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STABILIZED MINERAL OIL COMPOSITION

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6 Claims. (Cl. 252—51)

This invention is concerned with the stabilization of viscous mineral oil fractions against the harmful effects of oxidation or deterioration with use by the addition of an oxidation inhibitor or antioxidant to the oil. 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 normally 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 they are used as insulating or cooling oils in electrical equipment such as transformers or capacitors, an increase in acidic bodies results which tends to lower the dielectric strength of the oils 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—that is, 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 di-electric strength of these oils, but the principal objection to them is their tendency to deposit sludge which interferes with heat transfer in transformers and turbines and also causes plugging of oil feed lines in lubricating systems.

"Solvent-refined" oils such as have been prepared by treatment with selective solvents such as Chlorex, furfural, phenol, etc., in general 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 constitutents which are corrosive toward certain metals such as are typified by 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 upon 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.

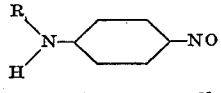
The use of oxidation inhibitors for the purpose of stabilizing a viscous mineral oil fraction against the deleterious effects of oxidation discussed above is well known. Since the action

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 versa. 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. Also, the action of a compound or class of compounds upon the oxidation of light distillates such as gasoline, kerosene, and the like gives no indication as to the effect which the same compound or class of compounds will have upon oxidation of a viscous mineral oil fraction.

The present invention is predicated upon the discovery that certain paranitroso N-monoalkyl anilines are effective to inhibit the deleterious effects of oxidation in viscous mineral oils of all the various types discussed hereinabove. In application Serial No. 257,097, filed February 18, 1939, now Patent No. 2,281,520, by Everett W. Fuller, one of the present joint applicants, the paranitroso dialkyl anilines are disclosed as oxidation inhibitors for mineral oils. As pointed out in that application, the paranitroso dialkyl anilines are of minor effectiveness in moderately refined oils, and preference is given to the highly refined oils and solvent-refined oils as the base stocks for making mineral oil compositions containing those compounds.

We have discovered the paranitroso N-monoalkyl anilines to be superior to the corresponding dialkyl anilines of the aforesaid application in that they are highly effective stabilizers for moderately refined oils as well as the highly refined and solvent-refined oils.

The paranitroso monoalkyl anilines contemplated herein are well known compounds whose properties and methods of synthesis are described in the literature (Ber. 19, 2991; Annalen 243, 291 and 286, 156). They are cheap and easy to produce and, as aforesaid, are effective in viscous mineral oil fractions in general irrespective of the refining treatment to which the oil has been subjected. The compounds contemplated herein have the general formula



in which R is an alkyl or an aralkyl radical.

The effectiveness of these compounds in the various viscous mineral oil fractions described above has been demonstrated by typical oxidation tests designed to bring out the characteristic properties of the different oils. A brief description of these tests, together with the results obtained with typical paranitroso monoalkyl anilines is set forth in the following examples.

EXAMPLE ONE

(Highly Refined Oils)

The oil used in this test was a highly refined mineral oil suitable for use in transformers and the like which had been prepared by treating a Coastal distillate with 40 pounds of 98 per cent sulfuric acid and 180 pounds of 103 per cent oleum per barrel, followed by washing and clay percolation. It had a specific gravity of 0.871, a flash point of 310° F., and a Saybolt Universal viscosity of 69 seconds at 100° F. This type of oil tends to form acidic products on oxidation. It was tested by heating samples to 120° C. and bubbling oxygen through the heated oil for a period of 70 hours. The acids thus formed were determined by titrating with alcoholic KOH, results being reported as neutralization number (N. N.), which represents the amount of KOH in milligrams necessary to neutralize one gram of oil. The results from the blank oil and samples thereof containing representative para-nitroso monoalkyl anilines are set forth in Table I below.

Table I

Inhibitor added	Per cent	N. N.
None		25.0
Paranitroso N-ethyl aniline	<.10	.01
Paranitroso N-n-butyl aniline	<.10	.00
Paranitroso N-amyl aniline	.10	.00

EXAMPLE TWO

(Moderately Refined Oils)

The oil used in this test was a mixed Midcontinent and Coastal distillate which had been refined by treatment with 70 pounds of 98 per cent sulfuric acid per barrel, neutralized, washed and percolated through clay. It had a specific gravity of 0.879, a flash point of 385° F. and a Saybolt Universal viscosity of 152 seconds at 100° F. It is an oil suitable for use in turbines. The test used involved maintaining at 25 cc. sample of the oil (or oil blend) at a temperature of 200° F. with 5 liters of air per hour bubbling through the oil. During this treatment the sample contained 24 inches of #18 gauge copper wire and 1 gram of iron granules. Two cc. of distilled water were added each day. The samples were tested for acidity (N. N.), color and sludge after varying time intervals. Results are given in Table II below.

Table II

Inhibitor added	Per cent	Time, hrs.	N. N.	Lov. color	Sludge, mg./25 cc.
None		168	.99	25	17
		240	2.5	110	246
		336	16.0	400	1,282
Paranitroso N-ethyl aniline	<.10	499	.01	2	7
		835	10.9	135	619
Paranitroso N-n-butyl aniline	<.10	499	.03	3	22
		1,004	6.1	75	190
Paranitroso N-amylaniline	.10	164	.02		1
		692	.70	33	4

EXAMPLE THREE

(Solvent-Refined Oils)

The oil used in this test was a distillate from a Rodessa crude refined with furfural, dewaxed, and filtered. The finished stock had a specific gravity of 0.856, a flash point of 420° F., and a Saybolt Universal viscosity of 151 seconds at 100° F. The oil was tested by the same method described under Example Two, and the results obtained are set forth in Table III below.

Table III

Inhibitor added	Per cent	Time, hrs.	N. N.	Lov. color	Sludge, Mg/25 cc.
None	-------	92	.91	9	33
		165	20.3	320	251
Para-nitroso N-ethyl aniline	<.10	499	.03	2	15
		1,003	.00	1	16
		1,339	14.3	105	68
Para-nitroso N-butyl aniline	<.10	499	.01	3	14
		1,005	.01	9	127
Para-nitroso N-amyl aniline	.10	164	.00	13	4
		692	.01	5	10

EXAMPLE FOUR

(BEARING CORROSION TEST)

The oil used in this test consisted of Pennsylvania neutral and residuum stocks separately refined by means of chlorex and then blended to give an S. A. E. No. 20 motor oil with a specific gravity of 0.872, a flash point of 435° F., and a Saybolt Universal viscosity of 318 seconds at 100° F. The oil was tested by adding a section of a bearing containing a cadmium-silver alloy surface and weighing about 6 grams, and heating it to 175° C. for 22 hours while a stream of air was bubbled against the surface of the bearing. The loss in weight of the bearing during this treatment measures the amount of corrosion that has taken place. A sample of the oil containing a stabilizer was run at the same time as a sample of the straight oil, and the loss in weight of the bearing section in the inhibited oil can thus be compared directly with the loss of the section in the uninhibited oil. The following results were obtained.

Table IV

Inhibitor added	Per cent	Mg. loss in weight	
		Inhibited	Uninhibited
Paranitroso N-ethyl aniline	<.25	0	35
Paranitroso N-n-butyl aniline	<.25	1	42
Paranitroso N-amyl aniline	.25	1	24

It will be observed from the foregoing test results that the compounds contemplated herein are effective in small amounts to inhibit the deleterious effects of oxidation in all of the various typical oils discussed in the fore part of this specification. The quantity of inhibitor used will depend upon the character of the oil and the conditions which it is to encounter in storage or use, but in general the desired results may be obtained with an amount ranging from 0.01 per cent to 1.00 per cent. Mutual solvents such as benzol, for example, may be used, if desirable or necessary, to facilitate blending the desired amount of the inhibitor with the oil.

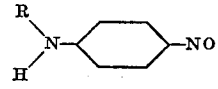
It is to be understood that the terms "highly refined," "moderately refined" and "solvent-refined" as used herein are not necessarily confined to viscous oil fractions which have been subjected to a particular refining treatment but are intended as inclusive of all viscous mineral oil fractions which are similar to the foregoing illustrative examples in their oxidation characteristics and inhibitor response. As aforesaid, these characteristics of a viscous mineral oil fraction are governed by the crude stock from which the oil is obtained as well as by the refining treatment, and it is possible, for example, to obtain a "highly refined" oil from a selected crude stock by a refining treatment which would yield a "moderately refined" oil from another crude stock.

We claim:

1. A viscous mineral oil fraction having in admixture therewith a minor proportion of a paranitroso monoalkyl aniline in an amount sufficient to inhibit the deleterious effects of oxidation on the oil.

2. A viscous mineral oil fraction having in admixture therewith a minor proportion, from about 0.01 per cent to about 1.00 per cent, of a paranitroso monoalkyl aniline.

3. A viscous mineral oil fraction having in admixture therewith a minor proportion of a compound having the general formula



in which R is a radical of the class consisting of alkyl and aralkyl radicals, the said compound being present in an amount sufficient to inhibit the deleterious effects of oxidation on the oil.

4. A viscous mineral oil fraction having in admixture therewith a minor proportion of paranitroso N-monoethyl aniline in an amount sufficient to inhibit the deleterious effects of oxidation on the oil.

5. A viscous mineral oil fraction having in admixture therewith a minor proportion of paranitroso N-monobutyl aniline in an amount sufficient to inhibit the deleterious effects of oxidation on the oil.

6. A viscous mineral oil fraction having in admixture therewith a minor proportion of paranitroso N-monoamyl aniline in an amount sufficient to inhibit the deleterious effects of oxidation on the oil.

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