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LUBRICATING COMPOSITION

Reginald G. Sloane, Elizabeth, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

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The present invention relates to improved lubricating oils and more specifically to oils of high stability both toward oxidation and sludge formation as in a continuation-in-part of the previous application Ser. No. 408,421 filed November 19, 1929, now Patent No. 1,966,050 issued July 10, 1934. The invention will be fully understood from the following description.

It has been observed that after lubricating oils have received a high degree of refinement they are often more unstable particularly toward oxidation than the impure or crude cuts from which they were obtained. The reason for this is thought to be that the refining process removes substances which act as inhibitors of oxidation. Furthermore, inhibitors of this type are known such as the cresols and naphthols which when added in relatively small amounts to lubricating oils showing a high oxidation rate cause a considerable reduction.

The present invention relates to a new class of inhibiting substances which are considerably more powerful than those previously known. This new class of inhibitors comprises in its broadest sense aromatic sulfur compounds in which the sulfur atom is attached directly to a carbon atom. These substances make up a rather large class and the ones of special commercial value are those boiling above 150° C. or preferably even higher, say above 180 or 200° C., and which for this reason will not be lost during the use of the lubricant at such temperatures as are likely to be encountered in the lubrication of automotive engines, or the like. Aromatic disulfides and mercaptans may be used such as phenyl, cresyl or higher alkylated disulfides, mercaptans and the corresponding naphthyl or anthryl, phenanthryl derivatives or their alkylated products and the relative positions of the sulfur and alkyl groups in the rings are of only minor significance, all being of good inhibiting power. More than one sulfur atom may be attached to a single ring if desired, as in the di or tri thio-phenols, cresols and naphthols.

All of the substances mentioned above consist only of the elements carbon, hydrogen and sulfur or, in other words, they are sulfurized hydrocarbons, and while these are generally preferred other elements may be present in the molecule without disadvantage, for example, oxygen or nitrogen and similar elements. As examples of such materials can be mentioned aromatic disulfides and mercaptans containing hydroxy, nitro, amino, azo and hydrazo groups. The presence of the hydroxy group is particularly desirable but the other groups mentioned, while not particularly desired, do not destroy the effect of the mercaptan or disulfide groups. In the same manner carboxyl, aldehyde and keto groups may be present. It will be understood that the compounds containing only carbon, hydrogen and sulfur are preferred, particularly disulfides and mercaptans.

While the above description has been limited entirely to sulfur compounds, it should be understood that in each case selenium or tellurium may be substituted for the sulfur atom, but for reasons of economy the sulfur derivatives are preferred. It is also usually the case that the sulfur compounds are more active.

The oils in which the present inhibitors are to be used are more especially those which are substantially paraffinic in type, for example, those obtained from paraffin or mixed base crudes which have been well refined with acid clay or by other means so that they are characterized by a higher oxidation rate than the crude oils from which they are obtained. Extracted oils such as are prepared by treatment with selective solvents of the type of phenol, cresol, sulfur dioxide, nitro-benzol and the like are also of a paraffinic type and these products are especially suitable for the new class of inhibitors. By an oil of high oxidation rate is meant an oil which has a maximum absorption rate in excess of about 50 cc. of oxygen per fifteen minute interval per 10 cc. of sample when agitated with oxygen at a temperature of about 200° C. The rates of oxidation for well refined oils of the type mentioned above may be far in excess of the figure mentioned, for example, they may be up to 100 or 180 cc. absorption or even up to 300 cc. in very pure paraffinic oils.

Other classes of oils in which the improved inhibitors are of great advantage are the highly refined white oils produced by the action of fuming or concentrated sulfuric acid, and also destructively hydrogenated oils or oils prepared by strong hydrogenation at low temperatures.

While the inhibitors mentioned above are of the greatest advantage with oils listed in the previous paragraphs because of their high oxidation rate, they have also been found to be so powerful as to likewise show a considerable reduction in the oxygen absorption rate of lower grade oils of more or less naphthenic or asphaltic types such as the Coastal or California oils which are characterized by a viscosity index below 50 or even 30 and by oxidation rates of the order of 30 cc. in the units mentioned above. It may well

be that the action of the present inhibitors is different from the ordinary naphtholic or cresolic inhibitors, since these latter show substantially no effect whatever on the naphthenic types of oils. On the other hand, the present inhibitors reduce the oxidation rate to a considerable degree, for example, by as much as one-half. It should be noted, however, as stated above, that the inhibitors are not of greatest value in connection with these oils since their oxidation rates are already low.

The amount of the various inhibitors which may be used depends upon the oil to which it is to be added, the particular inhibitor, and also to the conditions which are likely to be encountered. In general the substances are considerably more powerful than cresols or naphthols and for this reason may be used in smaller quantities. It may be said that if the oil is designed to stand higher temperatures, the amount of the inhibitors should be increased. The new inhibitors are effective when used in amounts as little as .01% in the case of very highly refined oil such as white oil or other less highly refined oils when used in the lower temperature range, for example, under 150° C., but ordinarily more is desired, for example .05 or .10%, or in some cases even more. Of the various compounds the disulfides are preferable to mercaptans because they have a less objectionable odor.

As illustrations of the materials used and their action in various lubricating oils, the following examples are given:

Example I

A well refined lubricating oil having a viscosity of approximately 145 seconds Saybolt at 100° F. is blown with a steady volume of air, 10 cu. ft. per hr. at 300° F. (149° C.). The sample was 300 gr. At intervals the free acid was determined by titration with alkali. The following table gives the rate of acid formation with time, in respect to the Blank sample containing no inhibitors, and the same oil containing specific inhibitors.

Time in hours	Acidity-MgKOH per qt. of oil			
	Blank	.1% thio beta naphthol	.3% thio beta naphthol	.3% diphenyl disulfide
3	1.4	.2	.2	.3
6	3.6	.2	.2	.5
9	5.7	.2	.2	.5
12	7.4	.2	.2	.5
15	10.0	.2	.2	.5
18	13.2	.2	.2	.5
21	13.4	.2	.2	.5
24	16.3	.2	.2	.5

Example II

In the following test the oxidation rate was determined in a different manner. The samples were 10 cc. and the amount of oxygen absorbed is measured at 15 minute intervals. The temperature of the test is 200° C. and the absorption rate is measured in cc. of absorbed oxygen. The Blank sample was a well refined motor oil.

Time 15-min. intervals	Oxygen absorption					
	Blank	.1% thio cresol	.1% dimercapto diphenyl	.1% alpha thio naphthol	.1% alpha naphthol disulfide	.1% of a mixture of the last two 60%-40%
1	180	67	12	24	9	18
2	135	42	8	15	10	11
3	65	23	8	13	6	8
4	42	----	8	10	6	4

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

I claim:

1. The combination, with a highly refined viscous mineral oil, of a sufficient quantity of a disulfide of an aromatic compound containing only the elements carbon, hydrogen and sulfur, to reduce substantially the tendency of the oil to form acidic material through oxidation.

2. The combination, with a highly refined viscous mineral oil, of a sufficient quantity of diphenyl disulfide to reduce substantially the tendency of the oil to form acidic material through oxidation.

3. A composition of matter comprising a petroleum lubricating oil characterized by a high initial rate of oxidation containing dissolved therein, in an amount sufficient to reduce substantially the tendency of the oil to form acidic material through oxidation, an oxidation inhibitor selected from the class consisting of alpha and beta naphthyl mercaptans.

4. The composition of matter according to claim 3, in which the inhibitor is beta naphthyl mercaptan.

5. A composition of matter comprising a white mineral oil obtained by strong acid refining containing dissolved therein, in an amount sufficient to reduce substantially the tendency of the oil to form acidic material through oxidation, beta naphthyl mercaptan.

REGINALD G. SLOANE.