Patented Apr. 2, 1940 2,195,539

UNITED STATES PATENT OFFICE

2,195,539

DI-ALKYL DIPHENOL SULPHIDES

Louis A. Mikeska and Charles A. Cohen, Elizabeth, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application August 12, 1938, Serial No. 224,540

8 Claims. (Cl. 260—609)

This invention relates to improved oxidation inhibitors which are particularly effective in the stabilization of mineral oils. This application is a continuation-in-part of Serial No. 51,827 filed November 27, 1935, by the present inventors.

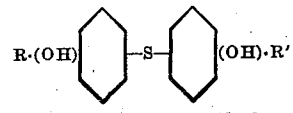
It is well known that many phenols and aromatic amines possess the property of retarding the oxidation of certain oils. The common impression exists that most, if not all such compounds will inhibit the oxidation of all oils, rubber, resins, etc. Recent systematic research on this subject, however, has shown that such a belief is without any reasonable grounds, since as many soluble compounds of the type given can be found to be ineffective or even detrimental in a particular oil, as there are compounds giving beneficial results.

In the case of lubricating oils, although it is generally desirable to employ an oil having a low oxidation rate, at ordinary temperatures, this is not the only important criterion to be considered. The oil must resist injurious oxidation at the high temperatures encountered in the engine as well. It must also be free of any tendency to settle out sludge or other solid matter in contact with metals (cone test), and must not cause ring sticking or gumming when employed in an engine. Naturally, any inhibitor must be soluble in the oil at the temperatures encountered in practice and not settle out even at —30 or —50° F. Other properties such as the lack of any detrimental effect upon demulsibility, color, color hold, Conradson carbon, corrosion, viscosity, viscosity index, and gravity are also desirable.

Heretofore, few, if any, single stabilizing agents for lubricants possessed these properties. As a general rule, most oxidation inhibitors seriously affect demulsibility, Conradson carbon and other important properties of lubricants. Attempts have been made by various investigators to employ mixtures of different inhibitors to eliminate this result, but apparently each compound possesses some detrimental property which cannot be overcome by the addition of an auxiliary compound. For instance, many organic compounds possess good inhibiting powers against oxygen absorption, but they form too great a deposit in the cone test (to be described later). Others possess good cone ratings but have little effect on the oxidation rate. If a mixture of both is employed, the cone rating is often worse, and furthermore, the Sligh value is generally increased considerably. Many compounds possess a good Sligh value but cause exceptionally bad ring sticking in actual engine tests.

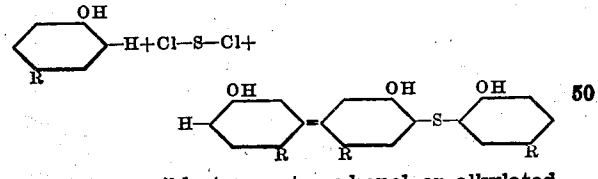
An object of this invention, therefore, is to prepare a stabilizing agent for lubricating oils which gives good oxidation inhibiting properties at engine temperature, a good cone rating, little if any ring sticking in engine tests, and substantially no effect upon other properties such as demulsibility, color, Conradson carbon, etc.

The improved oxidation inhibitors of this invention are certain higher alkyl phenol sulphides, and are represented as follows:



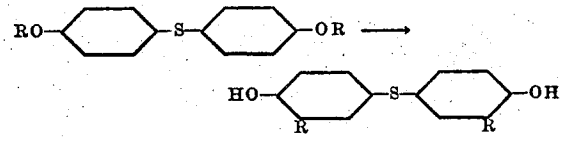
in which R and R' represent alkyl groups of 4 to about 8 carbon atoms although larger alkyl groups may also be used. R' is preferably the same as R, but may also be a different alkyl group from R. These alkyl groups may be normal or iso, and primary, secondary or tertiary groups. Either or both of the aromatic nuclei may be replaced by naphthyl, anthracyl or other condensed aromatic radicals. The formulae illustrated are purely diagrammatic and the substituent radicals, hydroxyl, alkyl and sulphur, 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 sulphur 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 sulphur group, are also included. For example, the alkyl groups may be aryl-alkyl groups, such as benzyl. Likewise, the sulphur may be replaced by selenium or tellurium.

The above materials may be prepared in a number of ways. For example, the corresponding phenol may be heated with sulphur dichloride, driving off HCl according to the reaction:



Or, it is possible to react a phenol or alkylated phenol with sulphur dichloride to give say, 4:4'

dihydroxy di-phenyl thio ethers which may then be alkylated either by reacting with an olefin in presence of a condensing agent such as sulphuric acid, boron fluoride, aluminum chloride, etc., or with an alcohol or alkyl chloride and a condensing agent. Another method of preparation is to first produce 4—4' dihydroxy di-phenyl thio ether by reacting phenol with sulphur chloride, and then prepare ethers by reaction in alkaline media with alkyl chlorides or dialkyl sulphates. These ethers, in turn, may then be isomerized in the presence of anhydrous aluminum chloride to produce dialkyl di-phenol thio ethers as in the example:



Superior stabilizing 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 thio ethers by any of the above processes. The secondary olefins may be separated from the tertiary, and condensed separately to produce corresponding mixed di-secondary or di-tertiary thio ethers.

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

The compounds prepared according to this invention 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, and to the greatest extent 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 210° 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 compounds prepared according to this invention may also be used as oxidation inhibitors generally in organic materials which are subject to degradation by oxidation during normal conditions, or which tend to deteriorate by absorption of oxygen from the air. Illustrations of such materials are fatty oils, petroleum oils and their derivatives, soaps, aldehydes, synthetic resins, rubber, synthetic rubber, paper, and the like.

The stabilizing agents prepared according to this invention are generally employed in proportions below 1%, say 0.5%, 0.2%, 0.1% or even 0.05% or less, although percentages up to 5% are often advantageous in the case of highly unstable oils.

The lubricants and other oxidizable organic materials to which these stabilizing 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, oiliness agents, resins, rubber, fatty oils, heat thickened fatty oils, sulphurized 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.

The following examples illustrate suitable methods for preparing the improved oxidation inhibitors, and also their use in various compositions:

EXAMPLE I

125 grams of p-tertiary amyl phenol were dissolved in 500 cc. of ethylene chloride ($ClCH_2CH_2Cl$) and the solution was heated to boiling under reflux. 40 grams (0.52 molal proportion) of sulphur dichloride (SCl_2) were dissolved in 100 cc. of ethylene chloride. This solution was added slowly, with stirring, to the boiling solution of amyl phenol. The hydrogen chloride gas evolved during the reaction was withdrawn from the reaction zone through the reflux condenser. When the addition of the sulphur dichloride solution was completed, the boiling of the reaction mixture under reflux was continued for six hours until no further emission of hydrogen chloride was detectable. By this means, all hydrogen chloride is removed and there is no need to wash the reaction product with water. 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, was then removed from the reaction mixture by distillation and the resulting product was distilled under a vacuum of 3 mm. mercury absolute pressure. There were thus obtained (1) a fraction distilled below 230° C., consisting of 20 gms. of unreacted phenol, (2) a fraction distilled between 230 and 235° C., and consisting of 108 gms. of amyl phenol sulphide, and (3) 10 gms. of residue.

The yield of amyl phenol sulphide recovered as distillate was 92.1%, based on the amount of amyl phenol reacting. It is a clear bright yellow liquid which on standing or being seeded crystallizes to a light yellow solid. Both the liquid and solid forms are soluble in ether, alcohol, acetone, carbon disulphide, liquid hydrocarbons, hydrocarbon halides, petroleum oils and fractions thereof, including gasoline, kerosene, burning and Diesel oils and lubricating oils, and in most organic solvents.

The residue was easily removable from the distilling flask with ordinary organic solvents such as ether or chloroform. There was no coke formation.

The reaction is preferably conducted under anhydrous conditions. To insure this the first reflux condensate may be withdrawn until the stream is clear, when it is returned to the reaction zone. Instead of adding the sulphur chloride in solution in the solvent, the entire volume of solvent may be added initially or as desired, and the sulphur chloride may be added slowly to the reflux stream.

The equipment in which the reaction is con-

ducted should be non-corrodible by the materials used and the reaction products. It is preferably made of or lined with glass or other acid and sulphur resistant ceramic material or metal, such as pure nickel and suitable alloys.

A description follows of a number of tests used to determine the effectiveness of the oxidation inhibitors described in the examples below:

Oxygen absorption test

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

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° C. 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.

Ring sticking test

This test is often employed to indicate the susceptibility of a lubricating oil to stick rings and gum up pistons in an aviation engine. The oil is employed to lubricate a C. F. R. (Cooperative Fuel Research) engine with a jacket temperature of 390° F. using 2½ lbs. of oil for 14 hours, a very severe test for performance under hot conditions. The piston demerit is the rating given based on the general appearance of the pistons; the worse the condition, the higher the value. Usually, a record is also made of the number of rings stuck as well as the number of degrees of the stuck portion of the piston rings.

Sligh 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.

Demulsibility test

Generally employed for ascertaining the emulsifiability of turbine lubricating oils. It is described in Bur. Mines Circ. 323A and B and in Federal Specif. Stock Catalog, section IV DV-L-791, October 3, 1933.

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 325° 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 weighed 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 oleate, 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

A lubricating oil obtained by phenol extraction and having a viscosity index of 90 was blended with 0.2% di-tertiary butyl diphenol thio ether. Cone tests on the blend as well as the blank showed that the thio ether stabilized the oil to an exceptional degree (almost 60% reduction in deposit) as can be seen from the data:

	Cone deposit	Reduction
		Percent
Blank	0.67	
Blend	0.27	59.5

The blend also showed a marked decrease in oxygen absorption at 200° C., reducing the rate from 218 to 12–13–14–17 cc. O_2 per 15 min. intervals.

EXAMPLE 3

A petroleum lubricating oil had the following inspection characteristics:

Saybolt viscosity @ 210° F	90
Ring sticking test:	
Piston demerit	6.33
Skirt demerit	4.0
No. rings stuck	5
Degrees	1710

This oil was blended with 0.2% di-tertiary butyl diphenol thio ether. The inspection characteristics of this blend were as follows:

Saybolt viscosity @ 210° F	90
Ring sticking test:	
Piston demerit	1.06
Skirt demerit	0
No. rings stuck	0
Degrees	0

The results show the effectiveness of di-tertiary butyl diphenol thio ether in reducing ring sticking to practically a zero value.

EXAMPLE 4

A sample of petroleum lubricating oil had the following properties:

A. P. I. gravity	29.9
Flash point	465° F.
Fire point	525° F.
Vis. Saybolt @ 100° F	523
Vis. Saybolt @ 210° F	73.0
Viscosity index	121
Color	12½ Rob.
Conradson carbon	0.04%
Corrosion @ 210° F	Pass
Demulsibility	1620
Oxidation rate @ 200° C	183 cc. O_2/15 min./10 gm. oil

In this oil was dissolved 0.1% of di-tertiary butyl diphenol thio ether. Another series of tests was

run on the blend, and the following data were obtained:

A. P. I. gravity	29.9
Flash point	465° F.
Fire point	525° F.
Vis. Saybolt @ 100° F.	523
Vis. Saybolt @ 210° F.	73.0
Viscosity index	121
Color	12½ Rob.
Conradson carbon	0.04%
Corrosion @ 210° F.	Pass
Demulsibility	1620
Oxidation rate @ 200° C.	44–28–26–26 cc. O_2/15 min./10 gm. oil

It will be noted that the oxidation rate of the oil at 200° C. was lowered considerably without affecting in the least any of the other properties of the oil.

EXAMPLE 5

A blend of 37% phenol treated oil in a neutral stock suitable as an aviation oil and having a viscosity at 210° F. of 118, showed the following results in the C. F. R. ring sticking test, with and without the addition of 0.2% di-tertiary butyl diphenol thio ether:

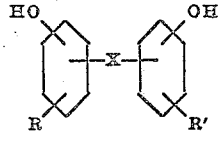
	Overall demerit		Degrees rings stuck		Gms. carbon in engine		Varnish demerit	
	15 hrs.	30 hrs.	15 hrs.	30 hrs.	15 hrs.	30 hrs.	15 hrs.	30 hrs.
Blank	3.10	------	180	------	2.35	------	4	------
Blend	1.32	1.41	0	0	1.00	1.35	1	2

As the above data show, the addition of the thio ether showed a great improvement in the appearance of the engine parts as expressed by the overall demerit rating. Also, no rings were stuck with the blend even after 30 hours operation, while in the case of the oil, 180° of the rings were stuck after 15 hours operation. Furthermore, the amount of carbon deposited in the engine was reduced to less than one-half, and the amount of varnish formed (as shown by the varnish demerit) was very little.

Although there have been shown and described certain specific embodiments of this invention, it is apparent that many modifications are possible. The invention, therefore, is not to be restricted except insofar as is necessitated by the prior art and by the spirit of the appended claims.

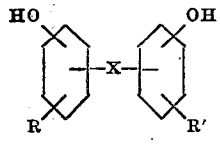
We claim:

1. Di-alkyl diphenol sulphides having the formula:



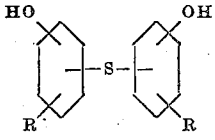
in which R and R' represent alkyl groups having at least four carbon atoms each, X represents an element of the sulphur family, consisting of sulphur, selenium and tellurium.

2. Di-alkyl diphenol sulphides having the formula:



in which R and R' represent alkyl groups having four to eight carbon atoms each, X represents an element of the sulphur family, consisting of sulphur, selenium and tellurium.

3. Di-alkyl diphenol sulphides having the formula:



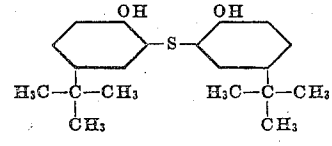
in which R represents an alkyl group having from four to five carbon atoms.

4. Di-alkyl diphenol sulphides according to claim 3 in which the carbon atom in each of the said two alkyl groups attached to the phenyl ring is also attached to at least two other carbon atoms of the alkyl group.

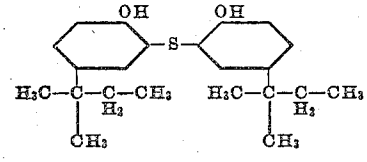
5. Di-secondary alkyl diphenol sulphides according to claim 3, in which R represents a secondary alkyl group.

6. Di-tertiary alkyl diphenol sulphides according to claim 3, in which R represents a tertiary alkyl group.

7. Di-tertiary butyl diphenol thio ether having the formula substantially as follows:



8. Di-tertiary amyl diphenol thio ether having the formula substantially as follows:



LOUIS A. MIKESKA.
CHARLES A. COHEN.