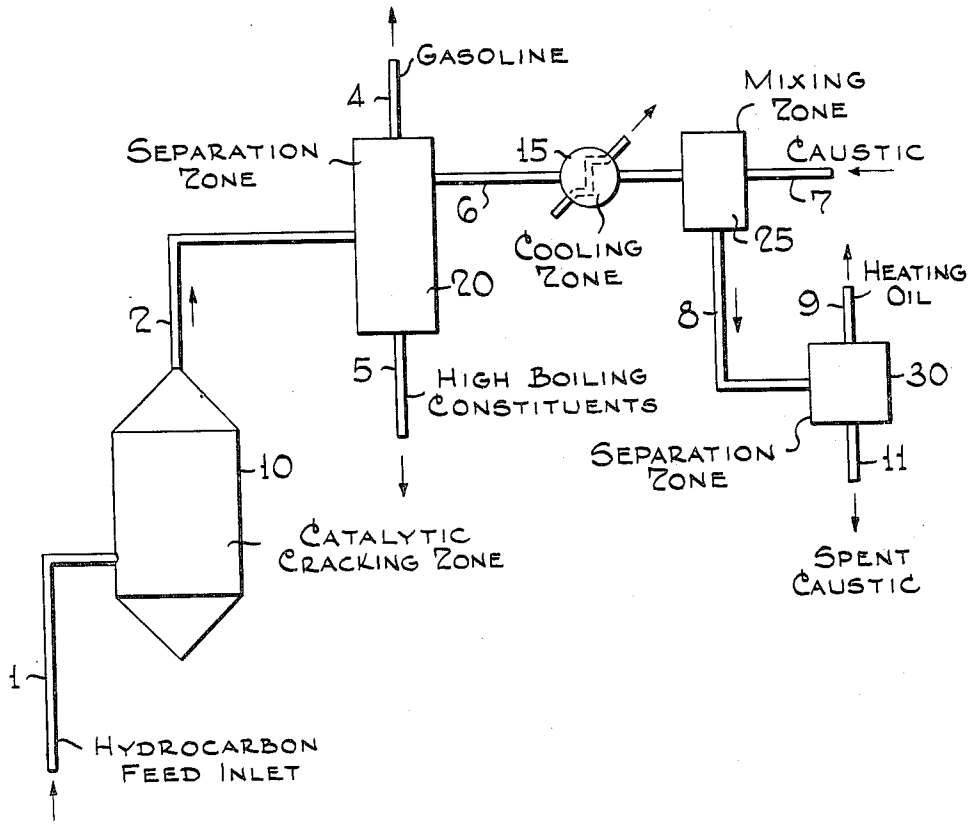
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PROCESS FOR STABILIZING CATALYTICALLY CRACKED HYDROCARBON DISTILLATES

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PROCESS FOR STABILIZING CATALYTICALLY CRACKED HYDROCARBON DISTILLATES

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This invention is concerned with the stabilization of catalytically cracked petroleum fractions. The present invention is a continuation-in-part of United States application 774,656 filed September 17, 1947 now Patent No. 2,525,152 which discloses and claims a process for stabilizing catalytically cracked gasoline. The present invention concerns a similar process for stabilizing catalytically cracked distillates boiling in the range of about 400 to 700° F.

It is known to produce hydrocarbons boiling in the heating oil range by various distillation and and cracking procedures. The heating oil distillates produced from such processes generally contain varying amounts of aliphatic and aromatic mercaptans. In general, however, the heating oil fractions produced by any process other than catalytic cracking contain substantially no aromatic mercaptans, although they may contain aliphatic mercaptans. However, in the case of catalytically cracked heating oils derived from high sulfur cracking feed stocks, it has been found that these particular heating oils contain relatively small quantities of aliphatic mercaptans and relatively large quantities of aromatic mercaptans. It has been found that the catalytic cracking operation, particularly as applied to a high sulfur feed stock, results in the production of aromatic mercaptans. Similarly, it has been found that the catalytic cracking operation causes formation of diolefins, so that catalytically cracked distillates contain both aromatic mercaptans and diolefins.

It has now been found that catalytically cracked heating oils containing aromatic mercaptans and diolefins undergo a peculiar phenomenon when exposed to air or oxygen. It has been determined that olefins and diolefins, present in the heating oils and produced by the catalytic cracking operation, are oxidized to form undesirable constituents in the presence of aromatic mercaptans. The probable mechanism involves the oxidation of olefins and diolefins to peroxides which in turn react with the aromatic mercaptans to provide constituents resulting in inferior burning properties. The aromatic mercaptans are strong promoters of the oxidation of olefins and diolefins.

The aromatic mercaptans which may be present are thiophenols, thiocresols, thioxylenols, or higher boiling derivatives of these compounds.

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These may all be considered as being mono or polyalkyl substituted thiophenols in which the alkyl group contains 1 to 10 carbon atoms.

The occurrence of aromatic mercaptans in catalytically cracked heating oils as related to the feed stock subjected to cracking is indicated by the following data:

EXAMPLE 1

A gas oil boiling in the range of 430 to 950° F., substantially free of aromatic mercaptans, and containing 0.5% sulfur was catalytically cracked under various conditions to provide yields of heating oil boiling in the range of 430 to 660° F. of 33 to 38 volume percent. It was found that the resultant catalytically cracked heating oils had sulfur contents varying from 0.3 to 0.4 weight percent. It was found that the average copper number of the heating oil fractions was 10. On analysis, it was found that the indicated mercaptan content consisted of 80% of aromatic mercaptans and 20% of aliphatic mercaptans. This example shows that a catalytically cracked heating oil contains a relatively low proportion of aliphatic mercaptans and a relatively high concentration of aromatic mercaptans, produced by the catalytic cracking operation.

EXAMPLE 2

A heavy gas oil boiling in the range of 720 to somewhat above 1100° F., and containing 1.3% of sulfur, although substantially no aromatic mercaptans, was catalytically cracked in a series of runs to provide heating oil fractions in yields of 15 to 20%. The heating oils were cut in the range of 430 to 660° F. It was found that these heating oils had sulfur contents of 0.9 to 1.5 weight percent. It was further found that these heating oils had a mercaptan content equivalent to a copper number of 40. On further analysis, it was found that substantially 90% of the mercaptans present were aromatic mercaptans while only about 10% of the mercaptans were aliphatic. These data again bear out the fact that relatively large proportions of aromatic mercaptans are produced by the catalytic cracking of a gas oil. Again, comparing this example to Example 1, it is demonstrated that the mercaptan content of a catalytically cracked heating oil is a function of the sulfur content of the gas oil subjected to cracking.

EXAMPLE 3

A West Texas gas oil obtained by vacuum distillation, boiling in the range of 720 to 930° F. and containing 1.6% sulfur, was catalytically cracked. The cracking operations were conducted to provide heating oil yields of 15 to 20 volume percent. It was found that the resultant heating oils had sulfur contents of 1.5 to 2.2 weight percent and copper numbers of about 60. Of this mercaptan content, expressed in copper numbers, the aromatic mercaptans comprised 55 while the aliphatic mercaptans comprised 5 copper numbers. Again, this example bears out the production of substantial quantities of aromatic mercaptans in cracked heating oils derived from gas oils containing substantial portions of sulfur.

As demonstrated by the data of Examples 1 to 3, therefore, in catalytically cracking a gas oil containing about 0.5 to 0.8% sulfur or more, cracked heating oil fractions resulting are characterized by inclusion of substantial quantities of aromatic mercaptans. The effect on the quality of the heatnig oil attributable to the presence of the aromatic mercaptans is shown by the following example:

EXAMPLE 4

A gas oil was catalytically cracked to provide a cracked heating oil boiling in the range of 400 to 580° F. The initial copper number of this heating oil, as determined under a protective blanket of nitrogen, to prevent exposure to oxygen, was 14. After two days exposure to air, the copper number was found to be less than 1, showing the conversion of aromatic mercaptans to disulfides due to exposure to air in a period of two days time. The peroxide number of this heating oil was similarly determined and it was found that the initial peroxide number, as determined under nitrogen, was 0.1, while the peroxide number after two days exposure to air was found to be 5.3. These data bear out the mechanism of degradation of a catalytically cracked heating oil. It thus appears that air is operative to cause the degradation in the presence of aromatic mercaptans with the resultant formation of peroxides. The effect of the peroxides and other probable oxidation products simultaneously formed on the burning quality of the cracked heating oil is shown by what is known as the carbon residue on 10% bottoms test. In this test, the heating oil is distilled to obtain a bottoms fraction consisting of 10% of the original heating oil. The Conradson carbon of this fraction is then determined. By a series of burning tests on heating oils, it has been found that this carbon residue based on the 10% bottoms fraction of the heating oil is correlated to the burning quality of the heating oil in the conventional oil burners currently employed. It has been found that the carbon residue on 10% bottoms is directly related to the burning quality so that the lower the carbon residue, the better the heating oil. Applying this test to the catalytically cracked heating oil of this example, it was found that the carbon residue on 10% bottoms, as determined initially, while maintaining the heating oil under nitrogen was 0.07, indicating a heating oil of good burning quality. However, after two days exposure to air, the carbon residue on 10% bottoms had increased to 0.27, and after seven days exposure to air, had increased to 0.34. Since the oil will normally be exposed to air, these data show the material degradation in burning quality of catalytically cracked heating oils due to the presence of aromatic mercaptans in the cracked heating oil.

In accordance with this invention, therefore, it has been found that the degradation of a cracked heating oil may be prevented by subjecting the cracked heating oil to a caustic washing process prior to permitting contact of the heating oil with air. The manner in which this process is conducted may be understood by reference to the accompanying diagrammatical drawing which illustrates one embodiment of the invention. Referring to this drawing, a hydrocarbon feed stock consisting of a gas oil boiling in the broad range from about 400 to above 1100° F., or preferably boiling in the range of 700 to about 1100° F., is introduced into catalytic cracking zone **10** through line **1**. It is to be understood that the gas oil employed has a sulfur content at least above about 0.5 weight percent sulfur. Catalytic cracking zone **10** contains a suitable cracking catalyst and is maintained under temperature and pressure conditions to secure the desired cracking of the feed stock. The cracked products are removed from cracking zone **10** through line **2**, and are conducted to distillation zone **20**. Distillation zone **20** is operated to permit removal overhead of a gasoline fraction through line **4** boiling below about 400° F. and to permit removal of a side stream product through line **6**, consisting of a heating oil fraction boiling in the range of about 400 to 700° F. Heavier fractions may be withdrawn through line **5**, as a bottoms product.

In accordance with this invention, the heating oil fraction of line **6** is conducted through cooling zone **15** to a caustic washing zone **25** wherein the heating oil is contacted with an aqueous caustic solution. Any desired type of apparatus to secure the contacting may be employed such as a countercurrent treating tower or any desired type of mixing equipment. The caustic employed should have a concentration of about 2 to 15° Baumé or somewhat greater and should be applied to provide a volumetric treat of about 2 to 10% or somewhat more. The mixture of caustic and heating oil is then removed from zone **25** through line **8** and is passed to separation zone **30** wherein the caustic and heating oil are separated by settling, permitting removal of the treated heating oil from line **9** and the spent caustic from line **11**. Thereafter the heating oil may be water washed if desired.

The caustic washing operation conducted in zone **25** must be critically operated to prevent the presence of oxygen during the washing operation. Thus, the caustic employed must be completely free of oxygen which frequently necessitates the purging of the caustic with inert gases such as light hydrocarbons or oxygen-free nitrogen gas to completely eliminate any possibility for oxygen entering the system. It is particularly preferred that caustic washing zone **25** be conducted at pressures somewhat above atmospheric to eliminate the possibility of air leaking into the system. These same considerations apply to the operation of separation zone **30**.

The effectiveness of the process of this invention is indicated by the following data:

EXAMPLE 5

A gas oil containing more than .5% of sulfur and boiling in the range of about 430 to 950° F. was catalytically cracked to provide a cracked heating oil boiling in the range of 400 to 580° F. One portion of the cracked heating oil was subjected to the process of this invention and was

washed in the absence of oxygen, with 10% of a caustic solution containing 10% of caustic. A control portion of the heating oil was not subjected to this caustic washing. Tests were then conducted on the two portions of heating oil, as indicated in the following table:

Table I

Caustic Wash	None	10% of 10%
Inspections:		
Copper Number—		
Initially, under Nitrogen	14	<1
After 2 days' exposure to air	<1	<1
After 7 days' exposure to air	<1	<1
Peroxide Number—		
Initially, under Nitrogen	0.1	0.05
After 2 days' exposure to air	5.3	0.15
After 7 days' exposure to air	5.1	0.20
Carbon Residue on 10% Btms.—		
Initially, under Nitrogen	0.07	0.07
After 2 days' exposure to air	0.27	0.04
After 7 days' exposure to air	0.34	0.08

Comparing columns 1 and 2 of Table I, the beneficial effects of the processing of this invention are apparent. Thus, it will be noted that the degradation promoted by the aromatic mercaptans in the case of the heating oil which was not caustic washed, as indicated by the drop in copper number after exposure to air, was eliminated by the caustic wash. Similarly, in the case of the portion of heating oil subjected to the caustic wash, it was found that the peroxide number did not greatly increase even after 7 days' exposure to air. Finally, and most important, the data of Table I show that the burning qualities of the caustic washed heating oil, as indicated by the carbon residue, were maintained substantially unchanged even after 7 days' exposure to air. These data therefore show the unexpected and material advantages of the caustic washing process of this invention. The data demonstrate that by subjecting a catalytically cracked heating oil to a caustic wash in the absence of oxygen, the burning qualities of this heating oil after a period of exposure to air are materially better than though caustic washing were not employed.

EXAMPLE 6

This effect is also shown by reference to the data of Table II below, which again compares inspections of comparative portions of a catalytically cracked heating oil when subjected to a caustic wash and when no caustic wash is employed. The catalytically cracked heating oil tested boiled in the range of 440° to 660° F. and was produced by the catalytic cracking of a gas oil containing 1.3% sulfur and boiling in the range of 720 to 1100+° F.

Table II

Caustic Wash	None	10% of 15° Bé.
Inspections:		
Copper Number—		
Initially [1]	35	5
After 16 hrs.[2]	2	1½
Peroxide Number—		
Initially [1]	Nil	
After 16 hrs.[2]	0.7	0.1
Carbon Residue on 10% Btms.—		
Initially [1]	0.13	
After 16 hrs.[2]	0.55	0.11
Color, Tag Robinson—		
Initially [1]	15	
After 16 hrs.[2]	13¼	13¼

[1] Under protective blanket of Seaford nitrogen.
[2] Exposed to 4 to 5 volumes of air for 16 hours.

Referring to the table, the data there presented illustrate the degradation occurring in the presence of aromatic mercaptans, the formation of peroxides, the increase in carbon residue, and the loss in color which occur when an untreated catalytically cracked heating oil is exposed to air. However, by comparison, the data show the stabilizing effect on each of these inspections caused by the caustic washing of this heating oil when conducted in the absence of oxygen.

What is claimed is:

1. A process for producing a stable cracked distillate comprising the steps of catalytically cracking a gas oil feed stock, substantially free of aromatic mercaptans and diolefins, boiling above about 400° F. and containing more than about 0.5% sulfur, whereby aromatic mercaptans, olefins, and diolefins are produced, separating a distillate fraction boiling in the range of about 400 to 700° F. characterized by the absence of oxygen and the inclusion of substantial portions of aromatic mercaptans, olefins and diolefins, and contacting said heating oil in the absence of oxygen with a treating agent consisting of an aqueous caustic solution free of oxygen, and thereafter, separating the heating oil from the spent caustic.

2. A process for producing a stable cracked distillate comprising the steps of catalytically cracking a gas oil feed stock, substantially free of aromatic mercaptans and diolefins, boiling above about 700° F. and containing more than about 0.5% sulfur, whereby aromatic mercaptans, olefins, and diolefins are produced, separating a distillate fraction boiling in the range of about 400 to 700° F. characterized by the absence of oxygen and the inclusion of substantial portions of aromatic mercaptans, olefins and diolefins, and contacting said heating oil in the absence of oxygen with a treating agent consisting of an aqueous caustic solution free of oxygen while maintaining the pressure during contacting above atmospheric, and thereafter, separating the heating oil from the spent caustic.

3. The process defined by claim 1 in which the said gas oil boils in the range of about 400 to 1100° F.

4. The process defined by claim 1 in which the said gas oil contains more than about 0.8% sulfur.

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