Patented Dec. 2, 1941

2,264,893

UNITED STATES PATENT OFFICE

2,264,893

STABILIZED PETROLEUM PRODUCT

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No Drawing. Application June 29, 1938, Serial No. 216,582

16 Claims. (Cl. 252—46)

This invention relates to improvements in stable mineral oils and more particularly to improvements in stable petroleum oils.

Many petroleum products, such as lubricating oils, electric insulating oils, turbine oils, spindle oils, medicinal oils and the like are refined by drastic chemical treatment and/or solvent extraction in order to meet certain specifications. It has been observed that such drastic treatment seriously impairs certain properties of the oils, and most seriously the property of resisting oxidation. Such drastically treated oils are normally susceptible to autocatalytic oxidation with the attendant sludge formation, high acidity and/or possible peroxide development. Oils which are readily oxidized develop bad odors, high acidity and large amounts of oil insoluble oxidation products which result in poor demulsifying and insulating properties and render them unsuitable for their intended use.

Heretofore, the oxidation of oils of this type has been inhibited to some extent by the addition thereto of from about 0.001% to about 0.25% of certain antioxidants such as the polyhydric phenols and the alkyl derivatives thereof, for example catechol, tertiary butyl catechol, cresol, pyrogallol, hydroquinol, and the like, and the hydroxy condensed poly ring compounds and their alkyl derivatives, such as beta-naphthol, octyl beta-naphthol, amyl beta-naphthol, lauryl beta-naphthol, alpha-naphthol, cetyl alpha-naphthol, butyl alpha-naphthol, amyl alpha-naphthol and other alkyl derivatives of alpha- and beta-naphthols. Other inhibitors such as phenyl alpha-naphthylamine, diphenylamine and butyl para aminophenol have been used. Although these antioxidants are effective to a degree, substantially complete inhibition is not obtained in many cases. For example, in some cases the inhibitor will retard sludging at elevated temperatures but will have little if any effect in inhibiting acidity formation.

It is the primary object of this invention to provide oils which are not susceptible to high acidity development, are less susceptible to sludging than prior art products, and which do not have a high oxygen absorption. It is another object of this invention to provide petroleum oils which have increased oxidation stability, which do not develop high acidity during service, and which retain their good demulsibility and insulating properties. It is still another object of the present invention to provide a method of increasing the oxidation stability of petroleum oils.

We have discovered that the foregoing objects can be attained by adding to highly refined petroleum oils, alone or in combination with the hereinbefore mentioned antioxidants, small amounts, preferably from about 0.005% to about 5%, of high sulfur petroleum fractions. For the most effective results fractions from sulfur bearing crude oils should be employed for this purpose, such as, for example, Winkler crude oil or other crude oils of the Winkler type. The distillates from Winkler crude oil contain from about 0.5% to about 2.5% sulfur, while the residuums contain higher percentages of sulfur. A particular fraction which has been found effective is a Winkler crude oil distillate having a gravity of from about 27.0° A. P. I. to about 27.4° A. P. I., a Saybolt viscosity at 100° F. of from about 50 seconds to about 80 seconds, and a sulfur content of from about 0.75% to about 2.0%. Similarly, the above type of distillate which has been treated and percolated through fuller's earth may be used.

We may also use the residue obtained in the distillation of high sulfur-containing light petroleum distillates, such as naphthas. An example of such a residue is that obtained by distilling a doctor sweetened Winkler stove distillate, which has a distillation range of from about 120° F. to about 400° F., to obtain a residue which is from about 1.0% to about 2.0% of the total charge to the still. This residue has a sulfur content of from about 0.5% to about 10.0%.

The effectiveness of the fractions from high sulfur crude oils in inhibiting the oxidation of petroleum oils normally susceptible to oxidation is well illustrated by the following examples which are intended only to exemplify and not limit the scope of the invention:

Example I.—The following samples

A. Control (a highly refined transformer oil)
B. Control+0.05% amyl beta-naphthol
C. Control+0.5% high sulfur distillate (1.5–2.0% sulfur)
D. Control+0.05% amyl beta-naphthol+0.5% high sulfur distillate (Winkler)

were heated at a temperature of about 284° F. while exposed to the atmosphere, and at stated periods samples withdrawn and tested for sludge, color, and acidity. The acidity is reported in milligrams of KOH per cubic centimeter of oil.

Sample	Time before sludge formed	Color (N. P. A.) after—			Acidity (mg. KOH)/cc. oil after—		
		66 hrs.	90 hrs.	114 hrs.	66 hrs.	90 hrs.	114 hrs.
	Hours						
A	*66	4	4½–5	5–6	.54	.94	1.24
B	*66	4	4½	5–6	.49	.55	.94
C	*66	3½	4	4½	.08	.10	.11
D	114	3½	4	4½	.06	.10	.09

*Less than 66 hrs.

It will be noted that the base oil and the base oil containing only amyl beta-naphthol devel-

oped sludge in a short period of time and acidity development was pronounced. The base oil containing Winkler distillate did not develop a high acidity but is inferior in that sludge development occurred in a short period of time. The oils containing both inhibitors were more stable with respect to acidity development and sludge formation.

Example II.—One method of obtaining an index of the oxidation stability of an oil is by the so-called Snyder life test which is determined by maintaining about 500 cc. of the oil at a temperature of about 120° C., and once every 24 hours withdrawing a 10 cc. sample, cooling and centrifuging the same for the purpose of determining when sludge first appears. The "life" of the oil is the number of days the oil can be maintained at 120° C. before visible sludge is formed. This test is fully described in the A. S. T. M. Proceedings, volume 24, part I, p. 638 (1924).

Submitting the following samples

A. Control (highly refined transformer oil)
B. Control+0.05% amyl beta-naphthol
C. Control+0.25% high sulfur distillate (Winkler)
D. Control+0.025% amyl beta-naphthol+0.25% high sulfur distillate

to the Snyder life test, the following results were obtained:

Oil	Snyder life test
	Days
A	3
B	5
C	7
D	24

The above data show the marked increase in the sludge stability of a highly treated transformer oil, normally susceptible to sludge formation, upon the addition of a small amount of a light sulfur distillate, alone and in combination with another antioxidant, amyl beta-naphthol.

Example III.—The effectiveness of small amounts of high sulfur naphtha bottoms in inhibiting oxidation is shown by the following data. The high sulfur naphtha bottoms were obtained by distilling a sweetened Winkler stove distillate which originally contained 0.09% mercaptan sulfur, to a residue of about 1.5% of the charge to the still. The maximum still temperature was 300° F. The effectiveness of the high sulfur sweetened naphtha bottoms, alone, and in combination with other inhibitors is shown by the following tests in which the following samples were tested:

A. Control (highly treated transformer oil)
B. Control+0.05% amyl beta-naphthol
C. Control+0.02% high sulfur naphtha bottoms
D. Control+0.05% amyl beta-naphthol+0.02% high sulfur naphtha bottoms.

These samples were then submitted to the Snyder life test with the following results:

Oil	Snyder life test
	Days
A	3
B	5
C	7
D	22

The acidities of the samples were also determined during the test. The following results were obtained:

Oil	Acidity mg. KOH / cc. oil	Days
A	0.31	3
B	0.72	7
C	0.09	7
D	0.06	7
	0.12	21

The Snyder life test data show the beneficial effect of small amounts of high sulfur naphtha bottoms in inhibiting the oxidation of highly refined oils, and the still marked inhibiting effect thereof when used in combination with other inhibitors such as amyl beta-naphthol.

The high sulfur distillate used as oxidation inhibitors should preferably be only lightly acid treated since we have found that the inhibiting effect of the distillates is greater with distillates which have not been subjected to a drastic acid treatment. Using high sulfur distillates which had been treated respectively with 1.0 pound of 104½% acid per gallon of oil, and with 0.25 pound of 93% acid per gallon of oil, the following samples were prepared:

A. Control (highly refined transformer oil)
B. Control+0.05% amyl beta-naphthol
C. Control+0.05% amyl beta-naphthol+2% high sulfur distillate treated with 1 lb./gal. of 104½% sulfuric acid
D. Control+0.05% amyl beta-naphthol+2% high sulfur distillate treated with ¼ lb./gal. of 93% sulfuric acid

and subjected to a temperature of about 284° F. while exposed to the atmosphere. At stated intervals samples were withdrawn and tested. The results are tabulated below.

Sample	Time before sludge formed	Color (N. P. A.) after— 66 hrs.	90 hrs.	114 hrs.	Acidity (mg. KOH)/cc. oil after— 66 hrs.	90 hrs.	114 hrs.	138 hrs.
	Hrs.							
A	*66	4	4½-5	5-6	.56	.94	1.24	------
B	*66	4	4½	5-6	.49	.55	.94	------
C	114	4	4½	4½+	.08	.13	.12	------
D	138	3-3½	3½-4	4½-	.07	------	------	.10

*Less than 66 hrs.

It will be observed that the distillate treated with 0.25 pound of 93% acid per gallon of distillate is more effective than the distillate treated with one pound of 104½% acid.

The distillates and naphtha bottoms from high sulfur crudes alone may be effectively employed as oxidation inhibitors, although we prefer to use them in combination with the hereinbefore mentioned inhibitors. While we have described our invention by the way of certain specific embodiments thereof, we do not limit the scope of the invention thereto, except insofar as the same is defined by the appended claims.

We claim:

1. The method of inhibiting the oxidation of a highly refined viscous hydrocarbon oil which comprises adding thereto, in combination, a high sulfur-containing fraction from a high sulfur crude oil and an organic compound selected from the class consisting of polyhydric phenols, alkyl polyhydric phenols, hydroxy condensed poly ring

compounds and alkyl hydroxy condensed poly ring compounds, said addition agents being added in small but sufficient quantities to inhibit the oxidation of said highly refined viscous hydrocarbon oil.

2. The method of inhibiting the oxidation of a highly refined viscous hydrocarbon oil which comprises adding thereto, in combination, a high sulfur-containing petroleum distillate obtained from a high sulfur crude oil and an organic compound selected from the class consisting of beta-naphthol, octyl beta-naphthol, amyl beta-naphthol, alpha-naphthol, cetyl alpha-naphthol, catechol, butyl catechol and cresol, said addition agents being added in small but sufficient quantities to adequately inhibit the oxidation of said highly refined viscous hydrocarbon oil.

3. The method of inhibiting the oxidation of a highly refined viscous hydrocarbon oil which comprises adding thereto, in combination, the residue obtained by the distillation of a high sulfur-containing sweetened distillate within the naphtha distillation range, and an organic compound selected from the class consisting of beta-naphthol, octyl beta-naphthol, amyl beta-naphthol, alpha-naphthol, cetyl alpha-naphthol, catechol, butyl catechol and cresol, said addition agents being added in small but sufficient quantities to adequately inhibit the oxidation of said highly refined viscous hydrocarbon oil.

4. The method of retarding the oxidation of a highly refined viscous hydrocarbon oil which comprises adding thereto, in combination, from about 0.5% to about 5% of a high sulfur distillate from a sulfur-containing crude oil and from about 0.001% to about 0.25% of amyl beta-naphthol.

5. The method of retarding the oxidation of a highly refined viscous hydrocarbon oil as defined in claim 3 in which the high sulfur distillate is a transformer oil distillate containing from about 0.5% to about 2.5% sulfur obtained from crude oils of the Winkler type.

6. The method of retarding oxidation of a highly refined viscous hydrocarbon oil which comprises adding thereto, in combination, from about 0.01% to about 2% of a high sulfur naphtha bottom and from about 0.001% to about 0.25% of amyl beta-naphthol.

7. A method of retarding the oxidation of a highly refined viscous hydrocarbon oil as defined in claim 6 in which the high sulfur naphtha bottoms is the residue obtained by distilling a sweetened Winkler stove distillate to about a 1.5 bottom.

8. A highly refined viscous hydrocarbon oil containing, in combination, a high sulfur-containing fraction of a high sulfur crude oil and an organic compound selected from the class consisting of polyhydric phenols, alkyl polyhydric phenols, hydroxy condensed poly ring compounds and alkyl hydroxy condensed poly ring compounds in small but sufficient quantities to inhibit the oxidation of said highly refined viscous hydrocarbon oil.

9. A highly refined viscous hydrocarbon oil containing, in combination, small proportions of a high sulfur fraction of a high sulfur crude oil and an organic compound selected from the class consisting of alpha-naphthols, beta-naphthols, catecols and cresols.

10. A highly refined viscous hydrocarbon oil containing from about 0.01% to about 5% of a petroleum distillate containing from about 0.5% to about 2.5% sulfur and from about 0.001% to about 0.25% amyl beta-naphthol.

11. An oxidation resistant highly refined viscous hydrocarbon oil containing, in combination, in small but oxidation inhibiting proportions a high sulfur containing naphtha residue and amyl beta-naphthol.

12. An oxidation resistant transformer oil containing, in combination, from about 0.01% to about 5% of a transformer oil distillate containing from about 1.5% to about 2% sulfur and from about 0.001% to about 0.25% amyl beta-naphthol.

13. A transformer oil highly resistant to oxidation containing from about 0.01% to about 2% of a high sulfur naphtha bottom and from about 0.001% to about 0.25% amyl beta-naphthol.

14. The method of inhibiting the oxidation of a highly refined viscous hydrocarbon oil which comprises adding thereto, in combination, the residue obtained by the distillation of a high sulfur-containing sweetened distillate within the naphtha distillation range, and an organic compound selected from the class consisting of polyhydric phenols, alkyl polyhydric phenols, hydroxy condensed polyring compounds and alkyl hydroxy condensed polyring compounds, said addition agents being added in small but sufficient quantities to inhibit the oxidation of said highly refined viscous hydrocarbon oil.

15. A highly refined viscous hydrocarbon oil containing, in combination, the residue obtained by the distillation of a high sulfur-containing sweetened distillate within the naphtha distillation range, and an organic compound selected from the class consisting of polyhydric phenols, alkyl polyhydric phenols, hydroxy condensed polyring compounds and alkyl hydroxy condensed polyring compounds, said addition agents being added in small but sufficient quantities to inhibit the oxidation of said highly refined viscous hydrocarbon oil.

16. A highly refined viscous hydrocarbon oil containing, in combination, the residue obtained by the distillation of a high sulfur-containing sweetened distillate within the naphtha distillation range, and an organic compound selected from the class consisting of alpha naphthols, beta naphthols, catechols and cresols, said addition agents being added in small but sufficient quantities to inhibit the oxidation of said highly refined viscous hydrocarbon oil.

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