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HYDROCARBON OIL CONTAINING ORGANIC POLYSULPHIDES AS OXIDATION INHIBITORS

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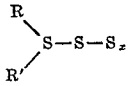
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6 Claims. (Cl. 252—46)

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 present application is a continuation-in-part of application Serial No. 220,005 filed July 19, 1938. 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 application 697,470 filed November 10, 1933, now Patent 2,153,973, by the present applicants, which was co-pending with application Serial No. 220,005. These materials comprise certain sulphur compounds specifically aliphatic and aromatic polysulphides and the corresponding polyselenids and polytellurides. By the term "polysulphide" we intend to include only substances of the following general formula:



This does not include, however, the well known disulphides of the general formula:



In each of the above formulas the R and R' denote alkyl or aryl groups. The x may represent 1 or more sulphur atoms. This is preferably under 3 since the penta and higher sulphides are corrosive, while those below 3 are not. The present application and the co-pending application Serial No. 220,005 are directed specifically to lubricating compositions containing organic polysulphides in which the organic radicals are relatively large, containing at least 10 carbon atoms and particularly to non-corrosive organic polysulphides in which the organic radicals correspond to unsaturated oils. Such organic polysulphides are conveniently prepared by sulphurizing unsaturated organic oils of suitably high molecular weight. This invention also includes the corresponding compounds in which selenium and tellurium are substituted for a part or all of the sulphur in the above-described organic polysulphides.

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% 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. These corrosive compounds usually contain relatively short organic groupings, such as butyl pentasulphide. Such corrosive compounds are claimed in Patent 2,153,973. Other compounds of the class which contain larger alkyl groupings are non-corrosive. These non-corrosive compounds are preferable. The use of these compounds in mineral lubricating oils is the subject matter of the present application. These compounds in fact reduce the tendency of highly refined lubricating oils to corrode alloy bearings in automobile engines operating with leaded fuels. They can be made by reaction of unsaturated hydrocarbons and sulphur or sulphur chloride or the corresponding selenium and tellurium compounds. Other suitable organic polysulphides can be prepared by sulphurizing corresponding unsaturated organic oils. Cracked oils, for example cracked wax, may be used to produce good non-corrosive substances. Also, fatty acid compounds containing an unsaturated organic group such as the unsaturated fatty acid glycerides, particularly lard oil may also be sulphurized to produce good non-corrosive substances. Another method of producing polysulphide is by treatment of a mercaptan with sodium plumbite adding enough sulphur to make the desired polysulphide.

The following examples are given to illustrate the use of the polysulphide containing organic groupings of at least ten carbon atoms and the properties of the inhibited oils:

Example I

The blank used in this experiment was a well refined motor oil S. A. E. grade 50. The polysulphide inhibitor was produced by reacting cracked wax fractions (boiling 200 to 600° F.) at 150 to 200° C. with 10% S_2Cl_2. According to boiling point analyses these cracked wax fractions consisted largely of C_{10} and C_{14} hydrocarbons. The product contained 2½% sulphur and a small amount of chlorine which was removed by treatment with alcoholic soda. The oxidation was conducted on a 10 cc. sample, agitating with a definite quantity of oxygen at 200° C. The absorption of oxygen was measured in cubic centimeters at 15 minute intervals.

Time intervals	Blank	1% polysulphide inhibitor
1	132	22
2	116	20
3	82	22
4	49	20

Example II

To the same blank as used in Example I an inhibitor is added prepared by cooking lard oil at 150 to 200° C. with approximately 10% sulphur. The tests were conducted as before.

Time intervals	Blank	0.1% inhibitor	0.25% inhibitor
1	132	32	15
2	116	47	20
3	82	56	21
4	49	----------	21

With the present inhibitor, 0.1% is too small to be effective for the entire test at the high temperature used but its influence is clearly perceptible. At lower temperatures this amount is sufficient but at 200° C. it is preferable to use .25% which is altogether satisfactory.

The sulphurized lard oil described in the above example was tested for corrosivity against copper by immersing a strip of bright copper metal for 3 hours in the oil at 212° F. The copper strip remained bright with no appreciable corrosion or tarnish. The sulphurized lard oil was also tested for free sulphur, a portion of the oil being diluted with naphtha and shaken with bright metallic mercury. No free sulphur was present.

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.

What is claimed is:

1. An improved, substantially non-corrosive lubricating composition resistant to deterioration at elevated temperatures of the order encountered in an internal combustion engine, consisting essentially of a viscous hydrocarbon oil to which has been added a small amount, below about 1% and sufficient to increase the resistance of said oil to oxidation, of an organic polysulphide prepared by sulphurizing an unsaturated organic oil.

2. An improved, substantially non-corrosive lubricating composition resistant to deterioration at elevated temperatures of the order encountered in an internal combustion engine, consisting essentially of a viscous hydrocarbon oil to which has been added a small amount, below about 1% and sufficient to increase the resistance of said oil to oxidation, of an organic polysulphide prepared by sulphurizing an unsaturated fatty oil.

3. An improved, substantially non-corrosive lubricating composition resistant to deterioration at elevated temperatures of the order encountered in an internal combustion engine, consisting essentially of a viscous hydrocarbon oil to which has been added a small amount, below about 1% and sufficient to increase the resistance of said oil to oxidation, of an organic polysulphide prepared by the direct addition of sulphur to an unsaturated fatty oil at a temperature of about 150° to 200° C.

4. An improved, substantially non-corrosive lubricating composition resistant to deterioration at elevated temperatures of the order encountered in an internal combusion engine, consisting essentially of a viscous hydrocarbon oil to which has been added a small amount, below about 1% and sufficient to increase the resistance of said oil to oxidation, of an organic polysulphide prepared by the direct addition of sul-

phur to a lard oil at a temperature of about 150° to 200° C., the polysulphide being non-corrosive.

5. An improved, substantially non-corrosive lubricating composition resistant to deterioration at elevated temperatures of the order encountered in an internal combustion engine, consisting essentially of a viscous hydrocarbon oil to which has been added a small amount, below about 1% and sufficient to increase the resistance of said oil to oxidation, of an organic polysulphide prepared by the action of sulphur monochloride on a cracked paraffin wax at a temperature of about 150 to 200° C.

6. An improved, substantially non-corrosive lubricating composition resistant to deterioration at elevated temperatures of the order encountered in an internal combustion engine, consisting essentially of a viscous hydrocarbon oil to which has been added a small amount, below about 1% and sufficient to increase the resistance of said oil to oxidation, of an organic non-corrosive higher polysulphide.

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