

UNITED STATES PATENT OFFICE

2,295,053

HYDROCARBON OILS CONTAINING ORGANIC TRISULPHIDES AS OXIDATION INHIBITORS

Raphael Rosen, Elizabeth, and Robert M. Thomas, Union, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application July 19, 1938,
Serial No. 220,004

10 Claims. (Cl. 252—45)

The present invention relates to improved lubricating oils and methods for producing them, and particularly to oils of low oxidation rate and low sludging tendency. The invention will be fully understood from the following description:

It has long been observed that well refined oils show a higher rate of oxidation than the unrefined oils from which they are obtained. This has been attributed to the fact that refining methods remove certain materials which inhibit oxidation and this apprehension seems to be plausible because inhibiting substances are known which can be added to oils to greatly reduce their oxidation rates. Among the known inhibitors are phenolic substances such as the cresols, naphthols and anthrols. For some purposes these materials serve excellently. However, it has been found that the addition of these materials always tends to increase the sludging tendency of the oil, for example, as measured by the Sligh test, see Proceedings of the American Society for Testing Materials, 24, 984, II (1924).

A new class of inhibitors which are not only much more powerful than the phenolic inhibitors, but which actually reduce the sludging tendency of the oils, has been described in the co-pending application 697,470, filed November 10, 1933, by the present applicants and which now has matured to Patent No. 2,153,973. These materials comprise certain sulphur compounds specifically aliphatic and aromatic polysulphides and the corresponding polyselenids and polytellurides. The present application is directed specifically to lubricating compositions containing the trisulphides and the corresponding compounds in which selenium and tellurium are substituted for a part or all of the sulphur.

The present inhibitors can be used in any type of well refined hydrocarbon oils from the light spindle to the heaviest lubricating oils. They are most desirable, however, when used in oils of a strongly paraffinic nature such as those derived from paraffin base crudes, or from oils which have been extracted with agents of the type of phenol, cresol, sulphur dioxide, nitrobenzol and dichlorethyl ether, all of which have the property of removing the non-paraffinic constituents. These inhibitors are also well suited to oils prepared by hydrogenation or destructive hydrogenation, and to oils refined by vigorous action with concentrated and even fuming sulphuric acid; in other words, the so-called white mineral oils. They are likewise useful in waxes and in the synthetic oils prepared by chemical

or electrical condensation and also in greases comprising mixtures of the above lubricating oils with soaps.

While the essentially paraffinic oils described above are the most important ones, it is worth noting that the present inhibitors are also effective in reducing the oxidation rate of naphthenic or asphaltic oils which have been well refined. This is a most unusual and unexpected property and may be taken as an indication that these inhibitors are different in their action from those formerly used, namely, the phenolic, because these latter show no appreciable reduction of the oxidation rate of naphthenic oils, whereas the present agents show a very substantial reduction.

The present inhibitors may be used in relatively small amounts, say as low as .01% for highly refined oils such as "white" oils or less refined oils in the lower range of temperatures, say below 150° C. but usually they are preferred in somewhat larger amounts, for example, .05 to 0.1% and as much as 1% or 2% can be used at higher temperatures although this is not necessary and is usually undesirable. They may be added directly to the finished lubricating oil in any desired form, for example, directly or in a suitable solvent, such as carbon disulphide or carbon tetrachloride or the like, and then incorporated with the oil. The solvent may be removed by distillation with steam, or under vacuum.

It is preferred to add pure agents but oils known to contain these materials may be added to the refined oils so as to incorporate the desired quantities of the inhibitors. It should also be understood that the sulphur compounds should be added after all of the refining steps have been completed because the usual refining methods will remove sulphur compounds and their equivalent. It will be understood, of course, that if the type of refinement is such as not to accomplish the removal of sulphur, then the agents may be added prior to such treatment.

Most of the above-mentioned substances are of the type known as corrosive in that they tarnish copper and brass but it has been determined that this is of little consequence, and especially where engines are run at elevated temperatures, for example, aeroplane engines, but some of the substances are not corrosive. These latter are, therefore, preferable.

The trisulphides in fact act as corrosion inhibitors in that they reduce the tendency of

highly refined lubricating oils to corrode alloy bearings in automobile engines operating with leaded fuels. The addition of trisulphides to lubricating oils is also advantageous in that these compounds increase the film strength or load-bearing properties of the lubricants.

The following examples are given to illustrate the use of the present inhibitors and the properties of the inhibited oils:

EXAMPLE

Highly refined petroleum lubricating oils were subjected to the oxidation rate and lead tolerance tests described below in order to determine their resistance to oxidation at elevated temperatures and their tendency to corrode alloy bearings in the presence of lead compounds. Blends of the same lubricants with 0.25% of organic polysulphides were subjected to the same tests. The results are indicated in the following table:

Lubricating oil	Oxidation rate cc. O ₂ abs./15 mins.	Lead tolerance
Blank oil	82-60-48	0.010.
Blank+diamyl disulphide	71-45-38-31	0.020.
Blank+dibenzyl disulphide	70-40-32-28	Not determined.
Blank+diethyl tetrasulphide	28-31-28-25	Greater than 0.210.
Blank	235-	0.005.
Blank+diamyl trisulphide	17-11-13-14	0.045.

The tests reported in the above table were conducted as follows:

Oxidation rate

Highly refined petroleum lubricating oil and blends thereof with the oxidation inhibitors were prepared in samples of 10 cc. each. The oil was heated to 200° C. and was agitated with a definite quantity of oxygen. The absorption of oxygen was measured in cubic centimeters at 15 minute intervals unless the amount absorbed in the first 15 minute interval was so high as to make further runs unnecessary.

Lead tolerance

1500 cc. of the oil being tested were maintained at 325° F. and were sprayed for five hours against two each of copper-lead and cadmium-silver alloy bearings, such as are used in automobile engines. The oil dripping from the bearings was recirculated. The bearings were weighed before and after the tests to determine any loss in weight. The test was then repeated with the addition of lead oleate in increments of 0.005% by weight (calculated as lead oxide). When the test results in a loss of weight of the bearings of 50 mg., it indicates that the lead tolerance of the oil has been exceeded and the amount of lead oxide added in the past previous test is recorded as the lead tolerance. By correlation of this test with the use of highly refined lubricating oils in actual operation of automobile engines under severe service conditions, it has been determined that a lead tolerance below 0.020 is unsatisfactory, this figure being marginal. Oils having much higher lead tolerances are considered far superior.

It is apparent from the above tests that the oxidation rate is reduced far more by the diamyl trisulphide than by either the disulphides or the tetrasulphides. The diamyl trisulphide also improved the lead tolerance to a much greater extent than the disulphide, but was not as good as the tetrasulphide in this respect.

The diamyl trisulphide described above was prepared as follows: 312 grams of amyl mercaptan were dissolved in 300 cc. of carbon disulfide and placed in a 2-liter 3-neck round bottom flask with stirrer, condenser and dropping funnel, with stirring. 154.5 grams of SCl₂ (dissolved in 150 cc. CS₂) were added slowly at room temperature over a period of 5 hours. The reaction mixture was stirred over night and then flushed with CO₂ while stirring for 4 hours, finally bringing up to reflux by heating on a water bath. The reaction mixture was poured into water, extracted with ether, washed free of acid, dried with Na₂SO₄ and filtered. The filtered solution was of bright yellow color. The solvent was removed on the water baths. A sample was heated under high vacuum on the water bath to remove the last traces of solvent. The residue weighed 335 grams. The residue was slowly percolated through a column of 140 grams of NaOH ground with fine sand. Yield=307 grams or 86%.

Other suitable trisulphides for use in place of the diamyl trisulphide in the above-described lubricating oil blends include diethyl trisulphide, di-isopropyl trisulphide, dibutyl trisulphide, dihexyl trisulphide, dibenzyl trisulphide, diphenyl trisulphide, and other aliphatic and aromatic trisulphides. The hydrocarbon radicals in such trisulphides may also be substituted with other elements in place of hydrogen, and trisulphide of nitrogen bases such as amines and anilines, and of hydroxy compounds such as alcohols and phenols, are also included.

The present invention is not to be limited by any theory of inhibitor action nor to any particular inhibitors nor to any particular oils containing them, but only to the following claims in which it is desired to claim all novelty inherent in the invention.

We claim:

1. Composition of matter comprising a well refined hydrocarbon lubricating oil to which is added a small amount less than 2%, sufficient to increase the resistance of said oil to oxidation, of a compound represented by the following formula



in which R represents organic radicals and X is an element selected from the group consisting of sulphur, selenium and tellurium.

2. Composition of matter comprising a well refined hydrocarbon lubricating oil to which is added a small amount less than 2%, sufficient to increase the resistance of said oil to oxidation, of an organic trisulphide.

3. Composition of matter comprising a well refined lubricating oil to which is added a small amount less than 2%, sufficient to increase the resistance of said oil to oxidation, of an alkyl trisulphide.

4. Composition of matter comprising a well refined hydrocarbon lubricating oil to which is added a small amount less than 2%, sufficient to increase the resistance of said oil to oxidation, of diamyl trisulphide.

5. An improved lubricating composition resistant to deterioration at elevated temperatures of the order encountered in an internal combustion engine, comprising a viscous hydrocarbon lubricating oil containing dissolved therein an amount, less than 2%, and sufficient to increase the resistance of said oil to oxidation, of an organic trisulphide.

6. An improved lubricating composition resist-

ant to deterioration at elevated temperatures of the order encountered in an internal combustion engine, comprising a viscous hydrocarbon lubricating oil containing dissolved therein about 0.01 to 1.0% of an organic trisulphide containing only carbon, hydrogen and sulphur.

7. An improved lubricating composition resistant to deterioration at elevated temperatures of the order encountered in an internal combustion engine, comprising a viscous hydrocarbon lubricating oil containing dissolved therein a small amount less than 2%, sufficient to increase the resistance of said oil to oxidation, of an alkyl trisulphide.

8. Composition according to claim 7 in which said alkyl trisulphide is diamyl trisulphide.

9. Composition of matter comprising a well refined hydrocarbon lubricating oil to which is added a small amount less than 2%, sufficient to increase the resistance of said oil to oxidation,

of a non-corrosive compound represented by the following formula



5 in which R represents organic radicals containing not more than six carbon atoms and X is an element selected from the group consisting of sulphur, selenium and tellurium.

10. Composition of matter comprising a well refined hydrocarbon lubricating oil to which is added a small amount less than 2%, sufficient to increase the resistance of said oil to oxidation, of a non-corrosive compound represented by the following formula,



15 in which R represents hydrocarbon radicals containing not more than six carbon atoms, and X is an element selected from the group consisting of sulphur, selenium and tellurium.

RAPHAEL ROSEN.

ROBERT M. THOMAS.