

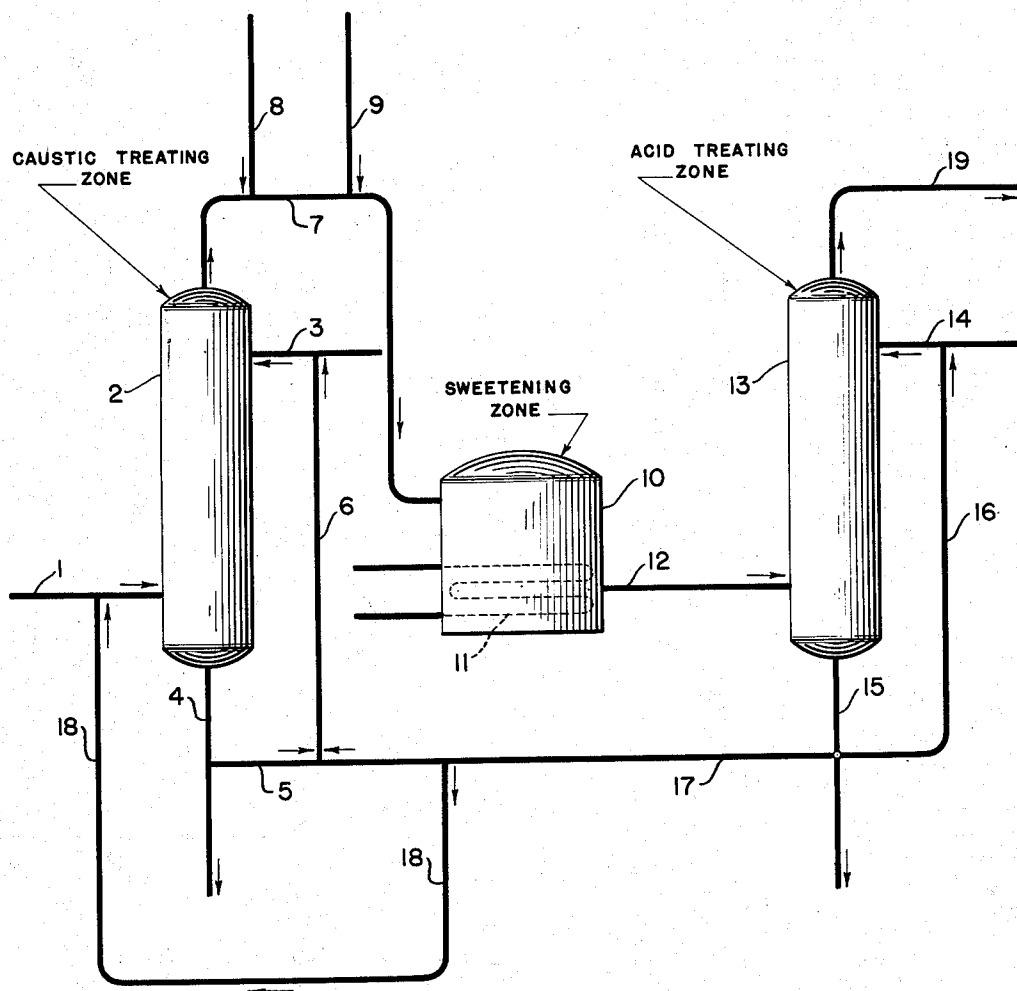
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SWEETENING OF SOUR HYDROCARBON DISTILLATES

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SWEETENING OF SOUR HYDROCARBON
DISTILLATES

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1

This invention relates to the sweetening of sour hydrocarbon distillates and more particularly to a combination process whereby the sweetening is effected in a novel and improved manner.

One method of removing mercaptans from a hydrocarbon distillate comprises treating the hydrocarbon distillate with an alkali metal hydroxide solution and particularly sodium hydroxide solution, potassium hydroxide solution, etc. In this method, the alkali metal hydroxide reacts with the mercaptans to form mercaptides, the latter being soluble in the alkali metal hydroxide solution and thereby is separated and withdrawn from the hydrocarbon distillate. A modification of this process is the use of a solutizer along with the alkali metal hydroxide solution in order to increase solubility of the mercaptans in the alkali metal hydroxide solution.

The process referred to above is satisfactory for use in removing a major proportion of the mercaptans from the hydrocarbon distillate. The treated hydrocarbon distillate is not sweet to the doctor test and, therefore, requires further treatment to remove or oxidize the last portion of mercaptans. In the past the practice has been to utilize such processes as doctor sweetening, copper treating, hypochlorite treating, etc. in order to obtain a sweet product.

Another method of treating a sour hydrocarbon distillate, and particularly a distillate which had been treated with caustic or the like to remove a major proportion of the mercaptans, is the process referred to as "inhibitor sweetening." In this process a phenylene diamine compound is commingled with the sour distillate and the distillate is allowed to remain in storage in the presence of air until the mercaptans contained therein are converted into disulfides, and a sweet product is obtained. This process has the objection that in many cases it is necessary for the hydrocarbon distillate to remain in storage for several days or more in order to become sweet. Due to the shortage of storage capacity or in order to meet shipping schedules or for other reasons, it often is necessary for the refiner to transport or use the hydrocarbon distillate within a very short time after it is produced, and the refiner does not wish to wait until sufficient time has elapsed for the hydrocarbon distillate to become sweet before transporting or using the same.

The rate at which inhibitor sweetening occurs depends, among other things, on the concentration of the phenylene diamine inhibitor added to the sour hydrocarbon distillate. Sweetening is accelerated by the use of larger concentra-

2

tions. However, the use of an excess of inhibitor over that normally required to obtain the necessary stability properties of the distillate is uneconomical, and the present invention is directed to a novel combination process whereby the excess inhibitor is recovered from the hydrocarbon distillate and is reused in the process.

In one embodiment the present invention relates to the method of sweetening a sour hydrocarbon distillate which comprises treating said distillate with a phenylene diamine compound in a molal quantity in excess of the molal quantity of mercaptans contained in said distillate, allowing the distillate to become substantially sweet, and thereafter removing excess phenylene diamine compound by treating the substantially sweet distillate with an acid.

In a specific embodiment the present invention relates to the method of sweetening sour gasoline which comprises treating said gasoline with caustic solution to remove a proportion of the mercaptans from said gasoline, introducing said gasoline to a sweetening zone wherein the gasoline undergoes sweetening in the presence of N,N'-di-secondary-butyl-p-phenylene diamine in a molal quantity in excess of the molal quantity of mercaptans contained in said gasoline, thereafter treating said gasoline with sulfuric acid to remove excess N,N' - di - secondary - butyl - p-phenylene diamine, separating an acidified phenylene diamine phase from gasoline, and commingling the acidified phenylene diamine with said caustic to liberate N,N'-di-secondary-butyl-p-phenylene diamine and to incorporate the liberated inhibitor in the gasoline being treated by said caustic.

The invention is further described in the accompanying diagrammatic flow drawing which illustrates several specific embodiments of the invention.

The process of the present invention is particularly applicable to the treatment of gasoline, which may be substantially olefinic or saturated. Olefinic gasolines include cracked gasoline, both catalytically and non-catalytically cracked, polymer gasoline, etc., and saturated gasolines include straight run gasoline, catalytically reformed gasoline, natural gasoline, etc. However, it is understood that the present invention also may be employed, with suitable modifications when necessary, for the treatment of higher boiling hydrocarbon distillates including both virgin and processed distillates such as kerosene, diesel fuel, light gas oil, etc.

In the interest of simplicity, the drawing will be described in connection with a process for the

treatment of sour gasoline utilizing caustic solution in the first step of the process. Referring to the drawing, the gasoline is introduced to the process through line 1 and is directed to caustic treating zone 2. It is understood that any suitable alkaline treating agent may be used in this step of the process and particularly comprises an alkali metal hydroxide solution. Caustic solution is preferred and generally will be utilized as an aqueous solution of from about 10° to about 50° Baumé gravity. The caustic solution will be employed in an amount sufficient to effect the removal of a proportion of the mercaptans contained in the gasoline and also to effect neutralization of the acidified phenylene diamine compound supplied to this zone in the manner to be hereinafter set forth.

It is understood that solutizers may be included along with the alkali metal hydroxide solution. Preferred solutizers comprise the low boiling alcohols including methyl alcohol, ethyl alcohol, propyl alcohol, etc., isobutyrate including potassium isobutyrate, sodium isobutyrate, etc., phenolic compounds including phenols, cresols, xlenols, etc. and their alkali metal salts.

Zone 2 may comprise any suitable zone for effecting intimate contact of the gasoline and caustic solution therein, and may be either of batch or continuous type operation. Zone 2 may contain suitable packing material, such as carbon Raschig rings, etc. and/or suitable contacting means including side to side pans, bubble decks, jets, baffle plates, etc. In the case here illustrated, zone 2 conveniently comprises a batch type operation in which the caustic solution originally is introduced to zone 2 through line 3, and the caustic solution from the bottom of zone 2 is continuously recirculated by way of lines 4, 5, 6 and 3 within zone 2. After the caustic solution is no longer active for the desired purpose, the introduction of gasoline through line 1 may be discontinued, and the caustic solution may be withdrawn from the process through line 4, after which fresh caustic solution is introduced into zone 2 through line 3. The life of the caustic solution will vary with the H₂S, mercaptan, and acid oil content of the sour gasoline charge, with the amount of phenylene diamine inhibitor employed and the acid required to extract it from the sweetened gasoline, with the temperature of operation, etc. In any event, the caustic solution should be discarded before it no longer is definitely alkaline and fails to neutralize the acid salt of the inhibitor.

The caustic treatment generally is effected at substantially atmospheric temperature which may range from 50° to 100° F., although, when desired, temperatures up to about 200° F. or more may be employed. Generally the pressure employed in zone 2 will be below about 25 pounds per square inch but higher pressures up to 200 pounds or more may be employed, when desired.

The gasoline substantially lower in mercaptan content is withdrawn from zone 2 through line 7. At the start of the operation or as subsequently required, a suitable phenylene diamine compound is introduced to the process through line 8 to commingle with the gasoline being withdrawn from zone 2. Any suitable phenylene diamine compound may be employed in accordance with the present invention. A preferred compound comprises N,N'-di-secondary-butyl-p-phenylene diamine. Other phenylene diamine compounds include N,N'-di-alkyl-p-phenylene diamines in which the alkyl groups contain from 1 to about 12 carbon atoms per molecule including such

compounds as N,N'-di-isopropyl-p-phenylene diamine, N,N'-di-secondary-amyl-p-phenylene diamine, N,N'-di-secondary-hexyl-p-phenylene diamine, N-isopropyl-N'-secondary-butyl-p-phenylene diamine, N-isopropyl-N'-secondary-amyl-p-phenylene diamine, etc.

In accordance with the present invention the phenylene diamine compound is employed in a molal quantity in an excess of the molal quantity of mercaptans contained in the gasoline. This in turn means that the quantity of phenylene diamine compound to be employed is in excess of that required to impart the necessary stability properties to the gasoline and also generally will be in excess of that stoichiometrically required to effect sweetening of the distillate. Thus the amount of phenylene diamine compound to be employed will depend upon the concentration of mercaptans in the gasoline but in general will be within the range of from about 0.008% to about 1% or more by weight of the gasoline. As hereinbefore set forth, the use of the excess quantity of phenylene diamine compound accelerates the sweetening reaction and thereby avoids the necessity of retaining the gasoline in storage for an excessive time.

As the conversion of mercaptans to disulfides is an oxidation reaction, the presence of air is essential in the sweetening zone. In some cases the gasoline will contain sufficient air dissolved or entrained therein to satisfy the requirements. When necessary, air from an extraneous source may be introduced to the process through line 9. It is understood that oxygen or other oxygen-containing gas mixtures may be employed in place of or in addition to air. In another embodiment, the phenylene diamine compound and/or air may be introduced directly to zone 10.

The gasoline containing phenylene diamine compound and air is directed by way of line 7 to inhibitor sweetening zone 10. While the inhibitor sweetening may be effected at substantially atmospheric temperatures, in a preferred embodiment of the present invention the inhibitor sweetening is effected at an elevated temperature which may range from about 100° to about 200° F. or more. Zone 10 may be heated in any suitable manner, when desired, as by means of steam coil 11. The use of elevated temperatures is particularly preferred when treating substantially saturated hydrocarbon distillates.

The gasoline remains in zone 10 until it is substantially sweet, which, in accordance with the present invention, will be for a shorter period of time than would be required when lower quantities of phenylene diamine compound are employed. The substantially sweet gasoline is withdrawn from zone 10 through line 12 and is directed to the acid treating zone 13. Any suitable acid may be employed for the purpose of extracting the phenylene diamine compound and to separate the same from the gasoline. Preferably a mineral acid is employed and in a concentration of such strength to avoid metal corrosion and olefin polymerization. Avoiding undesirable polymerization of the gasoline by the acid eliminates the necessity of subsequent re-running or distilling of the gasoline to remove the higher boiling polymers. A preferred acid for use in accordance with the invention comprises sulfuric acid of from about 70% to about 98% concentration. Other acids include weakly ionized solutions of hydrochloric acid, hydrofluoric acid, phosphoric acid, etc. Certain organic acids may be employed including, for ex-

ample, formic acid, acetic acid, alkane sulfonic acids, including methyl sulfonic acid, ethyl sulfonic acid, etc., aromatic sulfonic acids, including benzene sulfonic acid, toluene sulfonic acid, etc.

The acid is employed in an amount sufficient to acidify excess phenylene diamine compound but preferably is not used in an excessive amount. This is for the reason that the acidified phenylene diamine compound is subsequently neutralized with caustic solution in order to liberate the phenylene diamine compound, and the use of an excessive amount of acid means that excess caustic is required in its neutralization. Sulfuric acid generally will be used in an amount of from about 0.01 to about 0.5 pound or more per barrel of gasoline being treated.

Zone 13 may comprise any suitable zone for effecting intimate contact of the gasoline with the acid, and may comprise either batch or continuous operation. Zone 13 may contain packing and contacting means as heretofore described in connection with zone 2. In the case here illustrated, the acid is introduced to zone 13 through line 14 and acid is withdrawn from the lower portion of zone 13 through line 15 and is recirculated to the upper portion of zone 13 by way of lines 16 and 14. Although all or a portion of the acid may be removed from the process through line 15, in accordance with the invention at least a portion of the acidified phenylene diamine compound is directed by way of lines 17, 6 and 3 or by way of lines 17, 18 and 1 to caustic treating zone 2.

In zone 2 the acid salt of the phenylene diamine compound is neutralized, thereby releasing the phenylene diamine compound. The phenylene diamine compound dissolves in the hydrocarbon phase since it is insoluble in the caustic phase. By this means the phenylene diamine compound is recovered and reused in the process.

The substantially sweet gasoline is withdrawn from zone 13 through line 19. When the gasoline is an olefinic gasoline, it generally will be desirable to add additional inhibitor thereto in order to insure that the gasoline will have the necessary stability properties. The inhibitor to be added to the gasoline preferably comprises a phenylene diamine compound but, in another embodiment of the invention, may comprise any suitable inhibitor which will effect the desired stabilization of the gasoline.

In the interest of simplicity, valves, pumps, and similar appurtenances have been omitted from the drawing. These are conventional equipment and it is understood that they will be provided if necessary.

In the event that the gasoline charging stock contains hydrogen sulfide, the gasoline preferably is given a pretreatment with caustic solution or otherwise to remove the hydrogen sulfide prior to treatment within the process illustrated in the drawing. In another embodiment of the present invention, the gasoline may be given a preacidic wash, utilizing a caustic solution of from about 5° to about 25° Baumé gravity, then treated to remove a substantial proportion of the mercaptans in zone 2 which, in this embodiment of the invention, preferably is a regenerative caustic treating step and utilizes a conventional regenerator to renew the caustic for further use in the process. In this embodiment of the invention, the acidified phenylene diamine compound will be supplied to the caustic prewash zone rather than to the regenerative

caustic step of the process. As the caustic in the prewash step becomes unsatisfactory for further use, in the manner hereinbefore set forth, the caustic may be discarded or utilized for any other desired purpose.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

Example I

A West Texas thermally cracked gasoline having a mercaptan sulfur content of about 0.08% by weight may be treated with an aqueous caustic solution of 20° Baumé gravity at 75° F. to reduce the mercaptan sulfur content of the gasoline to about 0.009% by weight. The gasoline is stored in the presence of air and 0.01% by weight of N,N'-di-secondary-butyl-p-phenylene diamine at a temperature of 75° F. until the gasoline is substantially sweet. The substantially sweet gasoline containing excess phenylene diamine compound then is treated with 0.08 pound of 78% sulfuric acid per barrel of gasoline at a temperature of 75° F. The acid layer from the acid treating zone is introduced into the caustic treating step of the process and, in this manner, the phenylene diamine compound is released from the acid and is incorporated into the gasoline being treated in the process.

It will be found that, when operating in the manner hereinbefore set forth, the time required for sweetening of the gasoline is considerably reduced as compared to a process in which a smaller amount of the phenylene diamine compound is employed.

Example II

An Illinois straight run gasoline having a mercaptan sulfur content of 0.015% by weight and containing hydrogen sulfide is given a prewash treatment utilizing caustic solution of 15° Baumé gravity. The gasoline free of hydrogen sulfide is then treated in zone 2 with caustic solution of 30° Baumé gravity, and the mercaptan sulfur content of the gasoline is reduced to about 0.0075% by weight. The gasoline then is sweetened in the presence of 0.015% by weight of N,N'-di-secondary-amylyl-p-phenylene diamine at a temperature of 140° F. The sweetened gasoline containing excess phenylene diamine compound is treated with 90% sulfuric acid in an amount of 0.1 pound of acid per barrel of gasoline. The acid layer from the acid treating zone is supplied to the caustic prewash zone and the liberated phenylene diamine compound is incorporated into the gasoline being supplied to the subsequent steps of the process.

I claim as my invention:

1. The method of sweetening sour gasoline which comprises treating said gasoline with N,N'-di-secondary-butyl-p-phenylene diamine in a molal quantity in excess of the molal quantity of mercaptans contained in said gasoline, allowing the gasoline to remain in storage in the presence of air until it is substantially sweet, thereafter removing excess N,N'-di-secondary-butyl-p-phenylene diamine by treating the substantially sweet gasoline with sulfuric acid of a concentration of at least 70%, commingling the acidified N,N'-di-secondary-butyl-p-phenylene diamine with sour gasoline, and thereafter treating the last mentioned gasoline with an alkaline compound to release N,N'-di-secondary-butyl-p-phenylene diamine to said gasoline.

2. The method of sweetening a sour hydrocar-

bon distillate which comprises treating said distillate with a phenylene diamine sweetening agent in a molal quantity in an excess of the molal quantity of mercaptans contained in said distillate, allowing the distillate to remain in storage in the presence of air until it is substantially sweet, thereafter removing excess phenylene diamine sweetening agent by treating the substantially sweet distillate with an acid, commingling the acidified phenylene diamine sweetening agent with a sour hydrocarbon distillate, and thereafter treating the last mentioned distillate with an alkaline compound to release the phenylene diamine sweetening agent to said distillate.

3. The method of sweetening a sour hydrocarbon distillate which comprises treating said distillate with N,N'-di-secondary-butyl-p-phenylene diamine in a molal quantity in excess of the molal quantity of mercaptans contained in said distillate, allowing the distillate to remain in storage in the presence of air until it is substantially sweet, thereafter removing excess N,N'-di-secondary-butyl-p-phenylene diamine by treating the substantially sweet distillate with sulfuric acid of from about 70% to about 98% concentration, commingling the acidified N,N'-di-secondary-butyl-p-phenylene diamine with a sour hydrocarbon distillate, and thereafter treating the last mentioned distillate with caustic solution to release the N,N'-di-secondary-butyl-p-phenylene diamine to said distillate.

4. The method of sweetening sour gasoline which comprises treating said gasoline with N,N'-di-secondary-butyl-p-phenylene diamine in a molal quantity in excess of the molal quantity of mercaptans contained in said gasoline, allowing the gasoline to remain in storage in the presence of air until it is substantially sweet, thereafter removing excess N,N'-di-secondary-butyl-p-phenylene diamine by treating the substantially sweet gasoline with sulfuric acid of from about 70% to about 98% concentration, commingling the acidified N,N'-di-secondary-butyl-p-phenylene diamine with sour gasoline, and thereafter treating the last mentioned gasoline with caustic solution to release the N,N'-di-secondary-butyl-p-phenylene diamine to said gasoline.

5. The method of sweetening a sour hydrocarbon distillate which comprises treating said distillate with an alkaline reagent to remove a major proportion of the mercaptans from said distillate, introducing said distillate to a sweetening zone wherein the distillate undergoes sweetening in the presence of a phenylene diamine sweetening agent in a molal quantity in excess of the molal quantity of mercaptans contained in said distillate, thereafter treating said distillate with an acid to remove excess phenylene diamine sweetening agent, separating acidified phenylene diamine sweetening agent from hydrocarbon distillate, and commingling the acidified phenylene diamine sweetening agent with said alkaline reagent to liberate phenylene diamine sweetening agent and incorporate the liberated phenylene diamine sweetening agent in sour hydrocarbon distillate being treated with said alkaline reagent.

6. The method of sweetening sour gasoline

which comprises treating said gasoline with an alkaline reagent to remove a major proportion of the mercaptans from said gasoline, introducing the gasoline to a sweetening zone wherein the gasoline undergoes sweetening in the presence of air and a phenylene diamine sweetening agent in a molal quantity in excess of the molal quantity of mercaptans contained in the gasoline, thereafter treating the gasoline with an acid to remove excess phenylene diamine sweetening agent, separating acidified phenylene diamine sweetening agent from gasoline, and commingling the acidified phenylene diamine sweetening agent with said alkaline reagent to liberate phenylene diamine sweetening agent and to incorporate the liberated phenylene diamine sweetening agent in sour gasoline being treated with the alkaline reagent.

7. The method of sweetening sour gasoline which comprises treating said gasoline with caustic solution to remove a major proportion of the mercaptans from said gasoline, introducing the gasoline to a sweetening zone wherein the gasoline undergoes sweetening in the presence of air and N,N'-di-secondary-butyl-p-phenylene diamine in a molal quantity in excess of the molal quantity of mercaptans contained in the gasoline, thereafter treating the gasoline with sulfuric acid of at least 70% concentration to remove excess N,N'-di-secondary-butyl-p-phenylene diamine, separating acidified N,N'-di-secondary-butyl-p-phenylene diamine from gasoline, and commingling the acidified N,N'-di-secondary-butyl-p-phenylene diamine with said caustic solution to liberate N,N'-di-secondary-butyl-p-phenylene diamine and to incorporate the liberated N,N'-di-secondary-butyl-p-phenylene diamine in sour gasoline being treated with the alkaline reagent.

8. A method of refining a sour hydrocarbon distillate which comprises contacting the distillate with an alkaline reagent in a treating zone, maintaining the thus treated distillate in contact with air and a phenylene diamine sweetening agent in a molal quantity in excess of the molal quantity of mercaptans contained in said treated distillate, thereafter treating the distillate with an acid to remove excess sweetening agent from the distillate, and supplying the acidified sweetening agent to said treating zone to release the phenylene diamine sweetening agent and incorporate the same into sour distillate being contacted with alkaline reagent in said zone.

9. The method of claim 8 further characterized in that said sweetening agent comprises N,N'-di-secondary-butyl-p-phenylene diamine.

10. The method of claim 8 further characterized in that said acid is sulfuric acid.

WARREN W. JOHNSTONE.

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