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STABILIZED OIL COMPOSITION

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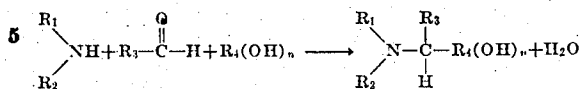
This invention has to do with hydrocarbon oil compositions and is more particularly concerned with the stabilization of viscous petroleum oils to inhibit the development of those undesirable products and properties, such as acid, sludge, discoloration, and corrosiveness toward alloy bearing metals, normally encountered under conditions of use.

As is well known to those familiar with the art, substantially all of the fractions obtained from petroleum oils and refined for their various uses are susceptible to oxidation. This susceptibility 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 unstable or catalytic constituents present in the unrefined oil and the extent to which these various unstable constituents or constituents which may act as oxidation catalysts have been removed by the refinery treatment.

The use of oxidation inhibitors for the purpose of stabilizing viscous petroleum oil fractions against the deleterious effects of oxidation 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 (one refined with large quantities of fuming sulfuric acid) against acid formation while the same inhibitor may have no appreciable effect upon acid, color, or sludge formation in a moderately refined oil (such as one refined with a moderate quantity of sulfuric acid), 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 solvent-refined oil toward metals such, for example, as the various normally corroded alloys typified by those used in cadmium-silver bearings.

The present invention is predicated upon the discovery of a class of compounds or reaction products which have the advantage of being effective oxidation-inhibitors for all types of viscous petroleum oils. The mineral oil-addition agents contemplated herein are obtained as the reaction products of substantially equimolecular proportions of a secondary amine, an aldehyde, and a mono-cyclic hydroxyaromatic (hydroxyphenyl) compound. Although I do not wish to be bound by any theory of reaction, it is thought that

the principal reaction which takes place in the formation of these oil addition agents may be represented by the following equation:



wherein R_1 and R_2 represent alkyl, aralkyl, aryl or alkaryl radicals; R_3 represents hydrogen or an alkyl, aralkyl, aryl or alkaryl radical; R_4 is a monocyclic aromatic radical; and n is a whole number from 1 to 3. The materials actually obtained as the reaction products contemplated herein are usually viscous oils probably consisting of mixtures of various compounds, and for that reason it is preferable to characterize and define these addition agents as reaction products rather than definite chemical compounds.

One general procedure for carrying out the reaction involves dissolving substantially equimolecular proportions of the secondary amine and the phenol in a suitable solvent such as alcohol and adding an equivalent amount of the aldehyde in solution with stirring at room temperature. This reaction mixture is then allowed to stand for a substantial period of time (from several hours to several days), after which it is drowned in water and the oil layer extracted as the reaction product.

Typical secondary amines which may be used in obtaining the reaction products contemplated herein are: dimethylamine; diethylamine; dibutylamine; diamylamine; methyl aniline; ethyl aniline; butyl aniline; amyl aniline; methyl naphthylamines; ethyl naphthylamines; butyl naphthylamines; diphenylamine; phenyl naphthylamines; dicyclohexylamine, etc. Typical phenols or monocyclic hydroxyaromatic compounds which may be used are: phenol; cresol; ethyl phenol; butyl phenol; amyl phenol; cyclohexyl phenol; catechol; butyl catechol; resorcinol; hydroquinone; amyl hydroquinone; pyrogallol, etc. Typical aldehydes which may be used are: formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, heptaldehyde, octylaldehyde, benzaldehyde, toluic aldehyde, phenylacetaldehyde, etc. Details in typical procedures for synthesizing the reaction products contemplated herein and test results showing their effectiveness as mineral oil-improving agents are given in the following examples.

EXAMPLE ONE

ETHYL ANILINE-PHENOL-FORMALDEHYDE PRODUCT

Twenty-four grams of ethyl aniline (0.2 mol) and 18.8 grams phenol (0.2 mol) were dissolved in 200 cc. methyl alcohol. 17 grams of a 38 per cent solution of formaldehyde (approx. 0.2) mol were added with stirring at room temperature.

The mixture was allowed to stand at room temperature for several days, and it was then poured into 1000 cc. of water. The oil separating was extracted with benzene; the benzene solution was well washed with water and then dried over CaCl_2 . By evaporating off the benzene, 36 grams of a very viscous liquid was obtained. This product was soluble in both 10 per cent NaOH and in dilute HCl , indicating the presence of both hydroxy and amine groups.

EXAMPLE TWO

DIAMYLAMINE-HYDROQUINONE-FORMALDEHYDE PRODUCT

31.4 grams diamylamine (0.2 mol) and 22 grams hydroquinone (0.2 mol) were dissolved in 150 cc. methyl alcohol. 17 grams of 38 per cent formaldehyde solution (approx. 0.2 mol) were added with stirring at room temperature. There was a slight rise in temperature. After standing over-night at room temperature, the mixture was poured into 1000 cc. of water. The oil separating was taken up in benzene, and the benzene solution was washed well with water, dried over CaCl_2 , and the benzene then evaporated off on the steam bath. This left about 29 grams of a viscous oil.

EXAMPLE THREE

ETHYL ANILINE-AMYL PHENOL-FORMALDEHYDE PRODUCT

Twenty-four grams of ethyl aniline (0.2 mol) and 32.8 grams of p-tert.-amyl phenol (0.2 mol) were dissolved in 200 cc. alcohol. Twenty-eight grams concentrated HCl (approximately 0.2 mol) were added. Seventeen grams of 38 per cent formaldehyde solution (approx. 0.2 mol) were added, and the mixture was allowed to stand at room temperature for several days. It was then poured into 1000 cc. of water containing sufficient NaOH to neutralize the HCl . The oil that separated was extracted with benzene, washed with water, dried, and the benzene then distilled off. Fifty-five grams of a fairly viscous oil remained. This was vacuum-distilled at 2 mm. pressure until the pot temperature reached 180°C ., and the residue in the flask, consisting of a viscous oil, was used as a stabilizer for petroleum oils.

Reaction products of the type obtained from the foregoing examples were blended with typical petroleum fractions resulting from various refining treatments and were subjected to typical test procedures to demonstrate their effectiveness as inhibitors of deterioration in the oil. These oils, together with the test procedures used and the results obtained, are described in the following examples.

EXAMPLE FOUR

OILS HIGHLY REFINED WITH SULFURIC ACID

A highly refined oil suitable for use in transformers 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 them for 70 hours. The acids thus formed were then determined by titrating with

alcoholic potash. Results for the oil alone and for the oil blends containing typical reaction products contemplated herein are given in Table I below in terms of neutralization numbers (N. N.), such numbers representing the acidity of the oil at the end of the test.

Table I

Agent added	Per cent used	N. N. value
None.....		25.0
Product of phenol-ethyl aniline-formaldehyde.....	.10	0.0
Product of phenol-amyl aniline-formaldehyde.....	.20	0.0
Product of para-amyl phenol-ethyl aniline-formaldehyde.....	.10	0.01
Product of hydroquinone-diamylamine-formaldehyde.....	.10	0.02
Product of para-amyl phenol-ethyl aniline-HCl-formaldehyde.....	.10	0.01
Product of phenol-ethylaniline-acetaldehyde.....	<.10	0.01
Product of phenol-phenyl alpha-naphthylamine-formaldehyde.....	<.10	0.02
Product of phenol-dicyclohexylamine-formaldehyde.....	.10	0.19
Product of phenol, ethylaniline-benzaldehyde.....	<.10	0.01

EXAMPLE FIVE

OILS MODERATELY REFINED WITH SULFURIC ACID

A mixed Mid-Continent and Coastal distillate 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. It was tested as follows:

Twenty-five cc.-samples of the oil were heated to 200°F . with 5 liters of air per hour bubbling through them. Twenty-four inches of No. 18 gauge copper wire and 1 gram of iron granules were added to each sample. Also, 2 cc. of distilled water were added each day. The samples were tested for acidity (N. N.), color, and sludge after varying periods of time. Results are given in Table II below.

Table II

Agent added	Per cent used	Time, hours	N. N.	Low. color	Sludge mg./25 cc.
None.....		72 168 240 336	.14 .99 2.5 16.0	6 25 110 400	68 17 246 1,282
Phenol-ethyl aniline-formaldehyde product.....	.10	162 498	.01 .01	1 3	29 49
Phenol-amyl aniline-formaldehyde product.....	.10	164 333 500	0 .01 2.5	1 4 55	0 77
Para-tert.-amyl phenol-ethyl aniline-formaldehyde product.....	.10	166 504	.4 3.4	9 77	6 158
Para-tert.-amyl phenol-ethyl aniline HCl-formaldehyde product.....	.10	162 499	.01 2.3	2 50	1 54
Hydroquinone-diamylamine-formaldehyde product.....	.10	162 490	0 0.7	2 17	0 6
Phenol-ethyl-aniline-acetaldehyde product.....	<.10	498 1002	0.6 4.4	11 110	10 242
Phenol-ethyl aniline-benzaldehyde product.....	<.10	162 503	.01 4.7	3 70	6 122

EXAMPLE SIX

OILS REFINED BY MEANS OF SOLVENTS

A distillate from a Rodessa crude was 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 sec. at 100° F. This oil was tested by the same method described in Example Five above. The results obtained are set forth in Table III below.

Table III

Agent added	Percent used	Time, hours	N. N.	Low. color	Sludge, mg./25 cc.
None		92 165	.91 20.3	9 320	33 251
Phenol-ethyl aniline-formaldehyde product	.10	162 498	0 .01	1 1	84 23
Phenol-diamylamine-formaldehyde product	.10	164 501	0 0	1 1	2 70
Phenol-amyl aniline-formaldehyde product	.10	164 500	0 .01	1 1	4
Para-tert.-amyl phenol-ethyl aniline formaldehyde product	.10	504 1007	.01 1.6	6 10	8 17
Para-tert.-amyl phenol-ethyl aniline HCl-formaldehyde product	.10	499 931	.07 .13	2 5	3 14
Hydroquinone-diamylamine-formaldehyde product	.10	162 499 835	0 .01 4.3	1 1 13	9 10 130
Phenol-ethyl aniline-acetaldehyde product	<.10	186 498	.01 .11	1 2	13
Phenol-ethyl aniline-benzaldehyde product	<.10	162	.02	2	18
Phenol-ethyl aniline-hexaldehyde product	<.10	164	2.8	3	14

EXAMPLE SEVEN

CORROSION TEST

Motor oils, especially those refined by certain solvent-extraction methods, tend to oxidize when submitted to high temperatures and to form products that are corrosive to metal bearings. This corrosive action may be quite severe with certain bearings, such as those having the corrosion-susceptibility of cadmium-silver alloys; and may cause their failure within a comparatively short time. The following test was used to determine the corrosive action of a motor oil on an automobile connecting rod bearing.

The oil used consisted of Pennsylvania neutral and residuum stocks separately refined by means of chlorex and then blended to give an S. A. E. 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 results obtained in this test are set forth in Table IV below.

Table IV

Agent added	Per cent used	Mg. loss in weight	
		Inhibited	Uninhibited
Phenol-ethyl aniline-formaldehyde product	<.25	0	33
Phenol-amyl aniline-formaldehyde product	.25	0	33
Para-tert.-amyl phenol-ethyl aniline-formaldehyde product	.25	1	42
Para-tert.-amyl phenol-ethyl aniline HCl-formaldehyde product	.25	0	34
Para-tert.-amyl phenol-amyl aniline-formaldehyde product	.25	0	33
Hydroquinone - diamylamine - formaldehyde product	.25	0	30
Phenol-ethyl aniline-acetaldehyde product	<.25	0	26
Phenol-ethyl aniline-benzaldehyde product	<.10	0	36
Phenol-ethyl aniline-hexaldehyde product	<.25	0	32

From the foregoing test results it will be observed that the reaction products contemplated herein are effective stabilizing agents for viscous petroleum oil fractions, irrespective of the refining treatment which the oil has received. The quantity of reaction product used to inhibit the deleterious effects of oxidation in the oil may be varied depending upon the character of the oil and the severity of the conditions to which it is exposed, but in general it appears that the desired results may be obtained with an amount ranging from 0.01 per cent to 1.0 per cent.

It is to be understood that while I have herein described in detail certain typical reaction procedures and several specific reactants which may be employed in synthesizing the reaction products contemplated herein, the invention is not confined to these specific procedural details or reactants but includes within its scope such changes and modifications as fairly come within the spirit of the appended claims.

I claim:

1. A viscous petroleum oil fraction having in admixture therewith a minor proportion of the reaction product obtained by reacting substantially equi-molecular proportions of a secondary amine, an aldehyde, and a monocyclic hydroxy-aromatic compound, the said reaction product possessing antioxidant properties and being present in an amount sufficient to inhibit the deleterious effects of oxidation on the oil.

2. A viscous petroleum oil fraction having in admixture therewith a minor proportion of the reaction product obtained by reacting substantially equi-molecular proportions of: a compound having the general formula



wherein R_1 and R_2 are selected from the group consisting of alkyl, aralkyl, aryl, and alkaryl radicals; a compound having the general formula



wherein R_3 is selected from the group consisting of hydrogen alkyl, aralkyl, aryl and alkaryl radicals; and a compound having the general formula $R_4(OH)_n$, wherein R_4 is a monocyclic aromatic radical and n is a whole number from 1 to 3; said reaction product possessing antioxidant

properties and being present in an amount sufficient to inhibit the deleterious effects of oxidation in the oil.

3. A viscous petroleum oil fraction having in admixture therewith a minor proportion of the reaction product obtained by reacting substantially equi-molecular proportions of methyl aniline, phenol and formaldehyde, the said reaction product being present in an amount sufficient to inhibit the deleterious effects of oxidation in the oil.

4. A viscous petroleum oil fraction having in admixture therewith a minor proportion of the reaction product obtained by reacting substantially equi-molecular proportions of diamylamine, hydroquinone and formaldehyde, the said reaction product being present in an amount sufficient to inhibit the deleterious effects of oxidation in the oil.

5. A viscous petroleum oil fraction having in admixture therewith a minor proportion of the reaction product obtained by reacting substantially equi-molecular proportion of ethyl aniline, p-tert.-amyl phenol, and formaldehyde, the said reaction product being present in an amount sufficient to inhibit the deleterious effects of oxidation in the oil.

6. A viscous petroleum oil fraction having in admixture therewith a minor proportion, from about 0.01 per cent to about 1.00 per cent, of the reaction product obtained by reacting substantially equi-molecular proportions of a secondary amine, an aldehyde, and a monocyclic hydroxyaromatic reaction, said reaction product possessing antioxidant properties.

7. A method of lubricating bearing surfaces one of which has the corrosion-susceptibility of a

cadmium-silver alloy, which comprises maintaining between the bearing surfaces a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid alloy, and maintaining the effectiveness of the lubricating oil by incorporating therein a small proportion, sufficient to substantially retard corrosion of the reaction product obtained by reacting substantially equi-molecular proportions of a secondary amine, an aldehyde, and a monocyclic hydroxyaromatic compound, said reaction product possessing anti-oxidant properties.

8. A viscous petroleum oil fraction having in admixture therewith a minor proportion of the reaction product obtained by reacting substantially equi-molecular proportions of: a phenol selected from the group consisting of phenol, para-tertiary-amyl phenol, and hydroquinone; a secondary amine selected from the group consisting of ethyl aniline, amyl aniline, and diamyl amine; and an aldehyde selected from the group consisting of formaldehyde and acetaldehyde, the said reaction product being present in an amount sufficient to inhibit the deleterious effects of oxidation in the oil.

9. A viscous petroleum oil fraction having in admixture therewith a minor proportion of the reaction product obtained by reacting substantially equimolecular proportions of a secondary amine, formaldehyde, and a monocyclic hydroxy aromatic compound, the said reaction product possessing anti-oxidant properties and being present in an amount sufficient to inhibit the deleterious effects of oxidation on the oil.

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