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SWEETENING HYDROCARBON MIXTURES

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1

The present invention relates to the sweetening of hydrocarbon mixtures and, more particularly, to the sweetening of petroleum distillates.

Sweetening may be broadly defined as an operation in which the concentration of the organic sulfur compounds in a hydrocarbon mixture is reduced to a value such that the doctor test is negative.

A hydrocarbon mixture containing sulfhydryls is said to be "sour," or to be positive in the common "doctor test," if it contains more than about 0.0004 per cent sulfur calculated as mercaptan and is free from hydrogen sulfide, it is said to be "sweet" or to be negative in the "doctor test" when the sulfur concentration is below that value.

The "doctor test" comprises adding 10 cubic centimeters of the oil to be tested to 5 cubic centimeters of sodium plumbite solution (made by dissolving 120 to 140 grams of sodium hydroxide and 20 to 30 grams of litharge in a liter of water) in a standard test bottle (4 ounce sample bottle, 33 millimeters inside diameter, fitted with a clean cork stopper). The bottle is stoppered, shaken for 15 seconds, and dry flowers of sulfur (ground and screened to 100 to 200 mesh) added to the mixture in quantity just sufficient to cover the interface (20 to 35 milligrams). The bottle is again stoppered and shaken for 15 seconds. The test is reported positive if either the oil or the sulfur becomes discolored.

The minimum amount of mercaptan sulfur required to give a positive doctor test in a sample of Stoddard cleaners' solvent is shown in Table I.

Table I

Mercaptan	Minimum per cent by weight of mercaptan sulfur in naptha required to give Positive Doctor Test
Ethyl	0.0006
n-Propyl	0.0003
n-Butyl	0.00015
n-Amyl	0.0002
Isoamyl	0.0001
n-Heptyl	0.0001
Phenyl	0.0010

Since hydrocarbon mixtures usually contain two or more mercaptans and since the distribution of the mercaptans in hydrocarbon mixtures is not constant, a practical value for the maximum per cent by weight of mercaptan sulfur which will

2

give a negative doctor test is usually accepted as 0.0004 per cent.

Mixture of hydrocarbons containing sulfhydryls can be treated in accordance with several procedures to produce a treated mixture which is negative to the "doctor test." However, all of these procedures do not produce the same result. For example, the so-called "doctor sweetening" and the "copper chloride" sweetening methods merely convert sufficient of the mercaptans present in the hydrocarbon mixture to disulfides that the treated mixture is negative in the "doctor test." For gasoline to which tetraethyl lead is not to be added the presence of the disulfides is not objectionable. On the other hand, the presence of disulfides in gasoline to which tetraethyl lead is to be added is objectionable because the presence of disulfides reduces the sensitivity of the gasoline to the addition of the lead to even a greater extent than a corresponding concentration of mercaptans. Since most gasolines now marketed are treated with tetraethyl lead, it follows that it is most desirable to remove the mercaptans rather than merely convert them to disulfides. As a consequence, the removal of mercaptans has become desirable. To meet this demand, methods have been devised which make it possible to remove substantially all of the mercaptans. However, while it is usually relatively easy to reduce the mercaptan sulfur content of cracked and straight run gasoline to a value of the order of 0.0007 to 0.003 per cent sulfur as mercaptan sulfur by treatment with the well-known solutizer solutions such as aqueous caustic-tannin and aqueous caustic cresylate-tannin solution or other caustic-solutizer solutions, the reduction of the mercaptan-sulfur content of gasoline from 0.0007 or 0.003 to 0.0004 is not accomplished as readily. On the other hand, gasoline containing 0.0007 to 0.003 per cent mercaptan sulfur is not "doctor sweet."

It has now been discovered that "sour" hydrocarbon mixtures containing organic sulfhydryls can be treated in a simple, inexpensive but efficacious manner to provide a "doctor sweet" mixture.

It is an object of the present invention to provide a method for "sweetening" "sour" hydrocarbon mixtures. It is another object of the present invention to provide a method for removing a portion of the mercaptan content of a "sour" hydrocarbon mixture and then to "sweeten" the partially demercaptanized, but sour, hydrocarbon mixture. It is a further object of the present invention to add a hydrocarbon soluble sweetening agent to hydrocarbon mixtures containing not more than about 0.02 weight per cent sulfur as organic sulfhydryls to produce a hydrocarbon mixture negative to the "doctor test." Other objects and advantages will become apparent from the following description.

Two conditions, in general, will be met in the treatment of "sour" mixtures of hydrocarbons. The "sour" mixture may contain only about 0.005 weight per cent mercaptan sulfur or the "sour" mixture may contain appreciably more than about 0.005 weight per cent mercaptan sulfur.

For the purpose of illustrating the present method, the treatment of sour gasoline containing not more than about 0.005 weight per cent mercaptan sulfur (including alkyl and aryl mercaptans, the latter often being termed thiophenols) first will be described. When the gasoline contains hydrogen sulfide as well as not more than about 0.005 weight per cent mercaptan sulfur, the hydrogen sulfide is removed in a conventional manner by washing the gasoline with an aqueous caustic solution. This caustic wash removes the hydrogen sulfide and a portion of the C_1 and C_2 mercaptans. However, the gasoline will still be positive in the "doctor test." The washed gasoline also contains a small amount of alkali metal hydroxide. The "sour" caustic washed gasoline containing not more than about 0.005 weight per cent mercaptan sulfur is sweetened by adding a small amount of a sweetening agent and the sweetening agent allowed to react with the mercaptans. After about 30 minutes to about 7 days at ambient temperatures, dependent upon the concentration of the sweetening agent, the so-treated gasoline is negative to the "doctor test." When it is unnecessary to wash the gasoline with an aqueous solution of alkali metal hydroxide, it is necessary to add a trace, say about 0.001 pound to about 0.02 pound of alkali metal hydroxide per barrel of gasoline.

Illustrative of the treatment of a "sour" mixture of hydrocarbons containing appreciably more than 0.005 weight per cent of mercaptan sulfur, is that of a sour gasoline containing say 0.03 weight per cent mercaptan sulfur but free from hydrogen sulfide. Such a gasoline is contacted with an aqueous solution of alkali metal hydroxide or an aqueous solution of alkali metal hydroxide containing a solutizer. Illustrative of such solutions are the commonly used sodium hydroxide-sodium cresylate solution which is 5.0 normal to sodium hydroxide and 2.0 normal sodium alkyl phenolates; or the well know aqueous solutions of potassium hydroxide and potassium alkyl phenolates, or an aqueous sodium hydroxide-sodium cresylate solution containing a polyhydroxy benzene or a polyhydroxy benzene carboxylic acid or a tannin or an aqueous potassium hydroxide-potassium cresylate-tannin solution or; in general, any of the aqueous alkaline solutizer solutions described in the voluminous literature on this subject and known to those skilled in the art may be used. The "sour" gasoline is treated with the aqueous alkaline solution until sufficient of the mercaptans have been extracted from the sour gasoline that although the treated gasoline is still positive in the "doctor test" it does not contain more than about 0.02 and preferably less than about 0.005 weight per cent mercaptan sulfur. The partially demercaptanized "sour" gasoline containing not more than about 0.02 weight per cent mercaptan sulfur is separated from the aqueous treating solution and sweetened by adding thereto a sweetening agent. The gasoline and added sweetening agent are reacted for a period of time dependent upon the temperature and concentration of the sweetening agent.

The preferred sweetening agent at this time is di-secondary butyl catechol. This catechol and several other compounds have been added to "sweetened" gasoline, i. e. gasoline negative in the "doctor test" in the past to inhibit the formation of gum during storage. However, the present method of sweetening "sour" mixtures of hydrocarbons distinguishes from this prior use of di-secondary butyl catechol. In the prior use of this catechol and other gum inhibitors the gum inhibitor was always added to "sweet" gasoline which was negative in the "doctor test," i. e. contained less than 0.0004 weight per cent of mercaptan sulfur. In the prior use of these gum inhibitors the "sweet" gasoline did not contain a trace of caustic. In contrast to the conditions attendant upon the prior use of alkyl catechols and other compounds in the inhibition of the formation of gum in "sweet" neutral gasoline, the alkyl catechols are employed under the following conditions: The gasoline is sour, i. e. positive in the "doctor test" and the gasoline contains at least a trace of alkali metal hydroxide and is probably saturated with water. Furthermore, all of the prior-art gum inhibitors are not effective in the present method of sweetening gasoline. This is established in the following tables.

Table II

Additive	lbs./1000 bbl.	Days at ambient temperature to sweeten gasoline containing 0.005 wt. % mercaptan and alkali metal hydroxide
None		12
Di-secondary butyl catechol	20	less than 1
Di-secondary butyl phenylene diamine	20	5
Trialkyl phenols	20	15
Normal butyl amino phenol	20	17
Alpha-naphthol	20	14
Quinone	20	5
Catechol	20	more than 19

Table III

Alkali metal hydroxide	Lbs. di-sec. butyl catechol per 1000 bbls. gasoline	Days at ambient temperatures to sweeten gasoline containing 0.005 wt. % mercaptan sulfur
present	0	>42
Do	10	7
absent	0	>42
Do	10	>42

Table IV

Lbs. alkyl catechol per 1000 bbls. of gasoline containing alkali metal hydroxide and 0.005 wt. % mercaptan sulfur	Days at ambient temperatures to sweeten; i. e. give a negative "doctor test"
0	13
0.25	7
0.50	7
0.75	6
1.0	4
2.0	3
3.0	2
4.0	0.83
5.0	0.13
10.0	0.04
20.0	0.02

The data presented in Table II establishes that of the common gum inhibitors tested the alkyl catechols are far superior in the present method of "sweetening" sour hydrocarbon mixtures containing about 0.005 weight per cent mercaptan sulfur. The data presented for catechol establishes that unsubstituted catechol is ineffective, if it does not actually retard, in sweetening of sour gasoline containing 0.005 weight per cent mercaptan sulfur.

The data presented in Table III establishes that in the absence of alkali metal hydroxide even di-secondary butyl catechol at a concentration of 10 pounds per 1000 barrels of gasoline is ineffective to sweeten sour gasoline containing about 0.005 weight per cent mercaptan sulfur but that in the presence of alkali metal hydroxide di-secondary butyl catechol is effective in sweetening sour gasoline containing about 0.005 weight per cent of mercaptan sulfur.

The data presented in Table IV establishes that in the presence of alkali metal hydroxide the rate of sweetening sour gasoline containing about 0.005 weight per cent mercaptan sulfur is dependent upon the concentration of alkyl catechol. A study of the data given in Table IV makes it manifest that the amount of alkyl catechol to be used in sweetening sour hydrocarbon mixtures containing not more than 0.02 weight per cent mercaptan sulfur will depend to a great extent upon local conditions, primarily local economic conditions. Thus, when a large volume of storage is available for a week at a time and the capacity exceeds the demand, it probably will be most practical to use about 0.25 pounds of alkyl catechol per 1000 barrels in treating gasoline containing about 0.005 weight per cent mercaptan sulfur and allow the reaction to proceed for several days at ambient temperatures. On the other hand, when sufficient storage capacity is not available or demand is practically equal to the capacity to produce the sour gasoline, it will probably be most practical to add about 4 to about 20 pounds of alkyl catechol per 1000 barrels of sour hydrocarbon mixture and allow the reaction to proceed at ambient temperatures or to use somewhat less, say 2 to 5 pounds, alkyl catechol and reflux the sour gasoline and alkyl catechol in the presence of a small amount of alkali metal hydroxide.

Furthermore, when storage capacity, production and consumption justify such procedure it is possible to sweeten gasoline and other mixtures of hydrocarbons such as kerosene, Diesel oil, and heating oil containing up to 0.02 weight per cent of mercaptan sulfur without first subjecting the mixture hydrocarbons to an operation for partially de-mercaptanizing the hydrocarbon mixture under such conditions larger amounts, say 3 to 5 times, of the predetermined additive and larger amounts of caustic can be added to the mixture of hydrocarbons and the mixture of hydrocarbons, sweetening additive, and caustic allowed to react for a longer period of time, say up to three or four times that required to sweeten a similar mixture of hydrocarbons containing about 0.005 weight per cent mercaptan sulfur.

The general procedure can be modified further with improved results. That is the rate of sweetening can be accelerated by adding the sweetening additive or agent before subjecting the mixture of hydrocarbons to a caustic wash. The data submitted in Table V is a basis for the foregoing statement.

Table V

Hydrocarbon mixture: tannin-solutizer treated gasoline containing 0.005 to 0.007 weight per cent mercaptan-sulfur.
Sweetening additive or agent: di-secondary butyl catechol.
Concentration of sweetening additive or agent: 5 and 10 pounds per 1000 barrels.

	Sequence of addition of reagents	Weight % mercaptan-sulfur in untreated gasoline	Sweetening time, hours	
			5 pounds per 1000 bbls.	10 pounds per 1000 bbls.
1	Gasoline+Sweetening agent+10% wash of aqueous 20% KOH	0.005	[1] 0	[1] 0
2	Gasoline+10% wash of aqueous 20% KOH+sweetening agent	0.005	3	1
3	Gasoline+Sweetening agent+30 parts per million of 3% alcoholic KOH	0.007	20	----------
4	Gasoline+sodium salt of sweetening agent	0.005	>90	1

[1] Practically instantaneous.

The data in Table V establish that the addition of the sweetening agent or additive to the mixture of hydrocarbons before subjecting the mixture to a caustic wash causes a much more rapid sweetening action than that achieved by adding the additive after a caustic wash. A further improvement can be achieved by carrying out the treatment in the presence of a gas containing free oxygen, for example air or even oxygen per se. The data presented in Table VI provide a basis for this conclusion.

Table VI

Mixture of hydrocarbons: gasoline.
Mercaptan-sulfur content, weight per cent mercaptan-sulfur: 0.005.
Pounds of di-secondary butyl-catechol per 1000 barrels of gasoline: 5.
Sequence of addition of reagents: gasoline plus sweetening agent plus contact with aqueous 20% KOH.

Condition	Sweetening time
	Hours
Air Present	2
Air Excluded	>96

Accordingly, the present invention comprises sweetening a sour mixture of hydrocarbons containing not more than about 0.02 per cent and preferably less than about 0.005 per cent by weight of mercaptan-sulfur by the action of a gum inhibitor selected from the group consisting of alkyl catechols, alkaryl diamines and quinones in the presence of alkali metal hydroxide. Preferably, the sweetening agent, i. e. the gum inhibitor, is added to the sour mixture of mercaptans before the mixture of hydrocarbons is contacted with air and aqueous solution of alkali metal hydroxide. In addition, it is preferred to sweeten the sour mixture of hydrocarbons in the presence of a gas containing free oxygen.

I claim:

1. A method of producing a petroleum fraction negative in the "doctor test" from a sour petroleum fraction containing not more than about 0.02 weight per cent of mercaptan sulfur which comprises mixing a sour petroleum fraction containing not more than about 0.02 weight per cent mercaptan sulfur with a di-secondary butyl catechol in the presence of alkali metal hydroxide.

2. The method described and set forth in claim 1 in which the sour petroleum fraction and di-secondary butyl catechol are maintained at ambient temperatures.

3. The method described and set forth in claim 1 in which the sour petroleum fraction and di-secondary butyl catechol are maintained at a temperature between ambient temperatures and the reflux temperature.

4. A method of sweetening a sour petroleum fraction which comprises partially demercaptanizing a sour petroleum fraction to obtain a treated petroleum fraction positive in the doctor test and containing not more than about 0.005 weight per cent mercaptan sulfur, separating said treated petroleum fraction from the treating medium and, mixing said treated petroleum fraction with a di-secondary butyl catechol in the presence of alkali metal hydroxide.

5. The method described in claim 4 in which the mixture of treated petroleum fraction and di-secondary butyl catechol is maintained at ambient temperatures.

6. The method described in claim 4 in which the mixture of treated petroleum fraction and di-secondary butyl catechol is heated to reflux in the presence of alkali metal hydroxide.

7. A method of sweetening a sour petroleum fraction which comprises contacting a sour petroleum fraction with an alkaline solutizer solution containing a tannin to demercaptanize partially said fraction and provide a treated fraction positive in the "doctor test" and containing not more than about 0.005 weight per cent mercaptan sulfur, separating said treated fraction from said alkaline solutizer solution, and mixing said treated fraction with di-secondary butyl catechol.

8. The method as set forth in claim 7 in which the butyl catechol and treated gasoline are heated to reflux temperatures.

9. A method of sweetening a sour petroleum fraction which comprises contacting a sour petroleum fraction with an alkaline solutizer solution containing a polyhydroxy benzene to demercaptanize partially said fraction and provide a treated fraction positive in the "doctor test" and containing not more than about 0.005 weight per cent mercaptan sulfur, separating said treated fraction from said alkaline solutizer solution, and mixing said treated fraction with di-secondary butyl catechol.

10. A method of sweetening a sour petroleum fraction which comprises contacting a sour petroleum fraction with an alkaline solutizer solution containing a polyhydroxy benzene carboxylic acid to demercaptanize partially said fraction and provide a treated fraction positive in the "doctor test" and containing not more than about 0.005 weight per cent mercaptan sulfur, separating said treated fraction from said alkaline solutizer solution, mixing said treated fraction with di-secondary butyl catechol and maintaining the mixture of sour hydrocarbon mixture and alkyl catechol at a temperature between ambient temperature and the reflux temperature.

11. A method of producing mixtures of hydrocarbons negative in the "doctor test" from sour mixtures of hydrocarbons containing not more than about 0.005 weight per cent mercaptan sulfur which comprises mixing a sour mixture of hydrocarbons containing not more than about 0.005 weight per cent mercaptan sulfur and di-secondary butyl catechol in the presence of alkali metal hydroxide.

12. A method of sweetening a sour mixture of hydrocarbons which comprises adding a gum inhibitor selected from the group consisting of di-secondary butyl catechol, di-secondary butyl phenylene diamine and quinone to a sour mixture of hydrocarbons containing not more than about 0.02 weight per cent of mercaptan-sulfur, and contacting said mixture of hydrocarbons and said gum inhibitor with an aqueous solution of alkali metal hydroxide.

13. The method described and set forth in claim 12 in which the sweetening of the sour mixture of hydrocarbons is carried out in the presence of a gas containing free oxygen.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,369,771	Bond	Feb. 20, 1945
2,413,945	Bolt	Jan. 7, 1947

FOREIGN PATENTS

Number	Country	Date
435,965	Great Britain	Oct. 2, 1935

OTHER REFERENCES

Bond: "Regeneration of Caustic Solutions for Gasoline—Oxidation," reprint from Oil & Gas. Jour., December 8, 1945.