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MINERAL OIL COMPOSITION

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This invention has to do with the stabilization of petroleum products such as viscous mineral oil fractions and refined paraffin waxes against the harmful effects of oxidation and deterioration with use. It 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. This 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 the oil 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 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 appreciably affect 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 where they come in contact with metals. These acidic materials are also injurious in textile lubricants and in spray oils.

Moderately refined oils, that is, oils which 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. They undergo material color depreciation and form considerable amounts of sludge and the changes taking place in these oils are appreciably accelerated by the presence of metal catalysts such as copper.

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 the 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 refined for use as internal combustion engine lubricants, under the conditions of use encountered in crankcases, develop constituents which are corrosive toward certain hard metal bearing surfaces such as the cadmium-silver or copper-lead alloys and the like which are sometimes used in these bearings.

It is to be understood that the foregoing classification of different "types" of viscous mineral oil fractions or hydrocarbon oils 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 discussed above. 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 on the crude from which it is obtained. 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 inhibitors or class of inhibitors may have no appreciable effect upon acid, color or sludge formation in a moderately refined oil and vice versa. The same inhibitor may or may not be effective to inhibit the corrosive action of a solvent-refined oil toward alloy bearing metals.

The present invention is chiefly concerned with

viscous hydrocarbon oil fractions of the "highly refined" type and has as its primary object the provision of a class of inhibitor compounds which, when blended in small amounts with highly refined oils, will inhibit the natural tendency of such oils to form acidic products under oxidizing conditions. The invention is predicated upon the discovery that the class of hydrocarbon derivatives of the type which may be obtained by reacting an organic compound containing the



group with a mercaptan under conditions such that water is released and mercaptan residual groups (SR') replace the oxygen in the



group, are effective inhibitors for highly refined oils.

Typical compounds containing the



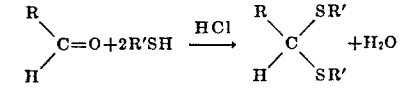
group which may be reacted with mercaptans to obtain the inhibitors contemplated herein are aldehydes, ketones, organic acids and esters, either aliphatic or cyclic (aromatic and alicyclic) and either unsubstituted or substituted with groups such as —NO_2, NR''_2, —Cl, CO—R'', CO—OR'' or other desired groups, wherein R'' represents a radical selected from the group consisting of alkyl, aryl, alkaryl and aralkyl radicals.

We have discovered that three types of organic compounds falling under the foregoing classifications, which type compounds we may call "organic mercaptals," "organic mercaptols," and "esters of trithio-ortho acids," are effective stabilizers for highly refined viscous petroleum oils. These types of compounds are, in general, prepared by reacting an aldehyde, a ketone or an acid (or ester), respectively, with a mercaptan in the presence of dry HCl gas. (See Posner, Ber. 33, 2987 (1900) and further articles by the same author.) The reactions by which these typical compounds can be obtained are illustrated by the following general examples and equations.

EXAMPLE I.—*Mercaptals*

One mol of aldehyde is mixed with 2 mols of mercaptan and the mixture saturated with HCl gas to complete the reaction. The reaction mixture is washed with water to free the product from acid and then topped under high vacuum to remove any unreacted aldehyde or mercaptan. Following this procedure, the following compounds have been prepared: 2-ethylhexaldehyde dibenzyl mercaptal; tolualdehyde dibenzyl mercaptal; benzaldehyde diamyl mercaptal; m-nitro benzaldehyde diamyl mercaptal; formaldehyde diphenyl mercaptal; and formaldehyde ditolyl mercaptal.

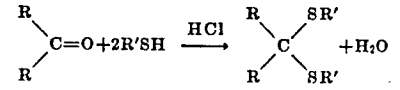
The reaction taking place in the procedure may be illustrated by the following equation:

A 

(Aldehyde) (mercaptan) (mercaptal)

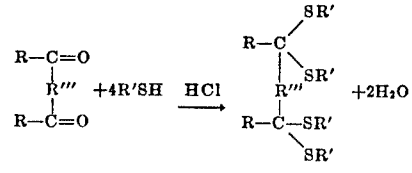
EXAMPLE II.—*Mercaptols*

The mercaptols may be prepared by following a procedure similar to that described in Example I, using 1 mol of a ketone instead of the aldehyde. Following this procedure we have prepared acetone dibenzyl mercaptol; acetophenone dibenzyl mercaptol; benzophenone dibenzyl mercaptol; mesityl oxide dibenzyl mercaptol; m-nitro acetophenone diphenyl mercaptol; benzil dibenzyl mercaptol; aceto acetic ester dibenzyl mercaptol; and benzoyl acetone diamyl mercaptol. The reaction taking place in this procedure may be illustrated by the following equation:

B 

(Ketone) (mercaptan) (mercaptol)

By using 1 mol of a diketone and 4 mols of mercaptan we have prepared acetyl acetone tetra-amyl mercaptol and acetonyl acetone tetra-phenyl mercaptol. This reaction and the general formula for the product are illustrated in the following equation:

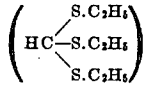
C 

(Diketone) (mercaptan) (tetra-mercaptol)

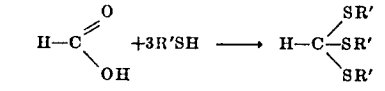
in which R''' is a bivalent hydrocarbon radical.

EXAMPLE III—*Esters of trithio-ortho acids*

These compounds are prepared by reacting 3 mols of a mercaptan with 1 mol of an organic acid or ester, following the general procedure described above under Example I. Using formic acid and 3 mols of ethyl mercaptan, trithioethyl formate

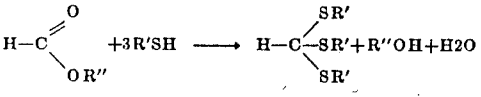


was obtained. The reaction is illustrated by the following equation:

D 

(Formic acid) (mercaptan) (esters of trithio-ortho formate)

Using a formic ester the following reaction takes place:

D' 

(Formic ester) (mercaptan) (esters of trithio-ortho formate) (alcohol)

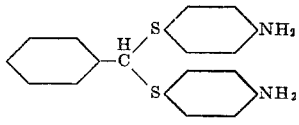
In the foregoing equations and the formulae therein, R and R' represent organic radicals selected from the group consisting of the hydrocarbon radicals, alkyl, aryl, alkaryl, and aralkyl radicals, and substituted hydrocarbon radicals containing substituents from the group consisting of: —NO_2, —NH_2, —NR''_2, —Cl, —CO—R'', and CO—OR'', in which R'' represents hydrocarbon radicals from the group consisting of alkyl, aryl, alkaryl and aralkyl radicals.

It will be observed from the products in equations A to D' inclusive that the compounds contemplated herein as mineral oil inhibitors are characterized by the presence of at least one carbon atom to which at least two mercaptan residual groups (SR') are attached. This general

class or group of compounds may be included under the general formula $R(SR')_n$, in which: R and R' are as defined above; n is a whole number from two to four, there being at least two SR' groups attached to one carbon atom of the radical R.

The preferred procedure for synthesizing the compounds contemplated herein may be illustrated by the preparation of 2-ethylhexaldehyde dibenzyl mercaptal, which was prepared by adding 24.8 parts by weight of benzyl mercaptan to 12.8 parts by weight of 2-ethylhexaldehyde. The mixture was cooled in an ice bath and saturated with dry HCl gas. After standing over night two layers formed, and both layers were poured into water and extracted with petroleum ether. The petroleum ether extract was washed with water, dried over anhydrous sodium sulfate, filtered, and the petroleum ether removed on a steam bath. The product was then topped at 2 mm. pressure to a pot temperature of 100° C.

Although the foregoing represents a preferred procedure for obtainig the majority of the compounds contemplated herein, it is to be understood that other methods may be followed. For example, benzaldehyde-di(4-aminophenyl) mercaptal was prepared according to the directions outlined by W. R. Waldron and E. E. Reid, J. A. C. S. 45, 2399 (1923), by reacting one mol of benzal chloride with two mols of the sodium salt of p-nitro-thio phenol, and then reducing the benzaldehyde-di(nitrophenyl) mercaptal with iron and acetic acid to obtain the amino derivative which has the formula:



The compounds contemplated herein are both cheap and easy to prepare and they are uniformly very effective in small amounts to inhibit the deteriorating effects of oxidation on highly refined oils Although these compounds, except perhaps for a few isolated examples, do not appear to be of outstanding eflectiveness as inhibitors for moderately refined and solvent-refined oil (for which reason the preferred mineral oil compositions contemplated herein are blends of highly refined oils), it is to be understood that our invention in its broadest aspect contemplates any mineral oil composition in which improvement has been effected by the addition thereto of one of the compounds falling within the broad class described herein.

To demonstrate the effectiveness of the compounds contemplated herein as inhibitors for highly refined oils, oil blends were prepared containing small quantities of representative compounds, such blends being subjected to a modified German tar test, which involved heating the oil samples to a temperature of 120° C. and bubbling oxygen gas therethrough for 70 hours, after which the neutralization number (N. N.) of the sample was obtained as an indication of acid formation therein. The oil used in this test was of the type used in transformers, obtained from a Coastal distillate and refined by treating first with 40 pounds per barrel of 98 per cent sulfuric acid, followed by 80 pounds per barrel of 103 per cent oleum and neutralization, washing and clay percolation. The finished oil had a specific gravity of 0.871, a flash point of 310° F. and a Saybolt viscosity of 69 seconds at 100° F. The results of these tests are tabulated in Table I below.

Table I

Inhibitor in sample	Conc.	N. N.
	Percent	
None		25.0
(1) 2-ethylhexaldehyde dibenzyl mercaptal	0.10	0.02
(2) Tolualdehyde dibenzyl mercaptal	0.10	0.05
(3) Benzaldehyde diamyl mercaptal	0.10	0.01
(4) m-Nitro benzaldehyde diamyl mercaptal	0.10	0.01
(5) Benzaldehyde-di (4-aminophenyl) mercaptal	<0.032	2.10
(6) Acetone dibenzyl mercaptol	0.10	0.04
(7) Acetophenone dibenzyl mercaptol	0.10	0.03
(8) Benzophenone dibenzyl mercaptol	0.10	0.02
(9) Mesityl oxide dibenzyl mercaptol	0.10	0.01
(10) m-Nitro acetophenone diphenyl mercaptol	0.10	0.01
(11) Benzil dibenzyl mercaptol	0.10	0.06
(12) Aceto acetic ester dibenzyl mercaptol	0.10	0.04
(13) Benzoyl acetone diamyl mercaptol	0.10	0.01
(14) Acetyl acetone tetra-amyl mercaptol	0.10	0.01
(15) Acetonyl acetone tetra-phenyl mercaptol	0.10	0.01
(16) Trithio-ethyl ortho formate	0.10	0.01

As we have previously indicated, the present invention is also concerned with the inhibition of acid formation in refined paraffin wax. To demonstrate the efficacy of the compounds contemplated herein for this purpose, blends containing representative compounds were prepared with a refined paraffin wax of 126° F. melting point, and such blends were tested by heating to 120° C. for 70 hours with oxygen gas bubbling therethrough and then determining the neutralization number (N. N.) of the sample. The results obtained, which are set forth in Table II below, show that these compounds are effective inhibitors of acid formation in paraffin wax.

Table II

Inhibitor in sample	Conc.	N. N.
	Percent	
None		35.6
Benzaldehyde diamyl mercaptal	0.10	.00
m-Nitro benzaldehyde diamyl mercaptal	0.10	.00
m-Nitro acetophenone diphenyl mercaptol	<0.10	.02
Benzophenone dibenzyl mercaptol	<0.10	.01
Acetonyl acetone tetra-phenyl mercaptol	0.10	.01
Trithio-ethyl ortho formate	0.10	.00

It will be seen from the foregoing table that the compounds contemplated herein are highly effective inhibitors of acid formation in highly refined oil and refined paraffin wax. Compound No. 5 (Table I) was only slightly soluble, but in this regard it is to be understood that our invention contemplates the use of suitable solvents, which may be aromatic hydrocarbons such as benzene, toluene, etc., ketones such as acetone, di-iso-butyl ketone, etc.; alcohols such as methyl, amyl, etc.; and esters such as ethyl acetate, etc., to facilitate blending of the less soluble compounds. These compounds may be used in amounts ranging from .01 per cent to 1.0 per cent, but in general it appears that the desired degree of inhibition is obtained with amounts in the neighborhood of 0.10 per cent.

It is to be understood that while we have described one preferred procedure for synthesizing the compounds contemplated herein, the invention is not confined to any particular method of preparing these compounds; also that the term "highly refined oil" as used herein is not restricted to oil prepared by a particular refining process but is intended rather to indicate oils having inhibitor response similar in general to

the oil used in the tested examples. In this regard it is again pointed out that the final properties and characteristics of an oil are derived from the crude oil source as well as the refining treatment, it being possible to obtain a "highly refined oil" from one crude, by a refining treatment which would yield a moderately refined oil with another crude. The invention, therefore, is not restricted to the specific procedures, compounds, or oils described hereinabove but includes within its scope whatever changes or modifications fairly come within the spirit of the appended claims.

We claim:

1. An improved petroleum product comprising a mineral oil fraction selected from the group consisting of highly refined viscous mineral oils and refined paraffin wax and in admixture therewith a minor proportion, from about 0.01 per cent to about 1.0 per cent, of a mercaptal, the said mercaptal being an organic sulfur-containing compound which is characterized by attachment of two sulfur atoms to a common carbon atom, said common carbon atom also being attached to a hydrogen atom and to a hydrocarbon radical, and the said compound being further characterized by attachment of each of said sulfur atoms to a hydrocarbon radical, and being free of sulfur-containing heterocyclic rings.

2. An improved petroleum product comprising a mineral oil fraction selected from the group consisting of a highly refined viscous mineral oils and refined paraffin wax and in admixture therewith a minor proportion, from about 0.01 percent to about 1.0 per cent, of a mercaptol, the said mercaptol being an organic sulfur-containing compound which is characterized by attachment of two sulfur atoms to a common carbon atom, said common carbon atom also being attached to two hydrocarbon radicals, and said compound being further characterized by attachment of each of said sulfur atoms to a hydrocarbon radical, and being free of sulfur-containing heterocyclic rings.

3. An improved petroleum product comprising a mineral oil fraction selected from the group consisting of highly refined viscous mineral oils and refined paraffin wax and in admixture therewith a minor proportion, from about 0.01 per cent to about 1.0 per cent, of a trithio ester of an ortho acid, said trithio ester being an organic sulfur-containing compound which is characterized by attachment of three sulfur atoms to a common carbon atom and is further characterized by attachment of each of said sulfur atoms to a hydrocarbon radical, and said trithio ester being free of sulfur-containing heterocyclic rings.

4. An improved petroleum product comprising a mineral oil fraction selected from the group consisting of highly refined viscous mineral oils and refined paraffin wax and in admixture therewith a minor proportion of a mercaptal, the said mercaptal being an organic sulfur-containing compound which is characterized by attachment of two sulfur atoms to a common carbon atom, said common carbon atom also being attached to a hydrogen atom and to a hydrocarbon radical, and the said compound being further characterized by attachment of each of said sulfur atoms to a hydrocarbon radical, and being free of sulfur-containing heterocyclic rings.

5. An improved petroleum product comprising a mineral oil fraction selected from the group consisting of highly refined viscous mineral oils and refined paraffin wax and in admixture therewith a minor proportion of a mercaptol, the said mercaptol being an organic sulfur-containing compound which is characterized by attachment of two sulfur atoms to a common carbon atom, said common carbon atom also being attached to two hydrocarbon radicals, and said compound being further characterized by attachment of each of said sulfur atoms to a hydrocarbon radical, and being free of sulfur-containing heterocyclic rings.

6. An improved petroleum product comprising a mineral oil fraction selected from the group consisting of highly refined viscous mineral oils and refined paraffin wax and in admixture therewith a minor proportion of a trithio ester of an ortho acid, said trithio ester being an organic sulfur-containing compound which is characterized by attachment of three sulfur atoms to a common carbon atom and is further characterized by attachment of each of said sulfur atoms to a hydrocarbon radical, and said trithio ester being free of sulfur-containing heterocyclic rings.

7. An improved petroleum product comprising a mineral oil fraction selected from the group consisting of highly refined viscous mineral oils and refined paraffin wax and in admixture therewith a minor proportion of a benzaldehyde diamyl mercaptal.

8. An improved petroleum product comprising a mineral oil fraction selected from the group consisting of highly refined viscous mineral oils and refined paraffin wax and in admixtnre therewith a minor proportion of an acetone dibenzyl mercaptol.

9. An improved petroleum product comprising a mineral oil fraction selected from the group consisting of highly refined viscous mineral oils and refined paraffin wax and in admixture therewith a minor proportion of a trithio ethyl ortho formate.

10. An improved petroleum product comprising a mineral oil fraction selected from the group consisting of highly refined viscous mineral oils and refined paraffin wax and in admixture therewith a minor proportion of a compound selected from the group of compounds consisting of mercaptals, mercaptols and trithio esters of ortho acids, which compound is characterized by attachment of at least two and not more than three sulfur atoms to a common carbon atom and is further characterized by attachment of each of said sulfur atoms to an organic radical selected from the group consisting of hydrocarbon radicals and substituted hydrocarbon radicals containing substituents from the group consisting of $—NO_2$, $—NH_2$, —CO—R'' and —COOR'' wherein R'' represents a hydrocarbon radical, said compound being free of sulfur-containing heterocyclic rings.

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