oils is preferred, particularly when the improved inhibitor is to be used in lubricating oils, in order to permit use of the treated oil and inhibitor mixture, without separation.

The following examples are presented in order to indicate suitable methods for carrying out the process of this invention and for preparing the improved products obtained thereby. These methods are purely illustrative and the invention is not to be limited thereby:

## Example 1

One molecular weight of tertiary amyl phenol was dissolved in about 20% concentration in ethylene chloride ( $\text{ClCH}_2\text{CH}_2\text{Cl}$ ) and the solution was heated to boiling under reflux, first removing the distillate until it became clear, in order to remove any water present. 60 parts (about 0.6 molecular weight) of sulfur dichloride were then dissolved in about 50% concentration in ethylene chloride and this solution was added slowly with stirring to the boiling solution of amyl phenol during a period of about three hours. When the addition of the sulfur dichloride solution was completed, the boiling of the reaction mixture under reflux was continued for about four hours to insure completion of the reaction. During the reaction  $\text{HCl}$  was given off and absorbed in water in a packed tower. The reaction mixture was then blown with an inert gas, such as nitrogen, for a few minutes to remove the last of the hydrogen chloride and the ethylene dichloride was removed by distillation up to a still temperature of about  $110^\circ\text{C}$ .

The distillation residue still contained a small trace of ethylene dichloride, which was removed by addition of an equal volume of a paraffin base petroleum lubricating oil fraction, and the mixture was then heated to about  $125^\circ\text{C}$ . under an absolute pressure of about 20 millimeters of mercury. Inert gas may again be used to strip out the last traces of low boiling materials.

The amyl phenol sulfide reaction product thus obtained was added in varying amounts from 0.1 to 1% to several different portions of a highly refined S. A. E. 20 petroleum lubricating oil. The color and cast of the resulting blends were observed to be good and the amyl phenol sulfide reaction product was found to be an effective oxidation inhibitor in each blend. These blends

were subjected to the "copper strip corrosion test." This involves placing a piece of bright-polished copper in the oil sample under test and then heating it for three hours at 212° F. For an oil to pass this test, there must be no darkening or discoloration of the copper strip when it is removed from the oil at the end of the test and is washed with sulfur-free naphtha. The maximum concentration of the inhibitor in the blends passing this corrosion test was 0.25% (based on the active inhibitor).

#### Example 2

The mixture of approximately equal volumes of amyl phenol sulfide reaction product and lubricating oil obtained from the vacuum-stripping step described in the above example was heated to a temperature of about 400° F. for 15 minutes. The mixture was then cooled and blends were made up as in Example 1 with the same lubricating oil used therein. These blends were also tested in the same manner described above and it was observed that the oxidation inhibitor was effective in all cases. Blends containing concentrations of the active inhibitor as high as 1%, passed the "copper strip corrosion test."

The blends showed a dark color and a poor cast, as compared to the original lubricating oil used. This can be remedied in the manner described in the following example:

#### Example 3

The heat treated mixture of equal volumes of inhibitor and lubricating oil prepared in Example 2 was percolated through 25% by weight of active decolorizing clay at 200° F. temperature. The thus treated product was then used to prepare blends with the same lubricating oil used in the above examples, and the products were similarly tested. The oxidation inhibitor was effective in all cases. Blends containing as high as 1% of the active inhibitor passed the "copper strip corrosion test." The color and cast of the blends were good, equaling that of the original oil.

#### Example 4

Amyl phenol disulfide was prepared by the same procedure used in Example 1 except that sulfur monochloride was used in place of sulfur dichloride. The resulting product after blending with an equal volume of a paraffin base petroleum lubricating oil and stripping under vacuum as described in Example 1, was used to prepare blends of varying concentrations from 0.1% inhibitor in lubricating oil in the same manner as described in Example 1. While all these blends showed effective oxidation inhibition and possessed good color and cast, all failed to pass the "copper strip corrosion test."

The mixture of equal volumes of inhibitor product and lubricating oil was then heated to 425° F. for 15 minutes and percolated through 40% of clay. The resulting product was used to prepare blends that were tested as before. A blend containing 0.4% of the inhibitor passed the "copper strip corrosion test." The color and cast were fairly good.

#### Example 5

The same product was used as in Example 4 except that the percolation was substituted by contact treatment with 5% by weight of clay at 250° F. A blend of this clay-contacted product in the same lubricating oil used in the above blends showed good color and cast and passed

the "copper strip corrosion test" when using a concentration of 0.20% of the inhibitor.

While the heat treatment of the inhibitor greatly decreases its tendency to corrode copper, it has the disadvantage of darkening the color of the inhibitor concentrate so that in many cases when the concentrate is added to lubricating oil, the resulting blend has a dark color and a poor cast. As is demonstrated in the above examples, this may be remedied by treating the inhibitor concentrate with clay after the heat treatment. This clay treatment can be conducted by percolating the concentrate through a bed of clay; it is done preferably and more efficiently by clay contacting, i. e., mixing the concentrate with clay and then filtering out the clay. The clay treatments may be conducted at ordinary or elevated temperatures up to about 250° F. The clay contacting is preferably conducted at such elevated temperatures.

It has also been found that the color formation during the heat treatment may be substantially decreased by selection of suitable oils in preparing the inhibitor concentrate. Color formation is marked with asphaltic and aromatic base oils, while it is greatly decreased when using highly paraffinic oils. This is illustrated in the following examples:

#### Example 6

A reaction product consisting substantially of tertiary amyl phenol disulfide was prepared by the process described in Example 4, except that the addition of lubricating oil was omitted prior to the vacuum stripping. A concentrate was prepared using one part by weight of this inhibitor to four parts of a high quality Pennsylvania residuum of 140 seconds Saybolt viscosity at 210° F., which had been phenol treated to remove non-paraffinic components. This concentrate was heated to 450° F. for 15 minutes and was then contacted with 5% of clay. Blends of the original concentrate, the heat-treated concentrate, and the final clay-treated concentrate were prepared in the same lubricating oil used in the above examples. The blends with the initial concentrate all failed to pass the "copper strip corrosion test," although the color and cast were good. The blends with the heat-treated concentrate showed fair color and cast, and blends having a concentration as high as 0.80% inhibitor passed the "copper strip corrosion test." The blends with the clay-contacted inhibitor concentrate were equal to those with the heat-treated concentrate in passing the "copper strip corrosion test" and were equal to those with the original concentrate in regard to color and cast.

#### Example 7

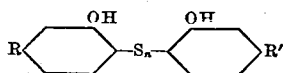
An inhibitor concentrate was prepared with one part of the same inhibitor used in Example 6 and four parts of a synthetic lubricating oil having a viscosity of 60 seconds Saybolt at 210° F. and prepared by polymerizing isobutylene with a catalyst such as boron fluoride or aluminum chloride suspended in an inert hydrocarbon liquid at a temperature of about 40° F. This concentrate was heated to a temperature of 450° F. for 15 minutes and was then blended with the same base lubricating oil used in the above tests. Blends containing 0.40% of the inhibitor passed the "copper strip corrosion test" and showed very good color and cast, substantially equal to that of the original oil. The concentrate used in preparing this blend was not clay treated after the heat treatment.

While the proportions of inhibitor to lubricating oil used in the concentrates which are subjected to the heat treating processes of this invention may be varied widely, it has been observed that concentrates containing about one part by weight of the inhibitor to form  $2\frac{1}{2}$  to  $17\frac{1}{2}$  parts of the oil are generally satisfactory for this treatment.

Substantially any lubricating oil may be used in preparing the inhibitor concentrates to be subjected to the heat treatment but oils which are predominately paraffinic in nature are preferred when it is desired to prepare a finished inhibitor of light color. Paraffin base lubricating oils such as those obtained from Pennsylvania crudes, and the highly refined concentrates obtained in general from lubricating oils by treatment with selective solvents, such as phenol, benzol-acetone, propane, dichlorethane, and other solvents exercising a selective action between paraffinic and non-paraffinic components of lubricating oils, may be used. Particularly light-colored concentrates are obtained when using synthetic oils prepared by the polymerization of olefins such as isobutylene or the olefins obtained by destructive distillation of wax.

The conditions for the heat treating will depend to some extent upon the nature of the inhibitor concentrate used. Heating to a temperature of above about  $375^{\circ}\text{F.}$  will generally be found necessary and it is undesirable in any case to heat to a temperature sufficiently high to cause decomposition of the lubricating oil present. Objectionable discoloration is also observed at the higher temperatures and temperatures above  $500^{\circ}\text{F.}$  will generally be avoided on this account. It has been observed that heating at temperatures of about  $425$  to  $475^{\circ}\text{F.}$  and for a period of time ranging from about 5 minutes at the higher temperature to about 30 minutes at the lower, gives very satisfactory results.

As indicated above, this invention applies particularly to the improvement of alkyl phenol thio ethers and disulfides. These are indicated as follows:



in which R is an alkyl group of preferably 2 to 8 carbon atoms, although larger and smaller alkyl groups are not excluded; R' is preferably the same as R, but may also be any other alkyl group or H; and n is an integer, which is usually 1 or 2. Compounds in which R and R' are alkyl radicals containing about 4 to 6 carbon atoms each 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. Either or both of the aromatic nuclei may be replaced by naphthyl, anthracyl, or other condensed aromatic radicals.

The formulae illustrated are purely diagrammatic and the substituent radicals, such as hydroxyl 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 in the hydroxy group are preferred. Derivatives of these compounds are also included. For example, the alkyl groups may be aryl-alkyl groups, such as benzyl. More than one alkyl group and/or more than one hydroxyl group may be connected to aromatic nucleus.

Likewise, the sulfur may be wholly or partially replaced by selenium or tellurium.

The improved inhibitor concentrates prepared according to this invention may be added to mineral lubricating oils to prepare blends which are highly resistant to oxidation and which show a decreased tendency to corrode bearings and to form sludge, particularly in service in internal combustion engines.

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, 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 stabilized by these compounds are other mineral oils of over 35 or 40 viscosity Saybolt at  $210^{\circ}\text{F.}$ , and even those having a viscosity of over 100 seconds at  $100^{\circ}\text{F.}$ , 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, cracked coal-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 soaps, pour inhibitors, sludge dispersers, oxidation inhibitors, thickeners, viscosity index improvers such as soluble linear polymers, oiliness agents, 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), 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 or explanation, all of which are presented herein solely for purpose of illustration, but is limited only by the following claims in which it is desired to claim all novelty insofar as the prior art permits.

We claim:

1. Process for preparing an improved oxidation inhibitor comprising heating an aryl sulfide in admixture with an oil reactive with sulfur to a temperature above about  $375^{\circ}\text{F.}$

2. Process according to claim 1 in which said heating treatment is conducted for about 5 to 30 minutes.

3. Process according to claim 1 in which the heat treated product is then treated with a decolorizing clay.

4. Process for preparing an improved oxidation inhibitor comprising heating an aryl sulfide in admixture with a viscous hydrocarbon oil to a temperature above about  $375^{\circ}\text{F.}$

5. Process for decreasing the tendency of alkyl phenol sulfides to corrode copper comprising heating a mixture of said sulfide and a hydrocarbon lubricating oil to a temperature of about 425 to 475° F. for a period of time of about 5 to 30 minutes.
6. Process according to claim 5 in which said lubricating oil is a paraffinic lubricating oil.
7. Process according to claim 5 in which said lubricating oil is a solvent treated residuum.
8. Process according to claim 5 in which said lubricating oil is a high quality synthetic lubricating oil prepared by polymerization of olefins.
9. Process for preparing improved oxidation inhibitors comprising reacting an alkyl phenol with a sulfur chloride to form an alkyl phenol sulfide reaction product soluble in viscous hydrocarbon oils, then heating a mixture containing about 1 part by weight of the said alkyl phenol sulfide and about 2½ to 17½ parts by weight of a viscous hydrocarbon oil to a temperature above about 375° F.
10. Process according to claim 9 in which said alkyl phenol is a tertiary alkyl phenol containing from 4 to 5 carbon atoms in the alkyl group.
11. Process according to claim 9 in which said heating step is conducted at a temperature of about 450° F. for about 15 minutes.
12. Process according to claim 9 in which said viscous hydrocarbon oil is a substantially paraffinic oil.
13. Process according to claim 9 in which said heated mixture is thereafter treated with clay.
14. Improved oxidation inhibitor according to claim 1.
15. Improved oxidation inhibitor according to claim 5.
16. Improved oxidation inhibitor according to claim 9.
17. A composition of matter comprising a mineral lubricating oil containing dissolved therein an aryl sulfide prepared according to claim 1.
18. An improved lubricating composition comprising a mineral lubricating oil containing dissolved therein a small amount of an alkyl phenol sulfide prepared according to claim 5.
19. Improved lubricating composition comprising a highly refined petroleum lubricating oil having dissolved therein a small amount of an alkyl phenol sulfide prepared according to claim 9.
20. Process for preparing an improved oxidation inhibitor comprising heating an aryl sulfide in admixture with an oil reactive with sulfur to a temperature above about 375° F. prior to use of the said mixture at temperatures as high as 375° F.

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