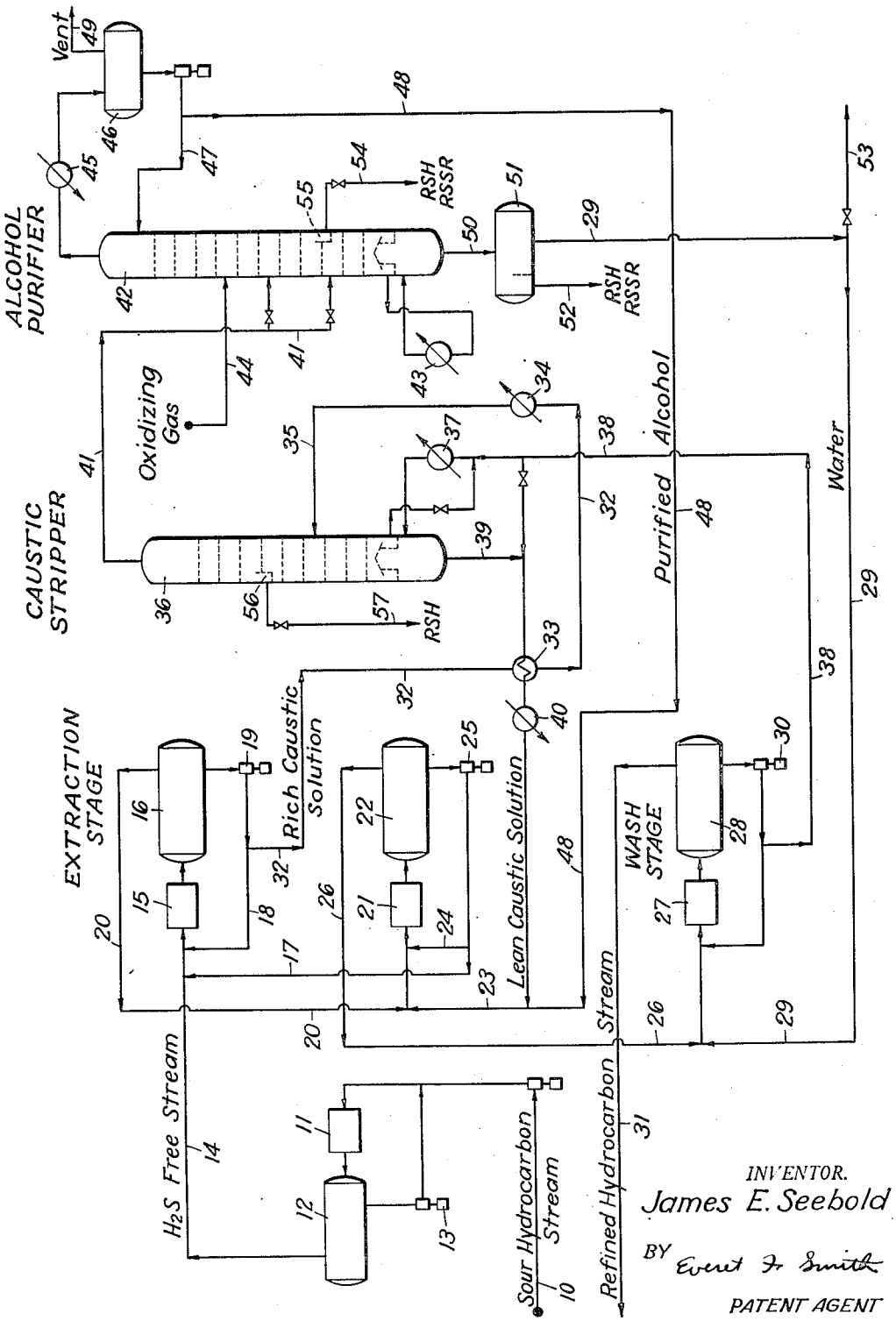
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MERCAPTAN REMOVAL FROM HYDROCARBONS

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INVENTOR.
James E. Seebold
BY Everett F. Smith
PATENT AGENT

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MERCAPTAN REMOVAL FROM HYDROCARBONS

James E. Seebold, Chicago, Ill., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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My invention relates to the extraction of mercaptans from hydrocarbon charging stocks, such as kerosene, gas oil, fuel oil, gasoline, naphthas, and the like, by extraction with an aqueous solution comprising a lower aliphatic alcohol and a caustic base, such as sodium hydroxide. More particularly, it relates to an improvement in the aforesaid process whereby the alcohol used in the extraction operation may be substantially freed from mercaptans and rendered suitable for being recycled. In an especially advantageous embodiment, my invention may be used to improve the burning characteristics of sour heater oils derived by distillation of crude petroleum or cracked petroleum products.

Many types of crude petroleums contain substantial quantities of sulfur in the form of mercaptans, disulfides, heterocyclic sulfur compounds, and the like. These materials are in general highly objectionable in refined petroleum products, owing to their unpleasant odor, corrosive qualities, and other undesirable characteristics. In heater oils, for example, the presence of small proportions of high-boiling sulfur compounds results in the rapid deposition of carbon or coke when burned, especially when burned in domestic sleeve-type space heaters, in which the vaporizing grooves of the burner tend to fill with the carbon, so that the oil flow is retarded, and more frequent shut-downs for cleaning are required. Heater oils derived from sour crudes are of this type, since they ordinarily contain substantial proportions of mercaptans, which result in unsatisfactory burning qualities. Moreover, when such oils are "doctor-sweetened" to remove the mercaptans, a part or all of the mercaptans are converted to disulfides, which have a considerably higher boiling range than that of the oil from which they were derived. These high-boiling disulfides are particularly undesirable in heating oils destined for use in critical space heaters, as the following tests demonstrate:

Fifty-gallon quantities of several heater oils of varying disulfide content were burned in a Jungers Model C sleeve-type space heater at a draft equivalent to 0.03 inch of water pressure and a flow rate of 0.3 gallon per hour. Under these conditions, an oil which deposits 6 grams or less of carbon on the heating surfaces in the course of a 50-gallon run is considered acceptable. The results of the tests are set forth in the following table:

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Treatment	Original Oil, Mercaptan No.	Refined Oil		
		Mercaptan No.	Disulfide No.	Carbon deposited
				Grams
None	90	90	0	4.0
Doctor-sweetened	89	0	89	20.3
Caustic-extracted to Mercaptan No. of 7; then doctored-sweetened	66	0	7	5.9

In the table, the mercaptan number (sometimes called the copper number) is the milligrams of mercaptan sulfur per 100 milliliters of oil, generally determined by titration with a standardized copper-salt solution. The disulfide number is the milligrams of disulfide sulfur per 100 milliliters of oil; this number is determined by reducing the disulfides to mercaptans with zinc and hydrochloric acid, and then determining the mercaptan number. The foregoing data demonstrate that it is necessary either to remove the disulfides from the oil or to prevent their formation during refining operations and even during storage, where disulfides may be produced by atmospheric oxidation of mercaptans.

Similar or related problems are encountered with other sulfur-containing hydrocarbon fractions obtained from sour crudes. This invention is concerned with a process for avoiding such difficulties by extraction of mercaptans, RSH from hydrocarbon stocks before the mercaptans have become oxidized to disulfides, RSSR, where R represents the same or different hydrocarbon radicals.

The prior art discloses numerous methods for extracting mercaptans from petroleum oils. In an especially effective process, the petroleum oil is extracted with an aqueous solution comprising a lower aliphatic alcohol such as methanol and a caustic alkali such as sodium hydroxide or potassium hydroxide. Mercaptans are freely soluble in such extractant solutions, and are readily removed thereby from hydrocarbon charging stocks comprised thereof. The resulting extraction solution may subsequently be stripped of all or the greater part of its alcohol content. After removal of the mercaptans, the regenerated

caustic liquor may be recycled, in combination with the recovered alcohol.

A major difficulty with the caustic-alcohol process lies in the fact that lower aliphatic alcohols form azeotropes with mercaptans, and the recovered alcohol is therefore contaminated with a substantial proportion of mercaptans. Alcohols contaminated in this manner are of course unsuitable for recycling, since they could not be used to produce a substantially mercaptan-free refined stock. I have now devised a means for avoiding this difficulty by fractionally distilling, in the presence of an oxidizing gas or oxygen-affording gasiform stream, the alcohol separated from the mercaptan-rich extract. In an especially advantageous embodiment of my invention, I distill the mercaptan-contaminated alcohol in a fractionating column while introducing into an upper section thereof an oxidizing gas. Any mercaptans within the upper section of the column are converted thereby into disulfides, from which the alcohol readily distills in purified form. The resulting disulfides flow downward through the column and further purify the ascending alcohol vapors by extracting mercaptans therefrom. If desired, this conversion of mercaptans to disulfides may be facilitated by introducing a small quantity of an alkaline agent, such as caustic or ammonia, to the treating zone.

One object of my invention is to provide an improved method for sweetening hydrocarbons. Another object of my invention is to separate mercaptans from lower aliphatic alcohols in an especially efficient and convenient manner. A further object of my invention is to purify a caustic-alcohol sweetening solution by means of an oxidative fractional distillation method. Other objects of my invention and its advantages over the prior art will be apparent from the description and claims.

It is to be understood that my invention is applicable broadly to the separation of mercaptans from hydrocarbons, including aliphatic, aromatic, and naphthenic hydrocarbons, and mixtures thereof. My invention is especially useful in connection with the purification of petroleum fractions, such as kerosene, gas oil, fuel oil, gasoline, naphthas, and the like.

It is also to be understood that my process is applicable broadly to the purification and regeneration of simple caustic-alcohol sweetening solutions and to various modifications thereof, as disclosed in the prior art, including solutions which contain various solutizers such as salts of phenols, cresols, carboxylic acids, and other organic acids. Suitable caustic alkalies include the class of alkali-metal hydroxides, preferably sodium hydroxide or potassium hydroxide. The alcohol should be a lower aliphatic alcohol, preferably methanol. Ethanol, isopropyl alcohol, or n-propyl alcohol can be used.

In the sweetening of sour hydrocarbon streams with caustic-alcohol solutions, the sour charging stock is first extracted with an aqueous caustic-alcohol solution wherein the proportion of caustic in the aqueous caustic portion of the solution is preferably within the range of about 35 to 60 percent by weight and the proportion of aqueous caustic in the total solution is preferably between about 20 and 80 percent by weight, the remainder being substantially all alcohol, exclusive of solutizer. Somewhat smaller proportions of water may be employed with potassium hydroxide than with sodium hydroxide. In general, potassium hydroxide solutions are somewhat more effective for removing mercaptans than sodium hydroxide solutions. Precautions should be taken to prevent contacting the caustic solution with carbon dioxide, since carbonates are formed thereby, unbalancing the composition of the solution and necessitating auxiliary filter equipment for their removal.

From the extraction step is withdrawn a refined hydrocarbon phase, lean in mercaptans, and an aqueous caustic-alcohol extract, rich in mercaptans. The latter may then be exhaustively stripped to separate substantially all mercaptans and alcohol therefrom, and the vaporous stream of mercaptans and alcohol is distilled in a fractionating column in the presence of an oxidizing gas, whereby the mercaptans are converted wholly or partly into disulfides, and the alcohol is withdrawn overhead in purified form, substantially free from mercaptants, or containing a greatly reduced proportion thereof. I prefer to use air as the oxidizing gas, but I may use oxygen, with or without diluents, and I may also use other oxidizing agents capable of converting mercaptans to disulfides, such as hydrogen peroxide. The distillation is preferably carried out at ordinary pressure and at the temperature required to operate the column at such pressure, generally from 10 to 25° F. above the boiling point of the alcohol. However, somewhat elevated pressures and temperatures may also be used, for example pressures up to around 200 pounds per square inch or somewhat higher, and corresponding temperatures.

Alternatively, I may fractionally distill the mercaptan-rich aqueous caustic-alcohol solution and separate therefrom all or substantiallly all of the alcohol, contaminated with mercaptans. The alcohol overhead stream may then be purified by oxidative distillation as described above. Thereafter, the aqueous caustic phase is freed from mercaptans by a further stripping operation, and is recycled to the extraction step in combination with the purified alcohol.

Ordinarily, in the stripping or fractionation of the mercaptan-rich aqueous caustic-alcohol solution, it is desirable to operate under rigidly controlled conditions such as will produce a substantially anhydrous overhead stream, since the proportion of mercaptans in the overhead stream is very greatly increased by operating under conditions which permit as little as one percent of water to be distilled simultaneously therewith. My process, however, makes it unnecessary to employ such conditions, since I am able to remove even much larger proportions of mercaptans with savings in costs and reduction of operating difficulties.

My invention will be more fully understood from the attached flowsheet, in which I have carefully set forth and described an advantageous embodiment thereof, together with illustrative alternatives.

A sour hydrocarbon stream, such as a sour heater oil boiling in the range of about 350 to 600° F. is charged to process by way of line 10 leading to mixer 11 and settler 12, in which an aqueous solution of an alkali is employed to remove hydrogen sulfide and carbon dioxide. For this purpose, a dilute solution of caustic soda is satisfactory. The caustic solution can be recycled by pump 13 from settler 12 to mixer 11 and discarded when spent.

The washed hydrocarbon stream, now free from hydrogen sulfiide and carbon dioxide, is conducted by line 14 to mixer 15 and settler 16, the first mercaptan extraction stage. The extraction

may be carried out in a baffled tower employing countercurrent flow of hydrocarbon and caustic-alcohol solution; but satisfactory extraction can be carried out batchwise with as few as two to five stages, or with only two to four stages where potassium hydroxide solutions are used. The drawing illustrates a process employing two extraction stages.

In mixer 15, caustic-alcohol solutions are introduced by lines 17 and 18. Therein, they are commingled with the hydrocarbon, and the mixture is allowed to stratify in settler 16. The quantities of fresh and recycled caustic-alcohol solutions are preferably adjusted to give a ratio of approximately 1:1 by volume of caustic-alcohol solution to hydrocarbon. Vigorous and intimate mixing should be carried out in mixer 15, suitably by use of an orifice-type mixer, a rapid agitator, or the like. The mixing and settling should preferably be carried out at a temperature below about 100° F., preferably around 90° F., and at autogenous or slightly elevated pressures, suitably from around atmospheric pressure to about 200 pounds per square inch. The caustic-alcohol solution from settler 16 may be recycled by pump 19 to mixer 15.

Treated hydrocarbon from the first extraction stage is conducted by line 20 to mixer 21, where it is commingled with another batch of caustic-alcohol solution, supplied through line 23 and recycle line 24. The mixture then flows into settler 22, where stratification takes place, and the separated caustic-alcohol phase is recycled by pump 25.

The treated hydrocarbon phase from settler 22, now substantially free from mercaptans, is conducted by line 26 to mixer 27, where the hydrocarbon stream is washed with water to remove the small proportion of alcohol dissolved therein. The quantity of dissolved alcohol is ordinarily quite small, usually from about .2 to 5 percent by volume or less, owing to the essentially oleophobic nature of the alcohols employed in the extraction process; however, it will be apparent that the recovery thereof is an important economic consideration. Wash water is supplied to mixer 27 by line 29, and a portion of the wash water from settler 28 may be recycled by pump 30 to mixer 27, if desired, to increase the volume of water for contacting the hydrocarbon stream. A refined, substantially mercaptan-free hydrocarbon stream is withdrawn from settler 28 through line 31.

The mercaptan-rich caustic-alcohol solution, sometimes called the spent caustic solution, is withdrawn from the first extraction stage by line 32 through heat exchanger 33 and heater 34, where its temperature is raised to around 210° F. or somewhat above. The hot caustic-alcohol solution is then introduced through line 35 into an intermediate point of stripper column 36, where the alcohol and mercaptans are substantially completely removed by the action of reboiler 37 and taken overhead as a vaporous stream, ordinarily with a substantial quantity of water. Water or free steam, preferably superheated steam, may be added at a low point in the stripper if desired to assist in removing the mercaptans from the caustic solution. For this purpose, the wash water from settler 28, containing recovered alcohol, may be supplied by line 38 to reboiler 37, where it is vaporized and the alcohol is stripped out. The temperature of the liquid in the base of stripper 36 is preferably within the range of about 250 to 350° F. From the bottom of the stripper, a hot stream of lean aqueous caustic solution emerges, now substantially free from mercaptans, and is recycled through line 39, heat exchanger 33, cooler 40, and line 23 to mixer 21.

From the top of stripper 36 vapors of alcohol, mercaptans, and water are withdrawn by line 41, and are introduced into an intermediate point of alcohol purifier column 42, equipped with reboiler 43. Therein, the stream is fractionally distilled, the water and the major proportion of the mercaptans passing downward, and the alcohol, contaminated with a small proportion of mercaptans, for example around .2 to 5 percent, passing upward. In order to purify the alcohol fraction, a stream of an oxidizing gas such as air is introduced through line 44 into an upper intermediate section of column 42, above the entry point of line 41, and preferably at the lowest point in the column at which the mercaptan-alcohol azeotrope composition exists. The oxidizing gas serves to convert substantially all mercaptans reaching the upper section of column 42 into the corresponding disulfides, from which the alcohol readily distills in pure form, because of the fact that the disulfides have much higher boiling points than the corresponding mercaptans. The disulfides therefore flow downward within column 42, where they perform the additional function of extracting mercaptans from the rising vapor stream, owing to the high solubility of mercaptans in disulfides.

The purified alcohol vapors emerge overhead through condenser 45 into reflux drum 46, from which a portion is refluxed to the top of column 42 through line 47, and the remainder is withdrawn and recycled through lines 48 and 23 to mixer 21. Gases are vented from reflux drum 46 through line 49, optionally through a scrubber or an activated charcoal adsorber to recover alcohol vapors contained therein.

From the bottom of column 42 emerges a heterogeneous mixture of mercaptans, disulfides, and water. This mixture flows through line 50 into decanter 51, from which an organic phase comprising substantially all of the mercaptans and disulfides is withdrawn through line 52. This phase may be subjected to further processing, such as by fractional distillation, to separate the components thereof in substantially pure form. The aqueous phase from decanter 51 is substantially free from sulfur compounds, owing to the low solubility of the latter in water. The aqueous phase may therefore be withdrawn and recycled through line 29 to mixer 27. Excess water may be withdrawn and discarded through line 53.

It will be apparent that the process set forth in the foregoing flowsheet may be modified in numerous ways without departing from the spirit of my invention. As an illustration, the mercaptans and disulfides may be withdrawn via line 54 from column 42 at trapout plate 55, located in the lower section of the column above or below the entry point of line 41. The trapout plate should preferably be located at a point sufficiently low in the column that substantially all of the alcohol has been removed from the descending liquid stream. This embodiment has the advantage that the aqueous stream reaching the bottom of column 42 may be stripped entirely free of mercaptans by reboiler 43, and decanter 51 may be dispensed with.

As a further alternative, caustic stripper 36 may be operated under suitable conditions to

produce a vaporous overhead stream comprising essentially alcohol with only a small proportion of mercaptans, for example around 1 to 5 percent. This can be done conveniently by withdrawing mercaptans from trapout plate 56 through line 57. The vapor stream emerging overhead through line 41 is purified in column 42 as hereinbefore described. In this embodiment, however, only a comparatively small proportion of the total sulfur compounds derived from the sour charging stock emerge from the bottom of column 42; consequently the load on column 42 is substantially reduced.

Typical heater oils, refined by caustic methanol extraction, have the following properties:

Gravity, API	39 to 43
Color, Saybolt Universal	8 to 18
Flash, TCC	115 to 150
Mercaptan No.	5
Copper Strip Corrosion, 3 hours at 212° F.	negative
Distillation, ASTM:	
Initial boiling point °F.	332
10% °F.	360
50% °F.	438
90% °F.	527
Maximum °F.	574

In a specific application of my invention, the total extract obtained in the caustic-methanol extraction of a sour heater oil was distilled in a column. When such an extract was fractionally distilled without treatment with an oxidizing gas according to my invention, a methanol fraction was obtained overhead having a mercaptan number around 300, corresponding to approximately 2 percent by volume of mercaptans. When 1863 parts by weight of such an extract were fractionally distilled while injecting approximately 15 cubic feet of air per hour per square foot of column cross section into the middle portion of the column, a purified methanol stream was obtained having a mercaptan number of only 51, corresponding to a mercaptan content of only 0.33 percent by volume.

While I have described my invention with reference to a specific example, it is to be distinctly understood that I am not limited to the charging stock, operating conditions, and manipulative steps set forth therein. My invention is to be construed broadly within the limits of my disclosure, and any modifications or equivalents that would ordinarily occur to one skilled in the art are to be considered as lying within the scope of my invention.

In accordance with the foregoing description, I claim as my invention:

1. A process for removing mercaptans from a mercaptan-containing lower aliphatic alcohol obtained by distillation from a caustic-alkali solution spent in desulfurizing a sour petroleum hydrocarbon which comprises fractionally distilling said mercaptan-containing lower aliphatic alcohol in contact with an oxidizing gas stream and withdrawing a vaporous alcohol stream of substantially reduced mercaptan content.

2. The process of claim 1 wherein said lower aliphatic alcohol is methanol.

3. The process of claim 1 wherein said lower aliphatic alcohol is ethanol.

4. The process of claim 1 wherein said lower aliphatic alcohol is isopropyl alcohol.

5. The process of claim 1 wherein said oxidizing gas is air.

6. A process for removing mercaptans from a mercaptan-containing lower aliphatic alcohol obtained by distillation from a caustic-alkali solution spent in desulfurizing a sour petroleum hydrocarbon which comprises distilling said mercaptan-containing lower aliphatic alcohol in a fractionating zone, introducing into an upper portion of said zone a stream of an oxidizing gas, and withdrawing from the top of said fractionating zone a vaporous alcohol stream of substantially reduced mercaptan content.

7. A process for removing mercaptans from mercaptan-contaminated methanol obtained by distillation from an aqueous caustic-alkali solution spent in desulfurizing a sour petroleum hydrocarbon which comprises distilling said mercaptan-containing methanol in a fractionating column, introducing into an upper portion of said column a stream of air, and withdrawing from the top of said column a vaporous stream of methanol substantially reduced in mercaptan content.

JAMES E. SEEBOLD.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,437,348	Brown et al.	Mar. 9, 1948
2,464,019	Bond et al.	Mar. 8, 1949
2,488,000	Bernard	Nov. 15, 1949