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TREATMENT OF CATALYTICALLY CRACKED DISTILLATES WITH POLYALKYLPHENOL PRIOR TO ALKALI TREATMENT

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This invention relates to a process for the preparation of hydrocarbon fractions of improved oxidation stability, particularly distillates obtained in the catalytic cracking of petroleum.

In the catalytic cracking of petroleum oils distillate fractions are produced which contain characteristically high concentrations of aryl mercaptans produced in the cracking process and relatively small concentrations of alkyl mercaptans, the form in which most of the mercaptan sulfur occurs in straight run, thermally cracked and thermally reformed distillates. Such aryl mercaptans, in which an —SH group is attached directly to a benzene ring, include thiophenol, thiocresols and thioxylenols. The presence of these compounds, together with the olefins and diolefins which always occur in high concentrations in catalytically cracked distillates, results in a serious refining problem. Upon contact with air, even in extremely small amounts, the distillate rapidly deteriorates because of the accelerating effect of the aryl mercaptans or (aryl disulfides into which they are converted) in the oxidation of olefins and diolefins. Intolerable amounts of peroxides and gum result, and oxidation products are formed which, especially in the case of gasoline, are precursors of engine induction system deposits.

Heretofore, it has been the practice to avoid this oxidative deterioration of catalytically cracked distillates by removing the aryl mercaptans contained therein by contacting the distillates with an aqueous solution of an alkali metal hydroxide, such as sodium hydroxide, before any oxygen in the form of air or otherwise is allowed to come in contact with the distillate. According to the process described in the Strickland patent, U.S. 2,525,152, "extreme precautions" must also be taken "to exclude all air or oxygen during the removal of the aromatic mercaptans" and it is recommended that the caustic solution used be freed of oxygen by purging with an inert gas.

Often, however, it is impossible, or at least inconvenient and expensive, to conduct commercial operations with such assiduous attention to the avoidance of any contact between the catalytically cracked distillate and air until after the aryl mercaptans have been entirely removed. Also, if the alkaline solution contacting plant is out of order or not available, the catalytically cracked distillates can be kept out of contact with air until the plant is again operating or available only by storing them in hermetically sealed vessels. If there are no such vessels available, the only way to avoid contact between the distillates and air is to shut down the cracking plant.

It is therefore a principal object of this invention to provide an improved process for the treatment of catalytically cracked distillates. A more particular object is to provide such a process wherein the quality of the treated product is improved with respect to oxidation stability, and content of gum, peroxides and other oxidation products. An important object is also to provide such a process which does not require the complete avoidance of contact of the cracked distillate with oxygen prior to its treatment with an alkali metal hydroxide solution. Other objects will be apparent in the description of the invention.

Contrary to the view hitherto held it has now been found that it is not necessary to bring the crude cracked products immediately into contact with alkali metal hydroxide solution. It has been found that the above objects are accomplished when one or more particular polyalkylphenols are added to the crude cracked products before they are brought into contact with the alkali metal hydroxide solution and before they come into contact with free oxygen.

The crude cracked distillate to which the polyalkylphenol is added according to the invention may remain exposed to the air for some time, e.g., 24 hours, without a troublesome amount of compounds being formed which might give rise to the formation of gum. If the crude cracked distillate is then afterwards washed with caustic alkali, most of the gum precursors which may have formed are removed. The presence of the polyalkylphenol also prevents any oxygen dissolved in the caustic alkali from oxidizing the aromatic mercaptans in the caustic alkali phase to disulfides. This is especially advantageous, as the disulfides are not readily soluble in caustic alkali but dissolve readily in the hydrocarbon oil, as a result of which there is a possibility that they will afterwards cause gum formation. If no disulfides are formed the total sulfur content of the cracked distillate is also reduced by the subsequent contacting with alkali metal hydroxide solution.

The catalytically cracked distillates to which the present invention is directed are those which are produced from petroleum derived straight run hydrocarbon feed stocks boiling above the gasoline boiling range, especially those which have relatively high total sulfur concentrations such as 0.5% by weight or more. Such distillates include gasoline and light and heavy gas oils and have boiling points (ASTM D–86) ranging from about 50° C. to about 410° C. Before any contact with air or alkaline solution, these distillates contain total mercaptan sulfur concentrations ranging from about 0.001 to about 0.05% by weight, at least one-tenth (by weight) of which, and often one-half or more of which is aryl mercaptan sulfur. The influence of the added polyalkylphenol is not sufficient to prevent the oxidation of hydrogen sulfide to free sulfur in the presence of oxygen, so it is preferred that any hydrogen sulfide present in the total product of the cracking operation be removed before the cracked distillate comes in contact with air. The advantages of the invention are most readily obtained when this is done by fractionation, as in the normal distillation of the total cracked product into one or more gas oil fractions, stabilized gasoline, and the lighter-than-gasoline fraction. The hydrogen sulfide in the total product will be recovered in the latter fraction. The gas oil fractions and the stabilized gasoline are then suitably treated in the process of the invention.

The particular polyalkylphenols which, according to the invention, are added to a catalytically cracked distillate before the distillate comes in contact with oxygen are the caustic-insoluble, sterically hindered, ortheo-disubstituted phenols in which at least one and preferably each ortho-substituent is a branched chain alkyl group containing at least 3, and preferably no more than 5 carbon atoms. Ortho-substituted alkyl groups attached to the phenol ring through a tertiary carbon atom are especially effective. Although the ortho-disubstituted mononuclear phenols are preferred, such dinuclear phenols are also operable; that is, those which contain two phenol rings linked together either directly or through an alkylene group. The polyalkylphenol compound should contain only carbon, hydrogen and oxygen atoms; it should contain at least 10, and preferably at least 14 carbon atoms, and not more than 40, preferably not more than 20 carbon atoms. Suitable polyalkylphenols include 2,6-di-tert.butyl-4-methylphenol, 2,4,6-tri-tert.butylphenol, 2,4-dimethyl-6-tert.butylphenol, 2,6-di-tert.butylphenol, 2, 6-di-tert.butyl-4-isopropylphenol, 3,3'-dimethyl-4,4'-dihydroxy-5,5'-di-tert.butylbiphenyl, 3,3',5,5'-tetraisopropyl-4,4'-dihydroxybiphenyl, bis(2-hydroxy-3-tert.butyl-5-methylphenyl)methane, 2,2-bis(3',5'-di-tert.butyl-4'-hydroxyphenyl)pentane, and the like.

The amount of the polyalkylphenol added is from about 0.001 to about 0.05% by weight of the catalytically cracked distillate. It is preferred, however, that at least about 0.01% by weight be used, and usually no more than 0.025% by weight will be required.

Besides the particular advantage in preventing deterioration of aryl mercaptan-containing cracked distillates upon contact with air, a further reason for selecting the particular polyalkylphenols described is that they are not removed by subsequent treatment of the distillate with aqueous alkaline solutions and they are especially effective inhibitors for the usual purpose of preventing oxidative deterioration of treated (e.g., sweetened or dethiolized) distillates. Therefore, in the practice of the invention, a double addition of inhibitor is unnecessary. Other compounds which are normally used as inhibitors in treated distillates are not only less suitable for the primary purpose of the invention but are often soluble in aqueous alkaline solutions, as are alkylaminophenols and alkylcatechols, which are often used to inhibit oxidative deterioration of treated distillates. The di(alkylamino)benzenes, such as N,N'-di-sec.butyl-para-phenylene diamine, while not soluble in aqueous alkaline solutions, are not suitable in the practice of the invention because they do not sufficiently avoid the formation of peroxides, and in the case of gasoline, give rise to induction system deposits.

While the distillate can be allowed to come in contact with oxygen as soon as the polyalkylphenol has been thoroughly dispersed in the distillate, it is desirable that any such contact not be unduly prolonged. It is preferred that the distillate be contacted with an aqueous alkali metal hydroxide solution, for the removal of the aryl mercaptans, within 2 to 3 days, and preferably within 24 hours, after the polyalkylphenol has been added. Sodium hydroxide and potassium hydroxide solutions are preferred, especially the former. Concentrations of such solutions can range from 5° to 50° Bé. and the amounts used can range from 5% to 50% by volume based on the amount of distillate contacted therewith.

The following example is illustrative of the invention:

EXAMPLE

A Kuwait straight run flashed distillate with a boiling range of 300° C. to 550° C. and a total sulfur content of 2.25 to 2.30% by weight was catalytically cracked. The gaseous cracked products, the hydrogen sulfide and the components heavier than gasoline were removed by distillation, after which the following experiments were carried out with the gasoline obtained.

The gasoline was drawn off in an oxygen-free, nitrogen atmosphere and immediately analyzed. In one case 0.020% by weight of 2,6-di-tert.butyl-4-methylphenol, calculated on the hydrocarbon oil, was previously added, while another sample was analyzed without this compound. The results are summarized in Table I.

Table I

	2,6-di-tert. butyl-4-methylphenol	
	With	Without
Percent by weight of aryl mercaptan sulfur content	0.0155	0.0150
Percent by weight of alkyl mercaptan sulfur content	0.0086	0.0086
Total percent by weight of mercaptan sulfur content	0.0241	0.0236
Peroxide number, meq. active oxygen per liter of hydrocarbon oil	0.006	0.019
Gum (ASTM D-381), mg./100 cc	5	10

The peroxide number was determined by the method of Yule and Wilson, Ind. Eng. Chemistry 23, 1254 (1931).

The results of Table I show that even during the analysis the aryl mercaptans were oxidized by atmospheric oxygen, however carefully the analysis was carried out.

The above samples were then exposed to the air for 24 hours before being again analyzed, and the results obtained are shown in Table II.

Table II

Exposed to Air for 24 Hours	2,6-di-tert. butyl-4-methylphenol	
	With	Without
Percent by weight of aryl mercaptan sulfur content	0.0126	0.0007
Percent by weight of alkyl mercaptan sulfur content	0.0074	0.0071
Total percent by weight of mercaptan sulfur content	0.0200	0.0078
Peroxide number, meq. active oxygen per liter of hydrocarbon oil	0.217	6.47
Gum (ASTM D-381) mg./100 cc	12	16

The results show that a cracked product which has been exposed to the air for 24 hours has obtained a peroxide number and a gum content which are both too high for a readily salable product.

The above samples were then washed with caustic alkali and again analyzed. The results obtained are summarized in Table III. In this case and in the following experiments the caustic alkali washing was carried out with 0.5% by volume of 6 N-sodium hydroxide solution (about 26° Bé.), calculated on the hydrocarbon oil treated.

Table III

Exposed to Air for 24 Hours and Then Caustic Washed	2,6-di-tert. butyl-4-methylphenol	
	With	Without
Percent by weight of aryl mercaptan sulfur content	nil	nil
Percent by weight of alkyl mercaptan sulfur content	0.0032	0.0025
Total percent by weight of mercaptan sulfur content	0.0032	0.0025
Peroxide number, meq. active oxygen per liter of hydrocarbon oil	0.106	0.317
Gum (ASTM D-381) mg./100 cc	7	14

The cracked gasoline which was exposed to the air for 24 hours without the polyalkylphenol is found to have too high a gum content, while the peroxide number is so high that it may be assumed that when stored and/or used an even much larger amount of gum will be formed. The gasoline treated with the inhibitor has, however, a reasonable ASTM gum content (10 mg./100 cc. is the permissible maximum) and, in addition, the peroxide number is not so high that too much gum formation is to be expected later.

Table IV shows the results of the experiments which were carried out with the cracked gasoline, mentioned in the commencement of the example, to which 0.005% by weight and 0.02% by weight of N,N'-di-sec.-butyl-para-phenylene diamine ("Inhibitor X") had been added, after which the gasoline was exposed to the air for 24 hours. At the same time an analysis is given of these two samples after they had been washed with caustic alkali. A comparison of the data of Table IV with the data of Tables II and III shows that the inhibiting effect of 2,6-di-tert.-butyl-4-methylphenol is very much better than that of Inhibitor X and that the cracked gasoline inhibited with the latter compound has too high a peroxide number even after a washing with caustic alkali.

Table IV

	With 0.005% by wt. of Inhibitor X, thereafter exposed to the air for 24 hours	With 0.02% by wt. of Inhibitor X, thereafter exposed to the air for 24 hours	With 0.005% by wt. of Inhibitor X, thereafter exposed to the air for 24 hours, subsequently washed with caustic alkali	With 0.02% by wt. of Inhibitor X, thereafter exposed to the air for 24 hours, subsequently washed with caustic alkali
Percent by weight of aryl mercaptan sulfur content	nil	0.0008	nil	nil
Percent by weight of alkyl mercaptan sulfur content	0.0068	0.0061	0.0019	0.0013
Percent by weight of total mercaptan sulfur content	0.0068	0.0069	0.0019	0.0013
Peroxide number, meq. of active oxygen per liter of hydrocarbon oil	6.49	6.33	0.558	0.651
Gum (ASTM D-381), mg./100 cc.	17	20	5	6

I claim as my invention:

1. A process for preparing a catalytically cracked distillate of improved oxidation stability which comprises adding to a catalytically cracked distillate containing aryl mercaptans and olefinic materials from about 0.001 to about 0.05% by weight of a caustic-insoluble polyalkylphenol before the distillate is allowed to come in contact with oxygen, thereafter contacting the distillate with an aqueous alkali metal hydroxide solution without the need of excluding air, said contacting being achieved without the occurrence of significant oxidative deterioration of the distillate and recovering a distillate of improved oxidation stability and having a reduced sulfur content.

2. A process for preparing a catalytically cracked distillate of improved oxidation stability which comprises distilling a total catalytically cracked product, before it is allowed to come in contact with oxygen, to recover a distillate boiling above about 50° C. and containing from about 0.001 to about 0.05% by weight mercaptan sulfur, at least one-tenth of which is aryl mercaptan sulfur and containing olefinic materials, adding to said distillate, before the distillate is allowed to come in contact with oxygen, from about 0.001 to about 0.05% by weight of a caustic-insoluble ortho-di-substituted polyalkylphenol containing only carbon, hydrogen and oxygen atoms and from 10 to 40 carbon atoms, at least one of the ortho substituents of which is a branched-chain alkyl group containing at least 3 carbon atoms, contacting the distillate with an aqueous alkali metal hydroxide solution without the need of excluding air, said contacting being achieved without the occurrence of significant oxidative deterioration of the distillate and recovering a distillate of improved oxidation stability and having a reduced sulfur content.

3. A process in accordance with claim 2, wherein the distillate is a gasoline fraction.

4. A process in accordance with claim 2, wherein the distillate is a gas oil fraction.

5. A process in accordance with claim 2, wherein the polyalkylphenol is a mononuclear phenol each of the ortho substituents of which is a branched-chain alkyl group containing from 3 to 5 carbon atoms.

6. A process in accordance with claim 5, wherein the polyalkylphenol is 2,6-di-tert.-butyl-4-methylphenol and the amount added to the distillate is from about 0.01 to about 0.025% by weight.

7. A process in accordance with claim 2 wherein the polyalkylphenol-containing distillate is contacted with the aqueous alkali metal hydroxide solution in the presence of air.

8. A process in accordance with claim 2 wherein the polyalkylphenol-containing distillate before treatment with the aqueous alkali metal hydroxide solution is exposed to air.

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