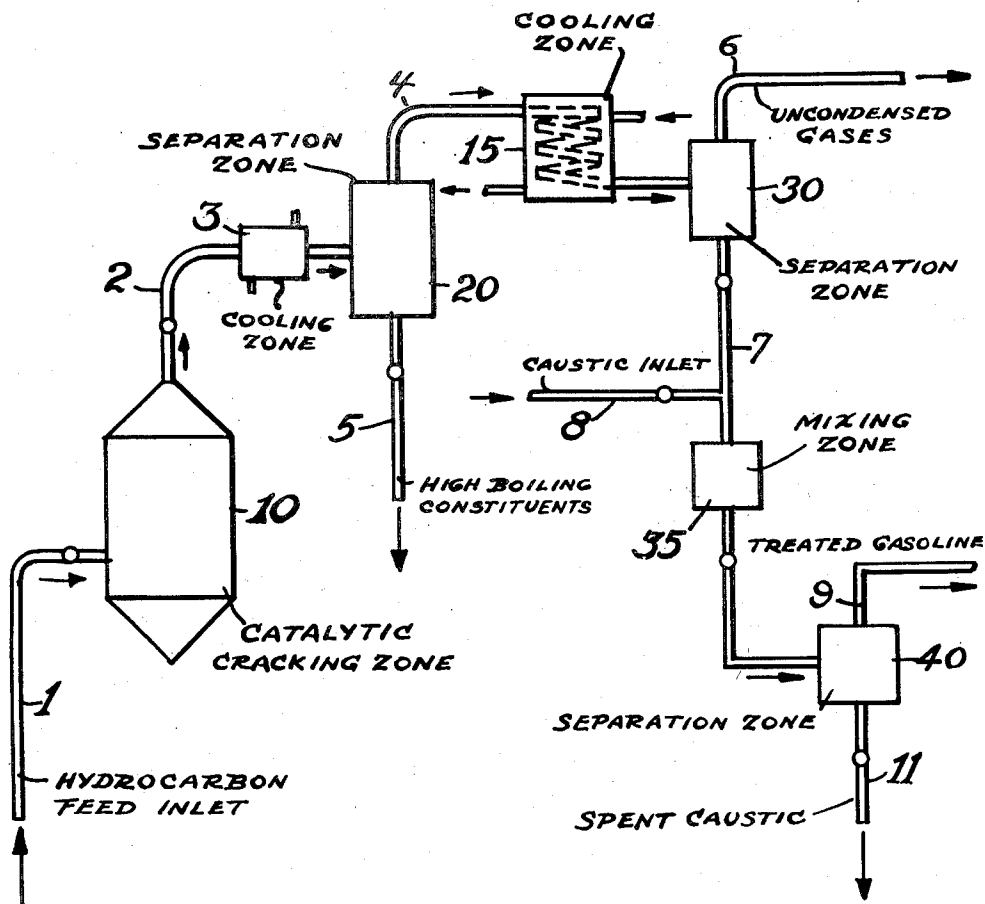


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PROCESS FOR STABILIZING GASOLINE

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PROCESS FOR STABILIZING GASOLINE

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The present invention is concerned with a process for the stabilization of hydrocarbon mixtures. The invention is more particularly concerned with the stabilization of hydrocarbon mixtures boiling in the gasoline boiling range and produced by cracking processes. In its specific adaptation the invention is particularly concerned with the stabilization of hydrocarbons of the aforesaid type which have been produced by catalytic cracking operations.

We have discovered that olefins and diolefins normally present in hydrocarbons boiling in the motor fuel boiling range, particularly as produced in a catalytic cracking operation, are oxidized to form peroxides. As a result, the presence of these compounds normally causes excessive gum formation in the hydrocarbon product. In order to remove this gum, additional processing steps, such as acid treating or distillation, are normally required. It is an object of this invention to avoid such processing steps by stabilizing the gasoline to prevent the formation of excessive gum.

In accordance with our invention, hydrocarbons boiling in the motor fuel boiling range, particularly as produced in a catalytic cracking operation, are treated with aqueous caustic solutions in the absence of oxygen. By means of this treatment such hydrocarbon mixtures are stabilized so as to substantially prevent the formation of gum.

It is known in the art to produce hydrocarbons boiling in the motor fuel boiling range by various distillation, reforming, and cracking procedures. No attempt will be made to outline or discuss these processes since they are well known. The products from such processes generally contain varying amounts of aliphatic and aromatic mercaptans. In general, thermally cracked stocks may contain minor amounts of aromatic mercaptans, such as thiocresols for example. However, in the case of catalytically cracked gasolines, it is found that these gasolines in general

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have a rather small amount of aliphatic mercaptans but a relatively large amount of aromatic mercaptans. This is particularly the situation when high sulfur stocks are employed. For example, when a West Texas gas oil, having a boiling range of about 400° F. to 700° F. and having a sulfur content of about 1.5%, is catalytically cracked to a 50 to 60% yield of 400° F. end point gasoline, the gasoline will have about a 30 copper number; that is, 30 milligrams of mercaptan sulfur per 100 milliliters of gasoline. This figure corresponds to approximately 0.035% sulfur as aromatic mercaptans. Or again, when a mixed gas oil of about 0.8% sulfur is catalytically cracked to a 50% yield of 400° F. end point gasoline, the amount of aromatic mercaptan sulfur in the gasoline is about 0.017 gram per 100 milliliters of gasoline.

As pointed out heretofore, catalytically cracked gasolines contain mercaptans, substantially all of which are aromatic in nature. We have now discovered a peculiar phenomenon with respect to catalytically cracked gasolines containing these aromatic mercaptans. We have discovered that when oxygen is present, oxidation of olefins and diolefins in the gasoline is catalyzed by the presence of these aromatic mercaptans. The olefins and diolefins are oxidized to peroxides, which in turn destroy the aromatic mercaptans and produce excessive gum in the hydrocarbon mixture.

The aromatic mercaptans which may be present are thiophenols, thiocresols, or thioxlenols. These may all be considered as being mono or di-alkyl substituted thiophenols in which the alkyl group contains one to three carbon atoms. Specifically, the aromatic mercaptans which may be present are thiophenol, methyl thiophenol, dimethyl thiophenol, ethyl thiophenol, diethyl thiophenol, propyl thiophenol, and dipropyl thiophenol.

This phenomenon is illustrated by the following table:

TABLE I

Effect of mercaptans¹ and hydrocarbon composition on peroxidation and air sweetening

Stock		Initial Inspections				Inspections after Air Contact		
		Per. No. ²	Cu No. ³	Cu Dish Gum ⁴	ASTM Gum ⁵	Per. No.	Cu No.	ASTM Gum
A	75% Diisobutylene (25% Dimethyl Butadiene) base	0	0	4	1	0	0	1
B	+n-Heptyl Mercaptan	0.6	29	6	0.2	0.3	26	3
C	+p-Thiocresol	7.1	27	120	17	13.7	0	34
D	n-Heptane (base)	0		4	3	0		1
E	+n-Heptyl Mercaptan	0	30	5	2	0	33	3
F	+p-Thiocresol	trace	28	7	3	trace	26	2

¹ Mercaptans added to theoretical copper number of 30.

² Yule, J. A. C. and Wilson, C. P. Jr. Ind. Eng. Chem. 23, 1254 (1931).

³ Francis, C. K., Oil & Gas Journal, 36, No. 11, 99 (1937).

⁴ Bureau of Mines, Reports of Investigations No. 3152, November 1931.

⁵ A. S. T. M. D381-44.

The table shows experiments with two base stocks A and D. Hydrocarbon base stock A was olefinic, consisting of 75% diisobutylene and 25% dimethylbutadiene, while base stock D was paraffinic consisting of normal heptane. It will be noted from the table that the base stocks contained no peroxides and substantially no gum, both before and after air contact.

Stocks B and C consisted of the base stock A, plus sufficient mercaptans to result in a theoretical copper number of 30. Similarly stocks E and F consisted of the base stock D, plus sufficient mercaptans to produce a theoretical copper number of 30. Two mercaptans were added to each fuel base; normal heptyl mercaptan which is an aliphatic mercaptan, and parathiocresol which is an aromatic mercaptan. It will be observed from the table that addition of the aliphatic mercaptan to either fuel base did not appreciably increase the gum content of the blend. The peroxide number after contacting with air as contrasted to before contacting with air, was also not increased, indicating that no oxidation took place.

However, in noting the effect of adding the aromatic mercaptan, parathiocresol, to the olefinic base stock A, it will be observed that this was effective in increasing the gum materially after contact with air, and also in increasing the peroxide number of the blend after air contact. This indicates oxidation of the diolefins and olefins while the decrease of the copper number indicates the destruction of the aromatic mercaptan. The resulting gum formation of 34 is excessively high and would necessitate further acid treating or redistillation. In the case where parathiocresol was added to normal heptane, it will be noted that the addition of this aromatic mercaptan was not effective in increasing the gum content or in changing the peroxide number of the stock.

These results show that when an aliphatic mercaptan is added to either a paraffinic or olefinic fuel base, no oxidation of the mercaptan occurs and no gum formation results from air contact. On the other hand, when an aromatic mercaptan is added to an olefinic fuel base, oxidation of the mercaptan does occur with resulting gum formation. The fact that these results do not occur with paraffinic base fuel stock, shows the importance of the hydrocarbon composition on these reactions.

These results are further substantiated by the following data secured with hydrocarbon mixtures boiling in the motor fuel boiling range derived from catalytically cracked gasoline.

TABLE II

Stock	Initial Inspections		Inspections after Air Contact	
	Cu No.	Peroxide Number	Cu No.	Peroxide Number
Low Pressure Distillate:				
Mix A.....	15	0	3	2.5
Mix B.....	27	0	1	8.9

The table shows the results of tests on two low pressure distillates, mixtures A and B. It will be observed that after air contact the copper number of these mixtures had decreased materially while the peroxide number had increased. These results show the oxidation of olefins and diolefins in the fuel mixtures with the accompanying destruction of aromatic mercaptans.

The exact mechanism of the reactions involved in this phenomenon is not known. However, it is believed that olefins and diolefins in the presence of oxygen, catalyzed by the aromatic mercaptans, form peroxides which destroy the aromatic mercaptans to form gum products. The result is a gasoline containing a relatively large amount of gum which necessitates further treatment of the product.

In accordance with our invention, therefore, we propose to remove these aromatic mercaptans, particularly from catalytically cracked gasolines, by treating these gasolines to remove the mercaptans before the cracked stock is allowed to contact oxygen. As aromatic mercaptans in the presence of olefinic hydrocarbons are very reactive with oxygen, extreme precautions must be taken in the practice of our invention to exclude all air or oxygen during the removal of the aromatic mercaptans.

Aromatic mercaptans may be readily and substantially completely removed by caustic washing, as indicated by the following table.

TABLE III

Gasoline	Copper Number	
	Initially	After Washing with 10% of 15° Bé. NaOH
Catalytically Cracked Gasoline Distillate:		
Sample A.....	15	2
Sample B.....	27	1

It will be observed from this table that washing the two samples with 10% of a 15° Bé. sodium hydroxide solution was effective in reducing the copper number of the samples treated to 2 or less showing substantial removal of aromatic mercaptans. Due to the susceptibility of the mercaptans to oxidation, it is essential that this process be carried out in the complete absence of oxygen. If carried out in the absence of oxygen, the aromatic mercaptans are extracted by the caustic solution in a recoverable form; if oxygen is present, however, the mercaptans are converted to a form not recoverable with caustic.

Our invention may be further understood by reference to the diagrammatical drawing illustrating one embodiment of the invention. Hydrocarbon feed, which for the purpose of illustration is assumed to be a high sulfur West Texas gas oil boiling in the range from about 400° to 700° F., is introduced into catalytic cracking zone 10 by means of line 1. Reaction zone 10 contains a suitable fluidized catalyst and is maintained under temperature and pressure conditions designed to secure the desired cracking of the feed stock. The cracked product, comprising hydrocarbons boiling in the gasoline boiling range, is removed from reaction zone 10 by means of line 2, cooled in cooling zone 3 and passed into separation zone 20. A hydrocarbon fraction having an end point of about 400° F. is removed overhead from zone 20 by means of line 4, while higher boiling constituents are removed by means of line 5. The hydrocarbon fraction removed by means of line 4 is passed through cooling zone 15 and passed into separation zone 30. Uncondensed gases, comprising hydrogen sulfide, are removed overhead from zone 30 by means of line 6, while the condensate is removed from zone 30 by means of line 7. In accordance with our in-

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vention, we introduce aqueous caustic by means of line 8 into the hydrocarbon stream of line 7 before this stream is allowed to contact oxygen or an oxygen-containing gas. The caustic used should preferably have been freed of oxygen by purging with an inert gas, such as light hydrocarbons, or oxygen-free nitrogen gas. After complete mixing of the caustic solution and gasoline in a suitable vessel 35, the mixture is passed into settling zone 40. The treated gasoline is allowed to separate from the aqueous caustic solution and is removed through line 9. The spent caustic solution is drawn off by means of line 11. It is essential that up to this point oxygen be excluded from the process. However, from this point on, the gasoline may be water washed and further processed as desired by conventional methods. The caustic used is preferably a solution of from 5° to 40° Bé. The amount of treating agent is preferably in the range from about 5% to 20% caustic per volume of oil. While the example given has referred to the treatment of gasoline with caustic solution, other hydroxides may be used. In general, any alkali metal hydroxide capable of dissolving the mercaptans may be used as the treating agent in this invention. For example, potassium hydroxide may be used in place of the sodium hydroxide specified.

The process of our invention is not to be limited by any theory as to mode of operation, but only in and by the following claims in which it is desired to claim all novelty insofar as the prior art permits.

Having now fully described our invention, we claim:

1. The process of producing a stable cracked gasoline which consists of the following steps:

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catalytically cracking a gas oil feed stock boiling above about 400° F. containing more than about 0.8% sulfur, fractionating the products of the said cracking step and separating a distillate fraction boiling in the gasoline boiling range substantially free of hydrogen sulfide but containing substantial quantities of mercaptans, said mercaptans consisting principally of aromatic mercaptans resulting from the cracking step to the substantial exclusion of aliphatic mercaptans, and said distillate stock containing both olefins and diolefins, thereafter contacting said distillate stock with an aqueous alkali hydroxide solution free of oxygen, said contact being conducted in the absence of oxygen, and thereafter separating the treated distillate stock from the spent caustic whereby a gum stable, substantially mercaptan sulfur free gasoline is obtained.

2. The process as defined by claim 1 wherein the hydroxide solution has a strength in the range from 5° to 40° Bé. and is used in an amount in the range of 5% to 20% per volume of catalytically cracked gasoline.

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