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STABILIZED MINERAL OIL COMPOSITION

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This invention is concerned with the stabilization of viscous mineral oil fractions against the harmful effects of oxidation or deterioration with use by means of an oxidation inhibitor or an antioxidant. The invention is more specifically related to the improvement or stabilization of such mineral oil fractions by the use of novel compounds, or a novel class of compounds, which when admixed with a viscous mineral oil in minor proportions will prevent or delay undesirable changes taking place in the oil.

As is well known to those familiar with the art, substantially all the various fractions obtained from mineral oils and refined for their various uses are susceptible to oxidation. The susceptibility of an oil fraction to oxidation and the manner in which oxidation manifests itself within the oil varies with the type and degree of refinement to which the oil has been subjected and with the conditions under which it is used or tested. In other words, the products formed in an oil fraction as a result of oxidation and the degree to which they are formed depends upon the extent to which the various unstable constituents or constituents which may act as oxidation catalysts have been removed by refining operations, and also upon the conditions of use.

A "highly refined" viscous oil, for example, which is one that has been refined by treatment with fuming sulfuric acid or other means or combinations such as $AlCl_3$, solvents and acids (or with large quantities of concentrated sulfuric acid), tends to form relatively large amounts of acidic constituents when subjected to oxidizing conditions. The presence of catalytic materials such as copper does not appear to affect appreciably the oxidation of highly refined oils and such oils are less prone to the formation of colored bodies or of insoluble sludge. The formation of acidic bodies, however, is highly undesirable for most applications of these oils. For example, when used as an insulating or cooling oil in electrical equipment such as transformers or capacitors an increase in acidic bodies tends to lower the dielectric strength of the oil and has other harmful effects which are undesirable. The acids are corrosive to metals and thus reduce the useful life of the oils as lubricants or for other purposes in which they come in contact with metals, and the acidic materials are also injurious in textile lubricants and in spray oils.

"Moderately refined" oils, which are normally oils that have been refined by treatment with only moderate amounts of sulfuric acid, or other refining agents, tend to form relatively small amounts of acidic oxidation products as compared with highly refined oils, but they undergo material color depreciation and form considerable amounts of sludge. The changes taking place in these oils are appreciably accelerated by the presence of metal catalysts such as copper. Sufficient acid is generally formed to cause some reduction in the dielectric strength of these oils, but the principal objection to them is their tendency to deposit sludge which interfers with heat transfer in transformers and turbines and also causes plugging of oil feed lines in lubricating systems.

"Solvent-refined" oils in general which have been prepared by treatment with selective solvents, such as chlorex, phenol, furfural, etc., resemble the moderately refined acid-treated oils in that their oxidation is accelerated by the presence of metals such as copper and further in that it is attended by substantial color depreciation and sludge formation. Acid formation is usually greater than in the case of moderately acid-refined oils, but considerably less than with highly refined oils. Both sludge and acid formation lower their value for many purposes, such as electrical insulation, lubrication, etc. Also, solvent-refined oils have found extensive use as lubricants for internal combustion engines because of their high viscosity index, but under the conditions of use encountered in crankcases such oils develop constituents which are corrosive toward certain metal bearings such as the cadmium-silver bearings, etc., which are sometimes used.

It is to be understood that this classification of oils as "highly refined," "moderately refined," and "solvent-refined" is by no means limiting and that there can exist oils whose refining and blending has been such as to make them intermediate in properties between the types set up. Thus, response to inhibitors may be said to depend entirely on the type of oxidation and end products of oxidation of an oil, which in turn depends largely upon the degree of refining this oil has had. Further, the degree of refining required to produce these types of oils varies with the crude source so that any one refining procedure may produce either a highly refined oil or a moderately refined oil, depending upon the crude source. Pennsylvania type oils, for example, require much less refining to produce highly refined oils than the Coastal type of oils.

The use of oxidation inhibitors for the purpose of stabilizing a viscous mineral oil fraction against the deleterious effects of oxidation discussed above is well known. Since the action of these inhibiting

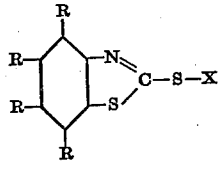
materials is apparently catalytic the problem of their development is a difficult one and is evidently influenced to a large degree by the oxidizable constituents which are in the oil following a particular refining treatment. Thus a particular inhibitor or class of inhibitors may be effective to stabilize a highly refined oil against acid formation while the same inhibitor may have no appreciable effect upon acid, color or sludge formation in a moderately refined oil and vice verse. This same inhibitor may or may not be effective in inhibiting acid, sludge and color formation in a solvent-refined oil and may or may not be effective to inhibit the corrosive action of a solvent-refined oil toward metals such as used in cadmium-silver bearings.

This invention is particularly concerned with the inhibition of oxidation in highly refined oils of the type used in transformers, turbines, and the like through the use of a novel class of compounds to be hereinafter described. The compounds contemplated herein do not appear to be effective negative catalysts toward the oxidation of "moderately refined" or "solvent-refined" oils of the turbine oil type, but I have found that certain of the compounds belonging to the general class contemplated herein are effective to inhibit corrosive action of solvent-refined motor oils toward alloy metals, such as cadmium-silver alloy bearings, under conditions encountered in crankcase use.

My invention is predicated upon the discovery that a class of organic compounds which may be broadly termed "mercapto benzo thiazoles and their derivatives" are effective negative catalysts toward the oxidation of viscous mineral oils of the "highly refined type."

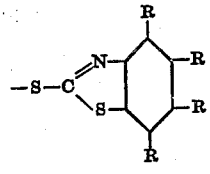
The mercapto benzo thiazoles and the derivatives thereof contemplated as oxidation inhibitors for the mineral oil blends contemplated herein may be represented by the general formula:

A



wherein R represents hydrogen, an alkyl group or an aryl group, and X represents hydrogen or the radical

A'



Compounds of the general type characterized by Formula A in which X represents hydrogen are the mercapto benzo thiazoles, such a compound in which R also represents hydrogen being 1-mercapto benzo thiazole. Compounds of the type characterized by Formula A where X represents the radical A' are benzo thiazyl disulfides, such last-mentioned compounds being oxidation products of the corresponding mercapto benzo thiazoles.

The mercapto benzo thiazoles can be prepared by heating an azobenzene with carbon disulfide (Ber. 24, 1403). On treating a solution of a mercapto benzo thiazole with an oxidizing agent, such as potassium dichromate, the corresponding benzo thiazyl disulfide is obtained (same reference). Other methods for preparing these compounds are given in the literature.

The following examples illustrate the effectiveness of the class of compounds contemplated herein as oxidation inhibitors for viscous mineral oils by certain specific compounds within the class.

EXAMPLE I

Highly refined oil

The oil employed in this test was of the "highly refined" type used in transformers and the like which had been obtained from a Coastal distillate by successive treatments with 40 lbs. per bbl. of 98 per cent sulfuric acid and 180 lbs. per bbl. of 103 per cent oleum, followed by neutralization, washing and clay percolation. It has a specific gravity of 0.871, a flash point of 310° F. and a Saybolt viscosity of 69 seconds at 100° F.

The test used, known as the Modified German tar test, involved heating a 150 gram sample of the oil at a temperature of 120° C. while bubbling oxygen gas through the oil for a period of 70 hours. The quantity of acidic oxidation products formed was determined by: (*a*) extracting the oil with alcoholic soda, neutralizing the extract, and then weighing the precipitated material, which is calculated as per cent acidic tar; and (*b*) by titrating the acids formed in the oil with alcoholic KOH and expressing the result as the neutralization number (N. N.) which represents the milligrams of KOH required to neutralize the acid in one gram of oil.

The results of this test, using representative compounds of the type contemplated by this invention, are listed in Tables I and II below. In Table I the compounds used are of the type indicated by general Formula A above, where R is hydrogen. In Table II the compounds are of the type represented by general Formula A, wherein at least one R represents an alkyl group or an aryl group and the remaining Rs represent hydrogen.

Table I

Oil	Acidic tar
	Percent
Oil alone	15
Oil+.03% mercapto benzo thiazole	0.02
Oil saturated (0.02+%) with benzo thiazyl disulfide	0.06

Table II

Oil	N. N.
Oil alone	25.0
Oil+<.10% methyl mercapto benzo thiazole	0.01
Oil+<.10% phenyl mercapto benzo thiazole	0.02
Oil+<.10% di(methyl benzo thiazyl) disulfide	0.01
Oil+<.10% di(phenyl benzo thiazyl) disulfide	0.01

From the foregoing results it will be seen that both the unsubstituted and the substituted mercapto benzo thiazoles and their corresponding oxidation products, the benzo thiazyl disulfides, are effective inhibitors of acid formation in oils of the "highly refined" type:

EXAMPLE II

Solvent-refined motor oil

The substituted mercapto benzo thiazoles and

their corresponding disulfides were also found to be of measurable effectiveness in inhibiting the corrosive action of solvent-refined motor oil toward alloy metals of the type used in cadmium-silver bearings. The oil used in this test was one obtained by separately refining Pennsylvania neutral and residuum stocks with chlorex and blending to give an oil of the following properties: specific gravity 0.872; flash point 435° F., and Saybolt viscosity of 318 seconds at 100° F.

The test used involved immersing a 6-gram section of a cadmium-silver bearing of the type used in connecting rods in a 30-gram sample of the oil, heating the oil to a temperature of 175° C. and bubbling air therethrough against the surface of the bearing for a period of 22 hours. Two specimens from the same bearing were tested simultaneously, one in the oil alone and the other in oil containing the inhibitor.

In Table III below the losses in weight of the respective metal specimens in the oil alone and the oil containing the inhibitor are listed in the columns headed "Not. inh." and "Inh.", respectively, such losses being a measure of corrosiveness of the oil or oil blend toward the alloy of the test specimen.

Table III

Inhibitor	Loss in weight (mgs.)		
	Amount	Not. inh.	Inh.
Methyl mercapto benzo thiazole	<.25%	78	28
Phenyl mercapto benzo thiazole	<.25%	78	40
Di(methyl benzo thiazyl) disulfide	<.25%	73	12
Di(phenyl benzo thiazyl) disulfide	<.25%	73	52

It will be understood that a suitable solvent such as benzene may be employed if desired to facilitate solution of the improving agent in the oil; also that the compounds contemplated herein may be used in varying amounts, depending upon the oil fraction, conditions of use, etc., but for the purposes contemplated herein it has been found that the use of these compounds in amounts ranging from about 0.01 per cent to about 0.5 per cent will give satisfactory results.

It is to be further understood that the terms "highly refined" and "solvent-refined" as used herein have reference to oils corresponding substantially in their manner of deterioration and inhibitor response to the examples given and are not necessarily restricted to oils obtained by particular refining operations. As has been previously pointed out, the final characteristics in an oil fraction are affected by the crude from which the oil is obtained as well as the refining treatment. For example, an oil of the "highly refined" type may be obtained from a selected crude by a refining treatment which with another crude stock would yield a "moderately refined" oil.

I claim:

1. An improved mineral oil composition comprising a highly refined viscous oil of the type used in turbines, transformers, and the like having in admixture therewith a minor proportion, sufficient to substantially inhibit the deleterious effects of oxidation on said oil, of a mercapto benzo thiazole.

2. An improved mineral oil composition comprising a solvent-refined viscous mineral oil fraction having in admixture therewith a minor proportion, sufficient to substantially inhibit the deleterious effects of oxidation on said oil, of a mercapto benzo thiazole in which the aryl nucleus has at least one substituent selected from the group consisting of alkyl and aryl hydrocarbon groups.

3. A viscous mineral oil fraction containing from about 0.01 per cent to about 0.5 per cent of a mercapto benzo thiazole.

4. A highly refined viscous mineral oil fraction normally tending to develop acidic products under oxidizing conditions and in admixture therewith a minor proportion of 1-mercapto benzo thiazole, sufficient to substantially inhibit the development of said acidic oxidation products.

5. A highly refined viscous mineral oil fraction normally tending to develop acidic products under oxidizing conditions and in admixture therewith a minor proportion of methyl mercapto benzo thiazole, sufficient to substantially inhibit the development of said acidic oxidation products.

6. A highly refined viscous mineral oil fraction normally tending to develop acidic products under oxidizing conditions and in admixture therewith a minor proportion of phenyl mercapto benzo thiazole, sufficient to substantially inhibit the development of said acidic oxidation products.

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