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STABILIZED PETROLEUM OILS

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This invention relates to the preparation of an improved oxidation inhibitor for petroleum oils, and to stabilized oil compositions containing a minor proportion of the inhibitor.

Petroleum oils, especially petroleum oils that have been highly refined by chemical means, tend to absorb and react with oxygen. This reaction is accelerated by the elevated temperatures and metal contact often employed with the refined oil. For example, treatment of a light lubricating oil with sulfuric acid, hydrofluoric acid, aluminum chloride, furfural, sulfur dioxide or the like, yields a highly refined oil having desirable properties, but which readily reacts with oxygen to form deleterious materials.

Various materials have heretofore been described as additives for petroleum oils, one or several properties of the oil being enhanced by relatively small quantities thereof. For example, the use of relatively high molecular weight fractions from petroleum operations, such as the residue from thermal cracking, as an additive for lubricating oils has been taught. Prior to incorporation in the oil, the additive may be subjected to a refining operation, such as hydrogenation or treating with an acid. Generally the purpose of such additives is to improve the color and bloom of the lubricating oil. While such additives have been described as successful in improving the color and bloom of lubricating oil, they have not been successful in providing an oxidation inhibitor which is effective in increasing the resistance of unstable oils toward oxidation. In some instances a multiplicity of additives have been employed in an attempt to prepare a stable oil.

An object of the invention is to provide a novel oil additive effective for increasing the resistance of an oleaginous material toward oxidation. Another object is to provide processes for the preparation of the oil additive of the invention. A further object is to provide a stable oil composition comprising an oil unstable toward oxidation and a stabilizing quantity of a novel oxidation inhibitor.

It has now been found that by subjecting a hydrocarbon fraction from a catalytically cracked petroleum oil, the components of which have molecular weights within a specific range, to certain treating steps, as hereinafter described, an oil additive remarkably effective, when incorporated in minor amounts in an unstable oil, for increasing the resistance of the oil to oxidation is obtained. While it is not desired to be limited by theoretical considerations, it is believed the effective constituents of the additive are polynuclear aromatic hydrocarbons having molecular weights within a rather narrow range, and that the specific treating steps employed in the present invention remove materials that exert a deleterious effect on the final oil composition.

Good results are obtained, in accordance with the invention, when oleaginous materials that are susceptible to oxidation are employed as the preponderant component of the compositions of the invention. Oils that have been

subjected to refining by chemical means, such as by acid treatment with, for example, sulfuric acid, or solvent extraction with, for example, furfural, are usually susceptible to oxidation and give excellent results in the present invention. It is preferred to employ oils of petroleum origin that have been refined by chemical means, and good results are obtained therewith, but synthetic oleaginous materials that are susceptible to oxidation, such as polyethylene oxide, also give good results.

As more fully described hereinafter, it is essential to the success of the invention that the additive be prepared from a catalytically cracked oil. From example, a fraction of comparable molecular weight range from a thermally cracked oil exhibits deleterious, rather than beneficial, effects when incorporated in an unstable oil. However, a thermally cracked or otherwise treated oil can be used so long as catalytic cracking is the last operation prior to preparation of the additive. By "catalytically cracked oil," and terms of similar import, as used herein, is meant an oil that has been contacted with a cracking catalyst under cracking conditions of temperature, pressure and space rate. Conventional cracking catalysts such as silica-alumina, silica-alumina-zirconia, silica-magnesia, activated clay, and the like can be employed. The cracking conditions can be those known to give good results in cracking operations, such as temperatures above about 600° F., pressures of from atmospheric to 500 p. s. i. g. and space rates of from 0.1 to 10 volumes of oil per volume of catalyst per hour.

It is also essential that the porition of the cracked oil employed, hereinafter defined, be subjected to specific treating steps. If the treating be omitted, an additive effective to an extent toward oxidation inhibition is obtained, but it is inoperative in the invention because of color deterioration of the oil composition and of the additive itself when stored for an appreciable time. It is further essential that the components of the fraction from the catalytically cracked oil have molecular weights within the range of from 200 to 400. This fraction may boil within different ranges depending on the treating steps as hereinafter described.

To illustrate the invention, a hydrocarbon oil is catalytically cracked by contact with a cracking catalyst under cracking conditions. The low boiling fractions are removed from the cracked oil and a residual fraction, boiling at least above 350° F., is obtained. This residual fraction contains a substantial quantity of polynuclear aromatic hydrocarbons which are believed to be the desirable components of the inhibitors of the invention. It is possible to employ different treating steps in converting the residual fraction into the additive of the invention, but it is essential, in the different steps, to observe certain critical limitations as described hereinafter.

In an embodiment of the invention, the residual fraction from catalytic cracking is agitated with from 0.5 to 5 pounds of concentrated (above 65° Bé.) sulfuric acid per barrel. After agitation, the acid is separated from the reaction mixture. Preferably acidic components of the oil are neutralized with a base, such as with an aqueous solution of sodium hydroxide, potassium hydroxide, sodium carbonate, or the like, the relatively strong bases such as those of the alkali metals being preferred. The residual fraction is then distilled to separate a fraction, the components of which have a molecular weight within the range of from about 200 to 400. This latter fraction is the inhibitor of the invention. It is sometimes desirable to use a preliminary distillation to separate components within the stated molecular weight range prior to

acid treatment, but the distillation after acid treatment should also be employed to separate high boiling materials formed in the acid treatment. To illustrate the importance of using a quantity of sulfuric acid within the stated range, it was found that using up to 5 pounds of 66° Bé. sulfuric acid per barrel of additive gave products that exhibited good results in inhibiting oil oxidation, whereas with larger amounts, poor results were obtained. For example, with 15 pounds of 66° Bé. sulfuric acid per barrel, additives which increased the rate of oxidation of oils compounded therewith were obtained.

As described above, it is essential that the residual fraction be from an operation involving catalytic cracking, that the quantity of concentrated sulfuric acid employed be within the stated ranges, and that the components of the additives have molecular weights within the stated range.

It is sometimes preferable to concentrate the aromatic constituents of the residual fraction from catalytic cracking prior to treatment with sulfuric acid. This can be accomplished by contacting the fraction boiling above about 350° F. with furfural, sulfur dioxide, silica gel, nitrobenzene, phenols or other extractant selective for separating aromatic hydrocarbons from non-aromatic hydrocarbons. The polynuclear aromatic hydrocarbons are then separated from the extractant and treated as above described. An advantage of concentrating the polynuclear aromatic constituents is that wax, which otherwise would be present in the additive when using a wax-containing crude oil, is removed. Other means of removing wax can be employed where necessary or desirable. When using stock which has been thermally cracked prior to the catalytic cracking, wax does not appear in the bottom fraction used to prepare the additive of the invention.

Another embodiment of the invention involves the distillation of the residual fraction from a catalytic cracked stock in the presence of a strong base, such as an alkali metal hydroxide or alkaline earth metal hydroxide, sodium hydroxide, potassium hydroxide or calcium hydroxide being preferred. It is of advantage in this embodiment to employ a polynuclear aromatic concentrate as above described. It is also of advantage during this distillation to separate the desired components having molecular weights within the range of 200 to 400. To illustrate this embodiment, an aromatic concentrate prepared by separating aromatic constituents from the residual fraction of a catalytically cracked oil is distilled while admixed with from 1% to 20% by weight, and preferably from 2% to 5% by weight, of about 50° Bé. sodium hydroxide. The concentration of caustic does not appear critical, and other concentrations can be employed, but in general the concentration will be above about 30° Bé. A fraction containing hydrocarbons having molecular weights within the range of from 200 to 400 is separated and is the inhibitor of the invention.

A stabilizing quantity of the oxidation inhibitor prepared as above described, which can vary from 0.5 to 5% by weight depending on the oil being stabilized, is incorporated in the oil. Smaller amounts do not achieve the desired results and higher quantities may cause the compostion to exhibit an increased tendency for oxidation, as shown by the examples described hereinafter. It is preferred to employ from 0.8 to 3% by weight of the inhibitor, since optimum results are obtained within these limitations. It is also preferred to employ the additive of the invention as the sole oxidation inhibitor in oil compositions since, as has been found, combining other materials heretofore described as oxidation inhibitors therewith does not enhance the oxidation stability of the oil to an extent greater than observed with the additive of the invention used above.

A still further embodiment of the invention is to prepare the composition of the invention by incorporating

in the oil to be stabilized an appropriate quantity, as above defined, of the residual fraction from catalytic cracking having a molecular weight within the range of from about 200 to 400. This compostion is then treated with from 0.1 to 4 pounds per barrel of concentrated sulfuric acid, say above about 65° Bé. After agitation, the phases are allowed to separate and the acid phase removed. The treated hydrocarbon layer is then treated with from about 4 to 25 pounds of clay per barrel. On separation of the clay, the finished product is obtained. It has been found, however, that clay contacting can be used in the invention only when the additive is incorporated with the oil to be stabilized prior to the acid contacting.

The following examples illustrate the several embodiments of the invention. In the examples, interfacial tension, between water and oil, and changes in this interfacial tension, are used to measure oxidation of the oil, ASTM D971–50 being used for this measurement. The oxidation procedure, unless otherwise designated in the examples, was to pass air for 96 hours at the rate of 7 ml. of air (measured at ambient temperature and pressure) per ml. of oil per minute through a 70 ml. oil sample maintained at 200° F. in contact with 25 cm. of iron wire (B. & S. No. 19) and 25 cm. of copper wire (B. & S. No. 18). The actual tensiometer readings, as determined by ASTM D971–50, are directly comparable for oils of similar density, such as those of the following examples, and hence the values in the examples given under the columns entitled "Interfacial tension after oxidation," are the tensiometer readings after oxidation, and usually these values are for a blend of oil plus additive, as also indicated in the column title, unless otherwise indicated in the examples. The values given in the columns entitled "Difference in interfacial tensions" are the differences between the tensiometer reading obtained with oil plus additive and the oil alone, both measured after oxidation for 96 hours at 200° F.

EXAMPLE 1

As above stated, it is essential that the residual fraction from which the oxidation inhibitor of the invention is prepared be from a catalytically cracked oil. This is shown by the present example. Four catalytically cracked and one thermally cracked tower bottoms (all boiling above 350° F.) were examined for activity toward oxidation inhibition. Sources A through D were from catalytic cracking as follows: Source A, from cracking catalytic gas oil over a fixed bed of commercial silica-alumina cracking catalyst; source B, from cracking fresh light gas oil in a moving bed of commercial silica-alumina cracking catalyst; source C, from cracking reduced crude over a fixed bed of commercial silica-alumina cracking catalyst; source D, from topping and cracking of crude petroleum over a fixed bed of commercial silica-alumina cracking catalyst. Source E was from the thermal cracking of fresh naphtha.

The boiling ranges of the additive fractions employed and data obtained are shown in the following Table I. In each instance 2.5% by weight of the additive from the indicated source was employed. The oil employed was a transformer oil prepared from a hydrocarbon fraction boiling from about 530° F. to 750° F. by contacting with sulfuric acid and subsequently with clay.

As above stated, the values in the column "Difference in interfacial tensions" were obtained by substracting the interfacial tension of the oil without the additive, determined after oxidation, from the interfacial tenson of the oil with the additive, i. e., of the blend, also determined after oxidation.

Table I

Source	Boiling range of additive, °F.	Interfacial tension of blend after oxidation	Difference in interfacial tensions
A	435–745	27.5	15.5
B	420–760	29.9	17.9
C	475–780	23.7	11.7
D	360–735	38.4	26.4
E	500–760	2.5	−9.5

In this example, the additive components had molecular weights within the range of from 200 to 400. It will be noted that the additive from source E exerted a deleterious effect, as shown by the negative value obtained for the change in surface tension, which shows that the oil plus additive was oxidized to an extent greater than the oil above. Although stabilization toward oxidation was obtained with the additives from sources A through D, the color of the compositions deteriorated to a substantial extent. This color deterioration is overcome by subjecting the additive to specific treating steps as described above and as shown in following examples. The treating steps also enhance the stabilizing value of the additives.

EXAMPLE 2

In order to demonstrate the range of effective materials of the residual fractions from catalytic cracking, fractions from source A and source B of Example 1 were separated into narrow boiling range fractions, and the narrow fractions tested for oxidation inhibition. Data and results obtained are shown in following Table II:

Table II

	Boiling Range (° F.)	Cut of Distillate (Percent)	Interfacial tension of blend after oxidation	Difference in Interfacial Tensions
Source A	525–570	10–20	11.2	−0.7
	570–585	20–30	19.8	7.9
	585–645	30–40	20.8	8.9
	645–655	40–50	21.5	9.6
	655–690	50–60	22.5	10.6
	690–710	60–70	35.4	23.4
	710–750	70–80	26.7	14.8
	750–820	80–90	10.1	−1.8
Source B	655–690	35–56	22.8	10.8
	690–710	56–62	32.6	20.6
	710–750	62–77	31.1	19.1

With the petroleum oil employed, the fractions boiling from 570 to about 750 had molecular weights within the range of from about 200 to 400, and gave especially good results in inhibiting oxidation. For example, the molecular weights of the 655–690° F. fraction and the 710–750° F. fraction, both of source A, were 275 and 320, respectively. These values are within the preferred molecular weight range of from 250 to 350, and good oxidation inhibition was obtained therewith. The molecular weight of the 585–645° F. fraction was about 210, and the results indicate this to be just above the lower permissible limit. When using an aromatic extract, the components having molecular weights within the stated ranges may boil within somewhat different temperature limits than those shown, probably due to an azeotropic effect.

In the foregoing data, the same difficulty encountered in Example 1 with color formation was observed. This is overcome as shown in the following examples.

EXAMPLE 3

A residual fraction from catalytic cracking was divided into 2 samples. Sample 1 was distilled to separate the fraction shown below in Table III. Sample 2 was distilled from 1% by weight of 50° Bé. sodium hydroxide. Various quantities of the additives were added to a transformer oil that had been treated with sulfuric acid and subsequently with clay. NPA color of the blends are shown both before oxidation (initial) and after oxidation (aged). Data and results obtained are shown in following Table III:

Table III

Sample	Boiling Range (°F.)	Quantity of Additive (Wt. Percent)	NPA color		Interfacial tension of blend after oxidation	Difference in Interfacial Tensions
			Initial	Aged		
1	585–870	0.5	3½	8	18.3	6.3
		1.0			20.3	8.3
		2.5			23.0	11.0
2	560–930	0.5	3	5−	19.0	7.0
		1.0			35.2	23.2
		2.5			31.7	19.7

These data show the improvement in color obtained by distilling from caustic the residual fraction from catalytic cracking, and also that the so-treated fraction is a more effective inhibitor toward oxidation than the comparable fraction from simple distillation, i. e., distillation without caustic.

EXAMPLE 4

This example demonstrates the remarkable effective resistance toward oxidation exhibited by the oil compositions of the invention. A residual fraction from catalytic cracking over a commercial silica-alumina catalyst was distilled from 2% by weight of 50° Bé. sodium hydroxide. Components of the resulting product had a molecular weight of from 250 to 350. Various amounts of the additive were incorporated in a transformer oil which had been treated with sulfuric acid and subsequently with clay. These compositions were oxidized according to ASTM–943, the procedure being modified by using 2% water, instead of 20% water, and by humidifying the oxygen, by bubbling through water, prior to passing it through the oil being tested. In the test, the oil composition is considered to be spent when the interfacial tension decreases to 15 dynes/cm. The following Table IV shows the interfacial tensions after various times using oil compositions having the indicated amount of additive. Without any additive, the oil becomes spent within about 65 hours.

Table IV

Time (hours)	Interfacial tension (dynes/cm.)		
	0.5% additive	1% additive	2% additive
100	14	17.5	26.0
200	----------	16.5	22.5
300	----------	15.0	19.0
400	----------	13.5	15.0

These data illustrate the remarkably long life of the oil compositions of the invention. The color of the compositions was good throughout the test, NPA colors of between 4 and 5 being observed.

EXAMPLE 5

An oil boiling in the lubricating oil range was extracted with furfural and subsequently treated with clay. Samples of the resulting oil, the oil with 1% additive, and with 2% additive were oxidized by air at 240° F. in the presence of iron and copper. Interfacial tension values were obtained as a function of time. The following Table V shows the data obtained. The additive employed was the same as used in Example IV.

Table V

Time (hours)	Interfacial tension		
	No additive	1% additive	2% additive
5	12	34	35
10	2	33	35
15		16	32
20			30
30			26

The remarkable resistance toward oxidation of oils containing small amounts of the additive of the invention is shown by these data. The colors of the oxidized mixtures were at all times superior to the color of the oxidized oil without the additive.

EXAMPLE 6

In order to demonstrate the effect of using various concentrations of the additive in oil compositions, varying quantities thereof were added to a transformer oil. The additive was prepared from the residue of an oil that had been subjected to thermal cracking and subsequently to catalytic cracking over a commercial silica-alumina cracking catalyst by treating with 3 pounds of 66° Bé. sulfuric acid per barrel of the fraction, neutralizing with aqueous sodium hydroxide, and distilling components having molecular weights within the range of from 200 to 400. Varying quantities of this additive were added to portions of the transformer oil described in Example 1. Following Table VI shows the data and results obtained:

Table VI

Concentration of additive (Wt. Percent)	Interfacial Tension of blend after oxidation	Difference in Interfacial Tensions	Color	
			NPA—Initial	NPA—96 hours
0	11.9			
1	35.1	23.2	1½−	4+
2	32.0	20.1	1½	6
3	5.5	−6.4	1½+	7

These data show that, with the additive employed, a concentration thereof of about 1% is optimum. The optimum will vary, however, with the particular additive and oil employed. In general, the optimum concentration will be from 0.8% to 3%, but concentrations of from 0.5% to 5% are operative. As shown by the example, use of a relative large quantity of the additive may result in deleterious effects.

The invention claimed is:

1. Method for the preparation of an oxidation inhibitor adapted to impart increased resistance to oxidation to oleaginous materials which comprises: (A) catalytically cracking a hydrocarbon oil by contact with a cracking catalyst under cracking conditions, (B) separating from the cracked oil a residual fraction boiling above 350° F., (C) contacting said residual fraction with an extractant selective for separating aromatic hydrocarbons from non-aromatic hydrocarbons thereby producing a fraction having a high aromatic hydrocarbon content, (D) contacting the fraction having a high aromatic hydrocarbon content with from 0.5 to 5 pounds of concentrated sulfuric acid per barrel of the fraction contacted, (E) separating acid from the residual fraction, (F) neutralizing acidic components of the separated residual fraction, and (G) distilling the separated residual fraction to separate components thereof having molecular weights within the range of 200 to 400.

2. Method according to claim 1 wherein the sulfuric acid has a concentration of at least 65° Bé.

3. Method according to claim 2 wherein acid components of the acid-treated fraction are neutralized with an aqueous solution of a strong base.

4. Method for the preparation of an oxidation inhibitor adapted to impart increased resistance to oxidation to oleaginous materials which comprises: (A) catalytically cracking a hydrocarbon oil by contact with a cracking catalyst under cracking conditions, (B) separating from the cracked oil a residual fraction boiling above 350° F., (C) contacting said residual fraction with an extractant selective for separating aromatic hydrocarbons from non-aromatic hydrocarbons thereby producing a fraction having a high aromatic hydrocarbon content, (D) separating from the fraction having a high aromatic content a fraction the components of which have molecular weights within the range of from 200 to 400, (E) incorporating from 0.5% by weight to 5% by weight of the last mentioned fraction in a hydrocarbon oil, (F) contacting the resulting composition with from 0.1 to 4 pounds of concentrated sulfuric acid per barrel of the composition, (G) separating sulfuric acid from the treated fraction, (H) contacting the acid-treated fraction with clay, and (I) separating clay from the hydrocarbon product.

5. Method according to claim 4 wherein the sulfuric acid has a concentration equivalent to at least 65° Bé.

6. Method for the preparation of an oxidation inhibitor adapted to impart increased resistance to oxidation to oleaginous materials which comprises: (A) catalytically cracking a hydrocarbon oil by contact with a cracking catalyst under cracking conditions, (B) separating from the cracked oil a residual fraction boiling above 350° F., (C) contacting said residual fraction with an extractant selective for separating aromatic hydrocarbons from non-aromatic hydrocarbons thereby producing a fraction having a high aromatic hydrocarbon content, and (D) distilling the high aromatic content fraction in the presence of a minor quantity of a strong base to separate a fraction consisting of components having molecular weights within the range of from 200 to 400.

7. Method according to claim 6 wherein said strong base is sodium hydroxide.

8. The oxidation inhibitor prepared by the method of claim 1.

9. A new composition of matter comprising an oleaginous material unstable toward oxidation and from 0.5% to 5% by weight of the oxidation inhibitor prepared by the method of claim 1.

10. A new composition of matter comprising a hydrocarbon oil unstable toward oxidation and from 0.5% to 5% by weight of the oxidation inhibitor prepared by the method of claim 1.

11. The oxidation inhibitor prepared by the method of claim 4.

12. A new composition of matter comprising an oleaginous material unstable toward oxidation and from 0.5% to 5% by weight of the oxidation inhibitor prepared by the method of claim 4.

13. A new composition of matter comprising a hydrocarbon oil unstable toward oxidation and from 0.5% to 5% by weight of the oxidation inhibitor prepared by the method of claim 4.

14. The oxidation inhibitor prepared by the method of claim 6.

15. A new composition of matter comprising an oleaginous material unstable toward oxidation and from 0.5% to 5% by weight of the oxidation inhibitor prepared by the method of claim 6.

16. A new composition of matter comprising a hydrocarbon oil unstable toward oxidation and from 0.5% to 5% by weight of the oxidation inhibitor prepared by the method of claim 6.

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