

March 8, 1949.

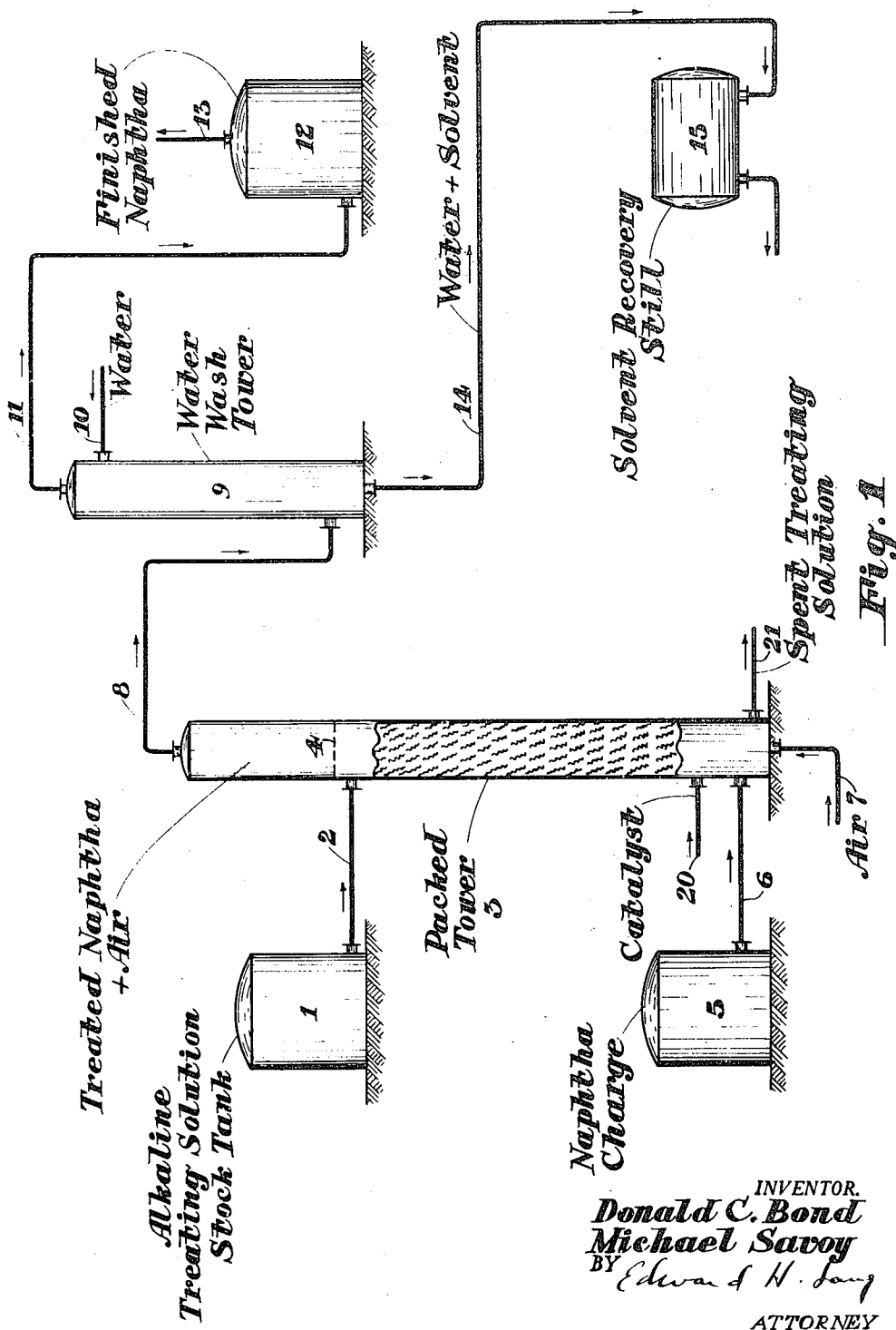
D. C. BOND ET AL

2,464,019

METHOD OF OXIDIZING ACIDIC SULFUR COMPOUNDS

Filed Nov. 13, 1946

2 Sheets-Sheet 1



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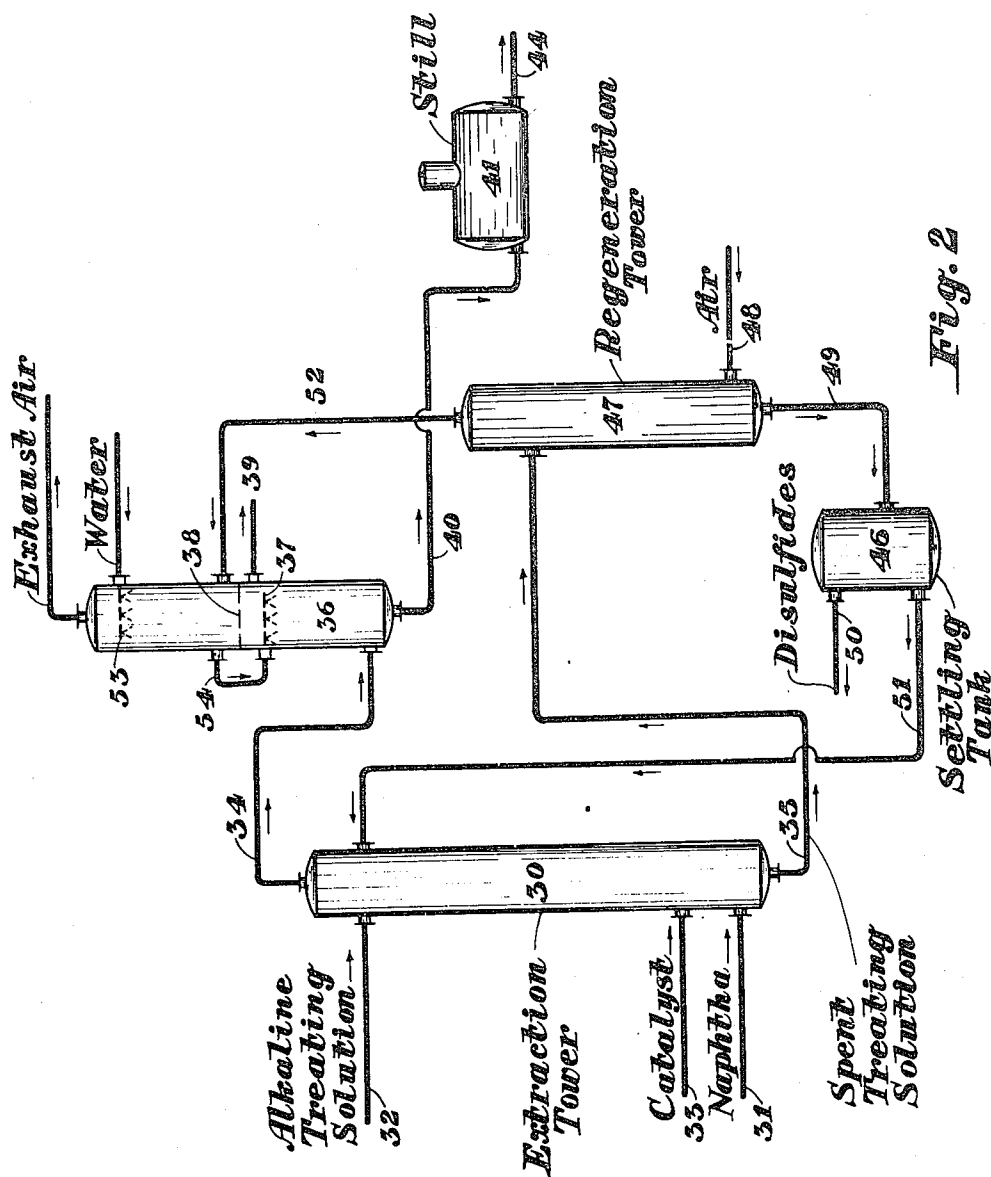


Fig. 2

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2,464,019

METHOD OF OXIDIZING ACIDIC SULFUR COMPOUNDS

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Application November 13, 1946, Serial No. 709,504

15 Claims. (Cl. 196—29)

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This invention relates to a method of removing acidic or malodorous sulfur compounds from hydrocarbon fluids such as low-boiling naphthas, kerosenes, and gasolines, and similar solvent materials, and to a method for converting such compounds in the hydrocarbon liquid to sulfur compounds of unobjectionable odor.

It is an object of the invention to provide an economical and convenient method of sweetening gasolines and hydrocarbon liquids of like boiling range, which method can be practiced in batch or continuous flow process.

It is another object of the invention to improve upon prior processes in respect to the amount of solvent recoverable from the treatment of the hydrocarbon fluid.

It is a further object of the invention to provide a relatively rapid continuous process for the oxidation of mercaptans contained in hydrocarbon liquids to disulfides.

It is a still further object of the invention to provide a catalytic process for the air oxidation of mercaptans occurring in low boiling hydrocarbons in which a minimum amount of water is used in the oxidation step.

Other objects and advantages of the invention will in part be obvious, and in part appear hereinafter.

We have discovered that sweetening of hydrocarbon oils by oxygen or air in the presence of catalysts and alkali solutions can be carried out with great convenience when a medium having properties like those of ethylene glycol or glycerine is used. Similar fluids of low volatility, miscible with water and substantially immiscible with hydrocarbon to be treated are good media. By employing such a medium for the alkaline catalytic oxidizing solution the process can be carried out so that there is a minimum amount of interdiffusion of phases, that is, little hydrocarbon is dissolved in the solvent, thereby materially simplifying auxiliary steps in the process which deal with solvent recovery and regeneration of the treating solution. In addition, because the process is carried out with very little water present, the retarding effect of water on the rate of the oxidation reaction is substantially avoided. We have found that the air regeneration of the catalyst-containing alkaline glycol or glycerine solutions used to oxidize the mercaptans and other acidic sulfur compounds occurring in the hydrocarbon fluid is greatly accelerated when the treating solution contains a small amount of a phenolic oxidation catalyst, such as pyrogallol, or the com-

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plex mixture of compounds known to the trade as wood tar distillates, or U. O. P. Inhibitor No. 1 which contains pyrogallol and derivatives. It is essential that the catalyst be soluble in an effective amount of the alkaline glycol solution. Effective catalysts having the proper degree of solubility in the treating solution include not only hard wood tar and pyrogallol, but such closely related quinone forming compounds as hydroquinone, n-butyl pyrogallol, anthragallol, gallic acid, tannic acid, 3,4-dihydroxy diphenyl, 2,5-dihydroxy diphenyl, butyl pyrogallol and monomethyl ether of pyrogallol.

As examples of hard wood tars which are particularly effective are U. O. P. Inhibitor No. 1 and I Tar Oil. U. O. P. Inhibitor No. 1 is the commercial designation of a product sold by the Universal Oil Products Company as a gasoline antioxidant. It is a hard wood tar fraction boiling between 240° and 300° C. I Tar Oil is a settled hard wood tar sold by the Tennessee Products Company. For the method for producing the wood tars, reference should be had to the article entitled "New Products from Wood Carbonization," by A. W. Goos and A. A. Reiter of the Cliffs Dow Chemical Company, Marquette, Michigan, which appeared in the February 1946, issue of The Journal of Industrial and Engineering Chemistry, pages 132 to 135, inclusive. The catalysts are effective when present in the alkaline glycol or glycerine solution in amounts of approximately 0.1 to 3 per cent by weight, although we prefer to use an amount equivalent to about 1 to 2 per cent by weight.

In accordance with the invention the alkaline treating agent may be a solution of an alkali metal hydroxide, for example, sodium, potassium or lithium hydroxide, in ethylene glycol, glycerine, polyethylene glycol or any mixtures thereof. Generally, it is desirable to have a small amount of water in the system to help prevent any substantial amount of the solvent medium from dissolving in the hydrocarbon undergoing treatment and to aid in bringing the hydroxide into solution. However, when water is present in the treating solution in amounts approaching about 25 per cent, a noticeable decrease in the rate of oxidation of mercaptans or other acidic sulfur compounds occurs. Accordingly, the amount of water in the system should be kept at a minimum, that is, balanced between the amount deemed necessary for making up the oxidizing solution and keeping the phases separated as against an amount which will adversely affect the rate of reaction. The amount of alkali in the solution may vary from

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approximately 5 per cent by weight to an amount sufficient to saturate the solution, although we prefer to use solutions containing between 5 and 25 per cent by weight of caustic alkali. Although oxidation proceeds more rapidly at elevated temperatures than at lower temperatures, treating temperatures above approximately 130° F. should be avoided and are best kept at about ambient atmospheric temperature in order to obviate the possibility of inducing undesirable oxidation.

In the accompanying drawing Figure 1 sets forth a flow diagram which illustrates an apparatus and method for sweetening hydrocarbons in accordance with the process of our invention;

Figure 2 likewise sets forth a flow diagram of an apparatus to illustrate the method for removing acidic sulfur compounds from hydrocarbons according to the process of our invention.

Referring particularly to Figure 1, storage tank 1 holding alkaline treating solution containing approximately 1 per cent by weight of a phenolic oxidation catalyst such as U. O. P. Inhibitor No. 1 or I Tar Oil feeds sufficient solution through line 2 into packed tower 3 to fill the tower to the level indicated by line 4. Naphtha from tank 5 is passed through line 6 into the bottom of tower 3. Air is bubbled into the bottom of the tower 3 through line 7. The mercaptans in the naphtha are oxidized to disulfides by the air in the presence of the alkaline treating solution containing the catalyst. The sweetened naphtha containing disulfides and the spent air pass over from the top of the tower 3 through line 8 to the lower portion of wash tower 9. Water is admitted to the top of the wash tower through line 10 in order to wash dissolved and entrained treating agent from the naphtha. About 1 to 5 per cent by volume of water based on the naphtha is sufficient to remove the little treating agent contained in solution in the naphtha. The washed naphtha and spent air pass from the top of the tower 9 through line 11 into finished naphtha tank 12 from which spent air escapes through line 13. The escaping air may be further washed with an absorbent such as gas oil or kerosene, if necessary, to remove any hydrocarbon vapors which may be contained therein.

Wash-water leaving the bottom of wash tower 9 through line 14 can be brought to a solvent recovery still 15, but since the amount of solvent carried from the oxidation stage is very small, it can be discarded without processing.

Make-up alkaline treating solution may be added to the tower 3 from time to time through line 2. Catalyst may be added to the tower as found necessary through line 20. A withdrawal line 21 is provided at the bottom of the tower 3 in order to permit periodic removal of treating solution as it becomes spent.

The amount of air fed to the tower 3 through line 7 is regulated so as to supply sufficient air to sweeten the naphtha, but care should be exercised not to bubble air through the tower at such rate or in such amount as to entrain excessive quantities of treating solution and hydrocarbon vapors.

Referring now to Figure 2, numeral 30 indicates a packed tower into the bottom of which line 31 feeds naphtha or other hydrocarbon fluid to be treated and to the top of which line 32 feeds alkaline treating solution. Line 33, is provided adjacent to the bottom of the tower to furnish catalyst as required. Sweetened naphtha leaves the top of the tower through line 34 and spent alkaline sweetening solution leaves the bottom of the

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tower through line 35. The naphtha passes from line 34 to the bottom of tower 36 where it is washed with a stream of water which enters the upper portion of the lower section of the tower through the spray head 37. The tower 36 is divided into two sections by the imperforate plate 38.

Washed naphtha leaves the upper portion of the lower section of tower 36 through line 39 and passes to storage. The wash-water, containing a small amount of solvent washed from the naphtha, leaves the bottom of tower 36 through line 40 and passes to solvent recovery still 41. Since very little solvent is dissolved in the naphtha, the solvent recovery can be omitted and the wash-water discarded.

The spent alkaline treating solution leaving the extraction tower 30 through line 35 passes to the upper portion of a packed regeneration tower 47. Air is bubbled into the lower portion of the tower 47 through line 48. The mixture of regenerated solution and disulfides leaves the bottom of tower 47 through line 49 and passes to the settling tank 46 in order to permit the disulfides and solution to stratify. The disulfides are withdrawn from the top of settling tank 46 through line 50. The regenerated solution together with the solvent recovered from still 41 is recycled through line 51 to the upper portion of extraction tower 30.

Spent air leaves the top of the regenerating tower 47 through line 52 and passes to the lower portion of the upper section of the water-wash tower 36. Water is sprayed into the upper portion of the upper section of wash-tower 36 through spray head 53. In this washing operation hydrocarbon vapors and solvent contained in the spent air are washed therefrom. The wash-water from the upper section of tower 36 passes through line 54 to the spray-head 37 in the lower section of the tower. Where the hydrocarbon undergoing treatment is a relatively high-boiling material, such as naphtha or kerosene, the washing of the spent air in the upper section of tower 36 may be dispensed with. Instead of water, a hydrocarbon absorbent such as gas oil or kerosene may be used to wash the air in the upper section of the tower. In that case the absorbent will be withdrawn through a line (not shown) in the bottom of the upper section of the tower and water fed into the upper portion of the lower section. The water leaving still 41 through line 44 may be used as wash water in either or both sections of tower 36.

The volume ratio of treating solution to hydrocarbon fluid treated may vary from about 1 to 20 to about 1 to 2. With an efficient contact tower a volume of treating solution equal to about 5 to 10 per cent by volume of the hydrocarbon fluid is sufficient to remove substantially all acidic sulfur compounds from the fluid.

The apparatus and method thus far described have dealt specifically with continuous flow processes. It is understood that in such a case the several rates of flow of hydrocarbon and treating solution will be adjusted to give the desired or needed time of contact in the treating tower. The practice of the process in batchwise operation involves merely contracting the hydrocarbon and the alkaline treating solution for the required time in a mixing tank, allowing the phases to separate, and decanting the sweetened hydrocarbon.

The effectiveness of our process for sweetening hydrocarbon fluids by using various glycols, poly-

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ethylene glycol fluids, glycerine and like organic compounds as vehicles for the alkaline treating solution and the economy of the method as shown by the efficacy of the reaction and immiscibility of the phases are demonstrated by the results and data summarized below:

EXAMPLE I

Five volumes of sour kerosene was agitated in the presence of air with 1 volume of 10 per cent potassium hydroxide solution in ethylene glycol

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hibitor No. 1 as the oxidation catalyst. After 30 minutes' agitation in air, the hydrocarbon was separated and found to be sweet according to the "doctor" test.

Similar results were obtained in like treatment processes using ethylene glycol as a vehicle for carrying alkali hydroxide in solution in amounts from 5 per cent to saturation and containing U. O. P. Inhibitor No. 1 and various hydroxy aromatic compounds in amounts from 0.5 to 3 per cent. Some typical results are tabulated below:

Table

	Treating Solution	Catalyst	Per cent mercaptan sulfur	
			Initial	After 30 min. Treatment
1	10 per cent NaOH in ethylene glycol.	Pyrogallol.....	0.019	0.009
2	do.....	Hydroquinone.....	0.019	0.0018
3	do.....	3,4 Dihydroxy diphenyl.....	0.019	0.0055
4	do.....	1,5 Dihydroxy naphthalene.....	0.019	0.0064
5	Isobutylene glycol satd. with NaOH.	Pyrogallol.....	0.019	0.0025
6	do.....	U. O. P. Inhibitor No. 1.....	0.019	(Dr. sweet)
7	Diethylene glycol satd. with NaOH.....	do.....	0.019	(Dr. sweet)

containing 2 per cent of Inhibitor No. 1 for a period of 15 minutes, after which hydrocarbon and treating solution were separated and the kerosene washed with water. It was determined by analysis that it was free of mercaptan sulfur and doctor sweet.

EXAMPLE II

One volume of a 10 per cent sodium hydroxide solution in ethylene glycol and containing 2 per cent by weight of U. O. P. Inhibitor No. 1 was used to contact 5 volumes of Stoddard solvent containing 0.034 per cent of mercaptan sulfur and having a boiling range of about 370-470° F. During the contact which lasted about 45 minutes the mixture was kept well agitated with air. After completion of the treatment the hydrocarbon and treating solution were allowed to stratify, separated, and the hydrocarbon analyzed and found free of mercaptan sulfur and sweet according to the "doctor" test.

EXAMPLE III

Five volumes of Stoddard solvent, boiling range 370-490° F., containing 0.019 per cent of mercaptan sulfur, was contacted with one volume of isobutylene glycol saturated with sodium hydroxide and containing 2 per cent of pyrogallol as an oxidation catalyst. After 30 minutes' agitation with air, the mixture was allowed to stratify, the hydrocarbon decanted and analyzed. As a result of the treatment the mercaptan sulfur content had been reduced to 0.0025 per cent.

EXAMPLE IV

Five volumes of Stoddard solvent, boiling range 370-490° F., containing 0.019 per cent of mercaptan sulfur, was contacted with one volume of isobutylene glycol saturated with sodium hydroxide and containing 2 per cent of U. O. P. Inhibitor No. 1 as the oxidation catalyst. After 30 minutes' agitation with air, the mixture was separated and the hydrocarbon found to be sweet according to the "doctor" test.

EXAMPLE V

Five volumes of Stoddard solvent, boiling range 370-490° F., containing 0.019 per cent of mercaptan sulfur, was contacted with one volume of diethylene glycol saturated with sodium hydroxide and containing 2 per cent of U. O. P. In-

In each of the tests summarized in the table, the amount of catalyst used was 0.2 gram per 10 cc. of treating solution.

EXAMPLE VI

Blank tests conducted to determine the efficacy of the glycol solutions without the catalyst and the solubility of the material in the hydrocarbon treated were made. It was found that the several alkaline glycol solutions are not very effective without the catalytic material to oxidize the sulfur compounds, as the following typical test will indicate: Five volumes, 300 cc., of Stoddard solvent containing 0.015 per cent of mercaptan sulfur was contacted with one volume, 60 cc., of alkaline treating solution for a period of 10 minutes in each case in the presence of about 10 volumes, 600 cc., of air. The results were as follows:

Table II

Composition of Treating Solution	Per cent mercaptan sulfur in Stoddard Solvent	
	Before	After
10 per cent aqueous KOH plus 2 per cent U. O. P. Inhibitor #1.....	0.015	0.010
10 per cent KOH in ethylene glycol.....	0.015	0.013
10 per cent KOH in Ethylene glycol with 2 per cent U. O. P. Inhibitor #1.....	0.015	<0.002 Doctor Sweet

Another advantage of employing the solvent vehicles indicated is shown by the following solubility data for ethylene glycol in the system ethylene glycol-water-sodium hydroxide-gasoline.

Table III

Ethylene glycol	Water	NaOH	Gasoline	Ethylene glycol in 200 cc. gasoline
Cc.	Cc.	Gm.	Cc.	Gm.
100	100	44	200	0.17
100	100	22	200	0.22
200	0	22	200	0.13
200	0	0	200	0.15

The other solvent materials described have solubilities in hydrocarbon similar to the figures listed for ethylene glycol.

The regeneration of the alkaline treating solu-

tion is carried out by blowing it with air. The process is conducted by running the spent treating solution into a regeneration tower counter-current to a stream of air, and in the process the regeneration of the alkaline treating solution is effected.

It is apparent, therefore, that by carrying out the sweetening operation by means of air or other oxygen-containing gas in the presence of alkaline treating solution containing a small amount of phenolic oxidation catalyst, sweetening of hydrocarbon liquids can be rapidly and effectively accomplished. Regeneration of the alkaline solutions can also be effectively carried out by means of air or other oxygen-containing gas if the regeneration is conducted in the presence of a small amount of a phenolic catalyst dissolved in the solution. The rate at which regeneration of the catalyst or sweetening of the hydrocarbon can be effected is far in excess of the rate which would be expected from the cumulative effect of air regeneration of the treating solutions in the presence of phenolic oxidation catalysts.

What is claimed is:

1. The method of oxidizing acidic sulfur compounds occurring in petroleum hydrocarbons comprising, contacting said compounds with a gas containing free oxygen in the presence of an alkaline polyhydroxy alcohol solution containing a phenolic material capable of forming a quinone upon oxidation, said solution containing less than 25% by weight of water.

2. The method of oxidizing acidic sulfur compounds in accordance with claim 1 in which said alkaline polyhydroxy alcohol solution is a solution of an alkali metal hydroxide in ethylene glycol.

3. The method of oxidizing acidic sulfur compounds in accordance with claim 1 in which the alkaline polyhydroxy alcohol solution is a solution of an alkali metal hydroxide in glycerine.

4. The method of oxidizing acidic sulfur compounds in accordance with claim 1 in which the alkaline polyhydroxy alcohol solution is a solution of an alkali metal hydroxide in diethylene glycol.

5. The method of oxidizing mercaptans to disulfides in petroleum hydrocarbons which comprises, contacting a mercaptan-containing petroleum fraction with a gas containing free oxygen in the presence of an alkaline polyhydroxy alcohol solution containing a minor amount of a phenolic material capable of being oxidized to a quinone.

6. The method of oxidizing mercaptans to disulfides in accordance with claim 5 in which the alkaline polyhydroxy alcohol solution is a solution of an alkali metal hydroxide in ethylene glycol.

7. The method of oxidizing mercaptans to disulfides in accordance with claim 5 in which the alkaline polyhydroxy alcohol solution is a solution of an alkali metal hydroxide in glycerine.

8. The method of oxidizing mercaptans to disulfides in accordance with claim 5 in which alkaline polyhydroxy alcohol solution is a solution of an alkali metal hydroxide in diethylene glycol.

9. The method in accordance with claim 5 in which the alkaline polyhydroxy alcohol solution is a solution of an alkali metal hydroxide in ethylene glycol and sufficient water to render the glycol substantially insoluble in said hydrocarbon but less than about 25 per cent by weight of the solution.

10. The method in accordance with claim 5 in which the phenolic material is a high-boiling hard wood tar fraction.

11. The method in accordance with claim 5 in which the phenolic material is pyrogallol.

12. The method of oxidizing mercaptans to disulfides in petroleum hydrocarbons which comprises, contacting a mercaptan-containing petroleum fraction with a gas containing free oxygen in the presence of an alkaline polyhydroxy alcohol solution containing about 5 to 25 per cent of alkali metal hydroxide and about 0.1 to 3 per cent of a phenolic material capable of being oxidized to a quinone, whereby the mercaptans are oxidized to disulfides.

13. The method of oxidizing mercaptans to disulfides in hydrocarbon fluids in accordance with claim 12, wherein the polyhydroxy alcohol is ethylene glycol and the phenolic material is a hard wood tar.

14. The method of oxidizing mercaptans to disulfides in hydrocarbon fluids in accordance with claim 12, wherein the polyhydroxy alcohol is glycerine and the phenolic material is hard wood tar.

15. The method of oxidizing mercaptans to disulfides in hydrocarbon fluids in accordance with claim 12, wherein the polyhydroxy alcohol is diethylene glycol, and the phenolic material is hard wood tar.

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