

UNITED STATES PATENT OFFICE

2,361,353

LUBRICATING COMPOSITION

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16 Claims. (Cl. 252—48)

This invention has to do with the development of improved lubricant compositions. More specifically, the present invention relates to the development of a novel class of characterizing agents which when incorporated in hydrocarbon lubricant oils inhibit the deleterious effects of oxidation upon the oils. This invention also contemplates the use of these characterizing agents in oils containing certain metal organic compounds, which, while effective to improve the oil in certain respects, may not have the necessary effectiveness in retarding the formation of acid and insoluble bodies in the oils. The characterizing agents of the present invention are effective to inhibit the formation of said acid and insoluble bodies in oils containing the said metal organic compounds and are contemplated for general use in retarding the deleterious effects of oxidation on mineral oil fractions.

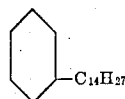
As is well known to those familiar with the art, various characterizing agents have been proposed for use in lubricants to counteract the chemical and physical shortcomings of the lubricants. Among such shortcomings are, for example, tendencies to: oxidize, form sludge and lacquer films on metal parts, deposit insoluble matter, form acid bodies, etc. The present invention is concerned with overcoming some of these tendencies, notably with fortifying lubricants against the deleterious effects of oxidation and the formation of acid and sludge.

The present invention is based upon the discovery of a novel class of sulphur-containing compounds which when used in lubricant oils will effectively increase the resistance of said oils to oxidation; and when used in lubricant oils containing certain metal organic compounds which tend to accelerate the formation of acid and insoluble bodies in the oils, will inhibit the formation of said acid and insoluble bodies and increase the resistance of the oils to oxidation. Thus, this invention is predicated upon the discovery that the sulphurized cardanol ethers, or sulphurized cardanyl ethers, will so characterize lubricant oils.

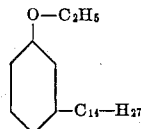
As described in U. S. Patent No. 2,181,119, the term "cardanol" denotes a phenol having an empirical formula of $C_{26}H_{32}O$, and a probable structural formula of $H_{27}C_{14}.C_6H_4.OH$ with one unsaturated bond in the $H_{27}C_{14}$ — group, which is meta to the $—OH$ group. The ethers of cardanol or cardanol ethers contemplated herein are those in which the hydrogen of the $—OH$ group has been replaced by an organic group, as, for example, an

aromatic or an aliphatic group. Preference is given to sulphurized cardanyl alkyl ethers.

The term "cardanyl" as used herein describes that group or radical which remains on the removal of the $—OH$ group from cardanol, as



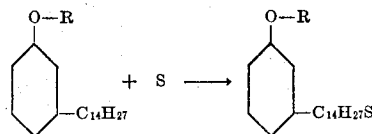
Making use of this term, the following structural formula represents cardanyl ethyl ether



Contemplated by the term "metal organic compounds" used herein are those compounds characterized by metal in combination with organic groups or radicals, such compounds as are characterized by attachment of the metal atom, or atoms, either directly or indirectly, as through the agency of a non-metal or metalloid, to a carbon atom of an organic group. Thus, a typical metal organic compound as described herein is the dicobalt salt of wax phenol carboxylic acid.

For further classification of terminology, the term "wax" connotes a long chain alkyl group having at least 20 carbon atoms. It is this connotation that is given in U. S. Patents Nos. 2,198,275 and 2,198,293, issued to O. M. Reiff.

While the mechanism of the reaction of cardanol ether with elementary sulphur is as yet not wholly understood, it is suggested that sulphur reacts with the carbon atoms of the unsaturated bond of the alkyl group, $—C_{14}H_{27}$, in the following way



wherein R is an aromatic or an aliphatic group.

The foregoing suggested explanation of the reaction mechanism is merely speculation and is not in any way to be construed so as to limit the scope of this invention, for the sulphurized cardanol ethers herein described are contemplated broadly as the reaction products of elementary sulphur and a cardanol ether.

A typical sulphurized cardanol ether, sulphurized cardanyl ethyl ether was prepared in the

following way: 160 grams of cardanyl ethyl ether with 16.2 grams of elementary sulphur were heated in the presence of a non-oxidizing gas, such as nitrogen, at approximately 175° C. for a period of 24 hours. During the reaction, practically no hydrogen sulphide is evolved, an indication that the major portion of the sulphur is reacting with the unsaturated group of the alkyl side chain of the cardanyl ethyl ether. A copper strip test on a 1 per cent blend of the reaction product in a mineral oil, heated for 3 hours at 150° C. gave no appreciable discoloration of the copper strip, therefore indicating that all of the sulphur had been chemically combined. The product may be improved in color by contacting it for approximately ½ hour with 10 per cent to 20 per cent of super-filtrol clay, followed by filtration through more clay to obtain the finished product, which is a light brown oil and contains about 9 per cent sulphur.

To demonstrate the effectiveness of such compounds as corrosion inhibitors in oils, a lubricant oil blend containing a typical sulphurized cardanol ether, the foregoing sulphurized cardanyl ethyl ether was subjected to the tests described below.

BUBBLE TEST

A section of a bearing containing a cadmium-silver alloy surface and weighing about 6.0 grams, was placed in 30 grams of a solvent-refined Pennsylvania oil of Saybolt Universal viscosity of 53 sec. at 210° F. The oil was heated to 175° C. for 22 hours while a stream of air was bubbled against the surface of the bearing. The loss in weight in milligrams of the bearing is indicative of the corrosiveness of the oil. In each case a sample of the oil containing the addition agent was run concurrently with a sample of straight oil. Each sample contained a section cut from the same bearing. The results are set forth in Table I below.

Table I

Reaction product added	Per cent	Milligrams wt. loss	
		Oil plus addition agent	Oil alone
Sulphurized cardanyl ethyl ether.....	1	0.0	27
Sulphurized cardanyl ethyl ether.....	½	3.0	51

LAUSON ENGINE TEST

The oil employed in this test was a solvent refined oil having a Saybolt Universal viscosity of 45 sec. at 210° F.

The test procedure was as follows:

The tests were carried out in a single-cylinder Lauson engine operated continuously over a time interval of 16 hours with the cooling medium held at a temperature of about 212° F. and the oil temperature held at about 280° F. The engine was operated at a speed of about 1830 R. P. M. At the end of the test the oil was tested for acidity (N. N.) and viscosity.

The results of this test are set forth in Table II below.

Table II

Reaction product added	Per cent	N. N.	K. V. @ 210° F.
None.....		5.2	8.80
Sulphurized cardanyl ethyl ether.....	½	2.8	7.19

Certain metal organic compounds have found extensive use in lubricant oil by virtue of their varied characterizing actions, as, for example, in preventing lacquer formation on metal parts and consequently retarding ring sticking in motors. Of these compounds, however, there are those that do not inhibit the formation of acid and insoluble bodies in lubricant oils, rather some of these compounds may, under certain conditions of use, accelerate the formation of such bodies in lubricant oils. In some cases, as is demonstrated in Table III below, small increases of acid and insoluble bodies are apparently caused by the metal organic compound incorporated in the lubricant oil. Thus, as aforesaid, one object of this invention is to remedy this effect by the addition of small amounts of sulphurized cardanol ethers to lubricant oil compounds containing metal organic compounds, thereby providing a combination which is superior to a similar oil containing either of the additives alone.

The effectiveness of sulphurized cardanyl ethers in lubricant oils containing metal organic compounds is demonstrated by the result of the Underwood Corrosion Test given in Table III below. The aforesaid sulphurized cardanyl ethyl ether was blended in a solvent refined motor oil having a Saybolt Universal viscosity (S. U. V.) of 45 sec. at 210° F. and containing a typical metal organic compound of the type contemplated herein, the dicobalt salt of wax phenol carboxylic acid. Tests were run on the blank oil, the oil containing the metal organic compound, and the aforesaid blend. The test employed is described in full in a publication of the General Motors Research Laboratory, December 9, 1940; and essentially involves the following:

The apparatus consists of a circulating arrangement whereby oil at 325° F. under 10 lbs. pressure is sprayed against a standard cadmium-silver bearing for a period of either 5, 10 or 15 hours. The amount of oil in the system under constant circulation is 1500 c. c. In passing through the system, the oil comes in contact with cast iron, steel, stainless steel, copper, and the cadmium-silver bearing; and is also exposed to aeration.

Table III

Compound added	Per cent	Gms. loss	N. N.	K. V. @ 130° F.	Per cent naphtha insolubles
None.....		1.3952	11.9	10.31	0.46
Dicobalt salt of wax phenol carboxylic acid.....	½	1.2374	12.6	11.6	0.76
Dicobalt salt of wax phenol carboxylic acid+ sulphurized cardanyl ethyl ether.....	½	0.0000	0.36	19.88	0.04

Similarly, the effectiveness of the sulphurized cardanyl ethers in lubricant oils with and without metal organic compounds is demonstrated by the results of the accelerated Underwood oxidation test given below in Table IV. Oil A is primarily an acid-treated oil having an S. U. V. of 55.5 seconds at 210° F.; and oil B is a solvent-refined oil having an S. U. V. of 65 seconds at 210° F.

The accelerated Underwood oxidation test is also described in full in the General Motors publication referred to above. An accelerator, iron naphthenate (commercially designated as Nuodex 6% Fe₂O₃), is added to the oil to be tested, and

the blended oil is subjected to the same test conditions as in the foregoing Underwood corrosion test.

amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

6. An improved lubricant composition compris-

Table IV

Compound added	Per cent	Oil	Initial N. N.	Final N. N.	Initial S. U. V. @ 130° F.	Final S. U. V. @ 130° F.	Per cent viscosity increase	Gms. loss
None		A	0.28	13.40	193	1,001	418	0.789
Sulphurized cardanyl ethyl ether	3	A	0.26	6.90	191	303	58	0.03
Barium phenate carboxylic wax phenolic acid disulfide	1 1/4	B	0.16	5.31	237	355	49.7	0.719
Barium phenate carboxylic wax phenolic acid disulfide + sulphurized cardanyl ethyl ether	1 1/4	B	0.16	0.27	233	236	1	0.002

¹ Alkaline.

Thus, the foregoing results of the accelerated Underwood oxidation tests clearly illustrate the effectiveness of our improving agents upon an oil (oil A) not containing a metal organic compound and upon an oil (oil B) containing a typical metal organic compound.

It is to be understood that the foregoing examples and tests are not to be interpreted as limiting in any way the scope of this invention. The sulphurized cardanyl ethyl ether is but one typical sulphurized cardanol ether of the class contemplated herein, and in place of the ethyl group the following hydrocarbon groups may be used: methyl, propyl, butyl, phenyl, naphthyl, tolyl, benzyl, etc.

For the purposes of this invention, the sulphurized cardanol ethers may be used in relatively small amounts in concentrations from about 0.25% to about 5%; and the metal organic salts, as is indicated by the examples shown in Tables III and IV above, may also be used in relatively small amounts such as from about 0.5 percent to about 1.25 percent.

I claim:

1. An improved lubricant composition comprising a hydrocarbon lubricant oil and in admixture therewith a minor proportion of a sulphurized cardanol ether obtained by reaction of a cardanol ether with elementary sulphur, said sulphurized cardanol ether being present in an amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

2. An improved lubricant composition comprising a hydrocarbon lubricant oil and in admixture therewith from about 0.25% to about 5% of a sulphurized cardanol ether obtained by reaction of a cardanol ether with elementary sulphur.

3. An improved lubricant composition comprising a hydrocarbon lubricant oil and in admixture therewith a minor proportion of sulphurized cardanyl alkyl ether obtained by reaction of a cardanyl alkyl ether with elementary sulphur, said sulphurized cardanyl alkyl ether being present in an amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

4. An improved lubricant composition comprising a hydrocarbon lubricant oil and in admixture therewith a minor proportion of sulphurized cardanyl ethyl ether obtained by reaction of cardanyl ethyl ether with elementary sulphur, said sulphurized cardanyl ethyl ether being present in an amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

5. An improved lubricant composition comprising a hydrocarbon lubricant oil and in admixture therewith a relatively small amount of an oil-miscible metal organic compound and a sulphurized cardanol ether obtained by reaction of a cardanol ether with elementary sulphur, said sulphurized cardanol ether being present in an

ing a hydrocarbon lubricant oil and in admixture therewith a relatively small amount of an oil-miscible metal salt of a wax phenol carboxylic acid and a sulphurized cardanol ether obtained by reaction of a cardanol ether with elementary sulphur, said sulphurized cardanol ether being present in an amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

7. An improved lubricant composition comprising a hydrocarbon lubricant oil and in admixture therewith a relatively small amount of the oil-miscible dicobalt salt of wax phenol carboxylic acid and a sulphurized cardanol ether obtained by reaction of the cardanol ether with elementary sulphur, said sulphurized cardanol ether being present in an amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

8. An improved lubricant comprising a hydrocarbon oil and in admixture therewith a relatively small amount of an oil-miscible metal organic compound and a sulphurized cardanyl alkyl ether obtained by reaction of the cardanyl alkyl ether with elementary sulphur, said sulphurized cardanyl alkyl ether being present in an amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

9. An improved lubricant composition comprising a hydrocarbon lubricant oil and in admixture therewith a relatively small amount of an oil-miscible metal salt of a wax phenol carboxylic acid and a sulphurized cardanyl alkyl ether obtained by reaction of a cardanyl alkyl ether with elementary sulphur, said sulphurized cardanyl alkyl ether being present in an amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

10. An improved lubricant composition comprising a hydrocarbon lubricant oil, and in admixture therewith a relatively small amount of the oil-miscible dicobalt salt of wax phenol carboxylic acid and a sulphurized cardanyl alkyl ether obtained by reaction of a cardanyl alkyl ether with elementary sulphur, said sulphurized cardanyl alkyl ether being present in an amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

11. An improved lubricant composition comprising a hydrocarbon lubricant oil and in admixture therewith an oil-miscible metal organic compound and sulphurized cardanyl ethyl ether obtained by reaction of cardanyl ethyl ether with elementary sulphur, said sulphurized cardanyl ethyl ether being present in an amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

12. An improved lubricant composition comprising a hydrocarbon lubricant oil and in admixture therewith a relatively small amount of an oil-miscible metal salt of a wax phenol carboxylic acid and sulphurized cardanyl ethyl ether

obtained by reaction of cardanyl ethyl ether with elementary sulphur, said sulphurized cardanyl ethyl ether being present in an amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

13. An improved lubricant composition comprising a hydrocarbon lubricant oil and in admixture therewith a relatively small amount of the oil-miscible dicobalt salt of wax phenol carboxylic acid and sulphurized cardanyl ethyl ether obtained by reaction of cardanyl ethyl ether with elementary sulphur, said sulphurized cardanyl ethyl ether being present in an amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

14. An improved lubricant composition comprising a hydrocarbon lubricant oil and in admixture therewith a relatively small amount, from about 0.25 percent to about 1.25 percent, of the oil-miscible dicobalt salt of wax phenol carboxylic acid and sulphurized cardanyl ethyl ether obtained by reaction of cardanyl ethyl ether with elementary sulphur, said sulphurized cardanyl ethyl ether being present in an amount of from about 0.25 per cent to about 5 per cent. 25

15. An improved lubricant composition comprising a hydrocarbon lubricant oil and in admixture therewith a relatively small amount of an oil-miscible metal organic compound selected from the group consisting of a metal salt of wax phenol carboxylic acid and a metal phenate carboxylate wax phenolic acid disulfide, and a sulfurized cardanol ether obtained by reaction of a cardanol ether with elementary sulfur, said cardanol ether being present in an amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

16. An improved lubricant composition comprising a hydrocarbon lubricant oil and in admixture therewith a relatively small amount of an oil-miscible barium phenate carboxylate wax phenolic acid disulfide and a sulfurized cardanol ether obtained by reaction of a cardanol ether with elementary sulfur, said cardanol ether being present in an amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

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CERTIFICATE OF CORRECTION.

Patent No. 2,361,353.

October 24, 1944.

FERDINAND P. OTTO.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 49, for "limt" read --limit--; page 2, second column, line 41, for "pediod" read --period--; line 59, Table III, fifth column thereof, for "19.88" read --19.82--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 6th day of February, A. D. 1945.

Leslie Frazer

(Seal)

Acting Commissioner of Patents.