

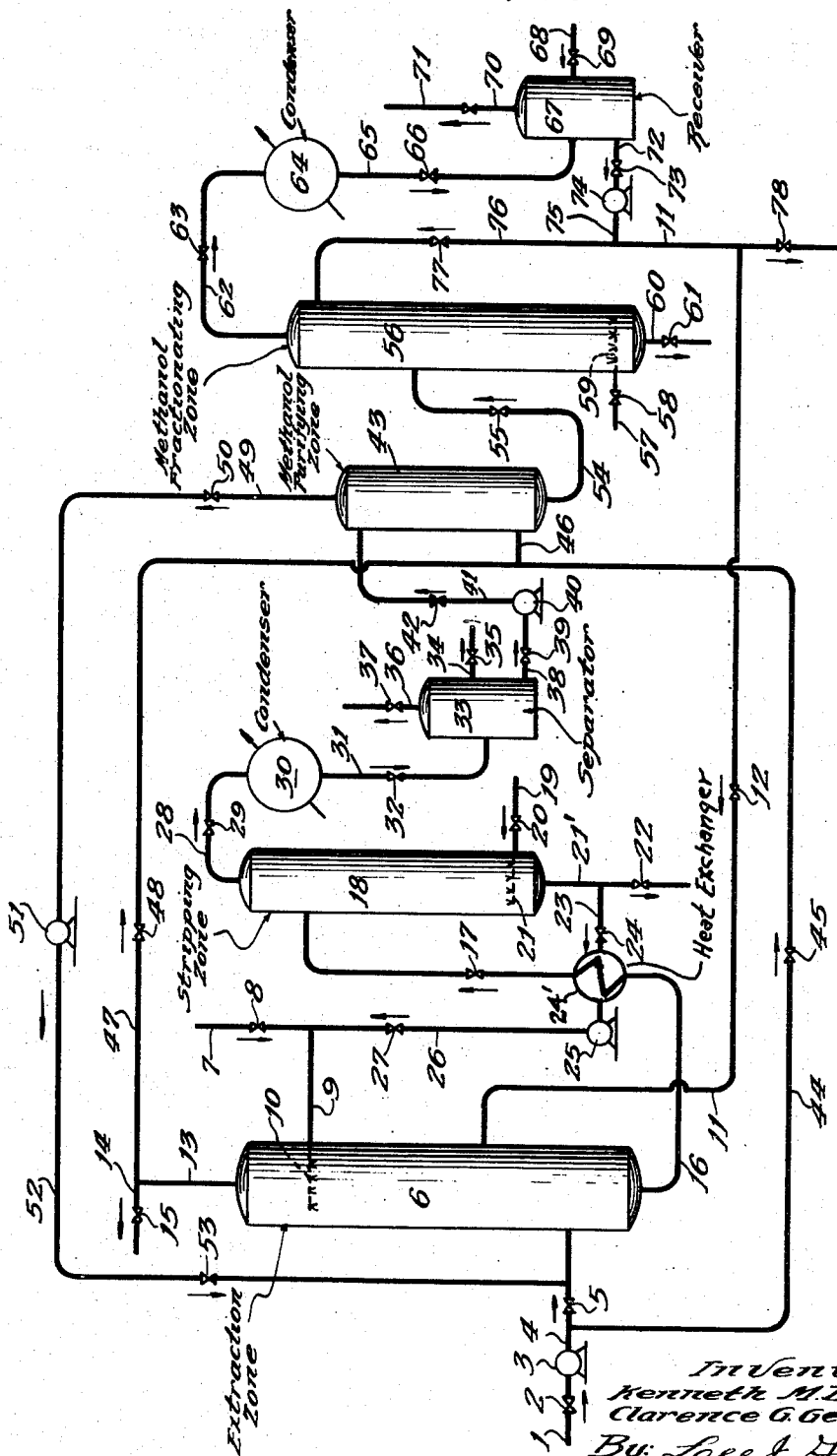
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PROCESS FOR THE REFINING OF HYDROCARBON OIL CONTAINING MERCAPTANS

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## PROCESS FOR THE REFINING OF HYDRO-CARBON OIL CONTAINING MERCAPTANS

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This invention relates particularly to the desulphurization of hydrocarbons and more particularly to the removal of acidic organic compounds from hydrocarbon oil by means of an alkaline-solvent solution.

In the removal of mercaptans from gasoline by means of an alkaline-solvent solution, as at present being practiced commercially, the treated gasoline in many cases is not doctor sweet. The present invention is directed to an improvement in processes of this nature in order to produce a treated gasoline which will be doctor sweet.

In a broad aspect, the present invention relates to a process for removing acidic organic compounds from hydrocarbons containing the same, which comprises treating said hydrocarbons with an alkaline-solvent solution, subsequently separating a solvent fraction containing a minute proportion of mercaptans, treating said solvent fraction to considerably lower its mercaptan content, and supplying the thus treated solvent to the first mentioned treating step.

In one specific embodiment, the present invention relates to a process for removing mercaptans from gasoline containing the same, which comprises introducing said gasoline into the lower portion of an extraction zone and therein contacting the gasoline with a caustic-methanol solution, subsequently separating a methanol fraction containing a minute proportion of mercaptans, treating said methanol fraction with gasoline to absorb a considerable portion of the mercaptans in the gasoline and to thereby remove them from the methanol, returning the gasoline containing the absorbed mercaptans to the lower portion of said extraction zone, and supplying the methanol to said extraction zone at a point above that at which said gasoline is introduced.

While any suitable alkaline reagent, including sodium hydroxide, potassium hydroxide, etc., and any suitable organic solvent which is more soluble in an aqueous solution of an alkaline reagent than in hydrocarbons, including methanol, ethanol, propanol, acetone, ethylene glycol, glycol ethers, etc., may be used, the preferred treating reagent comprises an aqueous solution of sodium hydroxide in methanol.

According to the present process hydrocarbon fractions containing acidic organic compounds are treated with the alkaline-solvent solution at a temperature above the freezing point of the solution, which temperature is generally within the range of 80° to 110° F., although in some cases lower or higher temperatures may be used but the temperature usually will not be below 25°

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F. and not above 200° F. When treating gasoline, the pressure employed is usually within the range of 25 to 200 pounds although lower or higher pressures may be used in some cases.

As heretofore set forth, the preferred treating reagent comprises an aqueous solution of sodium hydroxide in methanol. The quantity of sodium hydroxide may range from about 0.5% to 10% or more by volume based on the hydrocarbons to be treated, while the sodium hydroxide may be between about 35° and 50° Bé., and preferably between 45° and 50° Bé. The methanol employed may be anhydrous or it may contain varying amounts of water. However, as the water content of the methanol fraction increases, the concentration of the sodium hydroxide solution should be increased accordingly.

In accordance with the invention, gasoline containing mercaptans and usually phenols is contacted with the caustic-methanol solution under the conditions hereinbefore set forth. Sodium mercaptides and phenolates are formed and are dissolved in the caustic-methanol solution. This solution is then separated from the hydrocarbons. the caustic being regenerated, usually by stripping with steam, to convert the mercaptides into sodium hydroxide and mercaptans. The mercaptans, methanol and water are separated from the caustic, and the latter is returned to the first step of the process. The mercaptans are separated from the water-alcohol mixture usually by settling under carefully controlled conditions which prevent turbulence. However, we have found that the aqueous methanol layer thus separated and removed from the mercaptan layer contains mercaptans and, while the mercaptans are present in only minute quantities as, for example of the order of 0.6% by weight of the methanol-water fraction, the mercaptans remain in the methanol after separating from the water, and the mercaptans may then be of the order of 3% by weight of the methanol. In accordance with the invention, the aqueous methanol fraction is treated to remove a considerable portion of the mercaptans contained therein prior to recycling of the methanol for further use in the process. While any suitable method of removing the mercaptans may be employed, it is a particular feature of the present invention that a portion of the gasoline, either before or after treatment in the process, is utilized for this purpose. The mercaptans are more soluble in hydrocarbons than they are in an aqueous methanol solution and this fact is taken advantage of by contacting the aqueous methanol fraction with a portion of the gasoline to absorb the

mercaptans therein and to thereby purify the aqueous methanol solution. A particular advantage of this method of treatment is that the gasoline containing the absorbed mercaptans may be returned to the first step of the process and the mercaptans are therein removed from the gasoline.

The invention is further illustrated in the accompanying diagrammatic flow drawing and the following description of one specific operation of the process. In the interest of simplicity the following description will be limited to the treatment of gasoline by means of a caustic-methanol solution, although it is understood that other hydrocarbon fractions, either normally gaseous or normally liquid, may be treated in the process and that other suitable alkaline reagents and organic solvents may be employed but not necessarily with equivalent results.

Referring to the drawing, gasoline or other suitable charging stock is introduced to the process through line 1 and valve 2 to pump 3, by means of which it is supplied through line 4 and valve 5 into the lower portion of extraction zone 6. Extraction zone 6 may comprise one or a plurality of suitable extraction zones, preferably containing a suitable packing material. The packing material should not be detrimentally affected by the caustic, methanol and hydrocarbons at the operating conditions prevailing in this zone. A particularly suitable packing comprises carbon Raschig rings. Sodium hydroxide is introduced to the process through line 7 containing valve 8 and is directed through line 9 into the upper portion of zone 6, preferably through some sort of spray arrangement as indicated at 10. Usually sufficient sodium hydroxide is recycled within the process, in the manner to be hereinafter set forth in detail, and the sodium hydroxide introduced through line 7 from an external source will comprise the makeup reagent to replace that lost or withdrawn from the process. Similarly, methanol recycled from within the process is directed through line 11 and valve 12 into an intermediate portion of zone 6. Here again the methanol will comprise principally that recycled within the process and any makeup methanol introduced from an external source to replace that lost or withdrawn from the process.

In zone 6 the gasoline flows upwardly in intimate contact with the caustic-methanol solution, and the acidic organic compounds, such as mercaptans and phenols contained in the gasoline, are converted into sodium mercaptides and phenolates. The mercaptans and phenolates are dissolved in the caustic-methanol solution and the rate of flow of the gasoline, caustic and methanol, and the point of introduction of the methanol are so adjusted that the treated gasoline, being withdrawn from the top of zone 6 through line 13 and removed from the process through line 14 and valve 15, contains substantially less mercaptans than the gasoline introduced through line 1 and, in accordance with the present invention, the treated gasoline removed through line 14 will be doctor sweet. The treated gasoline may, if desired, be passed through a filter containing sand, pebbles or clay to remove traces of alkaline reagent, or such gasoline may be subjected to water washing, if desired.

Spent treating solution comprising an aqueous alcoholic solution containing unreacted sodium hydroxide, sodium mercaptides, sodium phenolates and methanol, is withdrawn from the bottom of zone 6 through line 16 and is directed

through heat exchanger 24' and valve 17 into stripping zone 18. Zone 18 preferably contains a suitable packing material which may conveniently comprise carbon Raschig rings. In zone 18 the treating solution is subjected to regeneration by heating, which, in the case here illustrated, comprises stripping with steam introduced through line 19 and valve 20 and is preferably directed through a suitable spray arrangement indicated at 21. The temperature maintained in the lower portion of the stripping zone is substantially the boiling point of the treating solution which, with a 48° Bé. sodium hydroxide solution, will be of the order of about 285° F. The temperature at the top of the stripping zone may be of the order of 200° to 250° F., depending in part on the temperature of the spent treating solution introduced thereto through line 16.

As a result of the heating, the sodium mercaptides are decomposed to mercaptans, with the liberation of an equivalent amount of sodium hydroxide. The sodium hydroxide is withdrawn from the lower portion of zone 18 through line 21' and may be removed from the process through valve 22, but preferably all or a portion of the sodium hydroxide is directed through line 23, valve 24 and heat exchanger 24' to pump 25, by means of which it is recycled through line 26, valve 27 and line 9 to zone 6 for further use therein. The mercaptans, methanol and water are vaporized in zone 18 and are directed therefrom through line 28 and valve 29, into and through condenser 30, line 31 and valve 32, into separator 33. The condensate is permitted to settle and stratify in separator 33, whereby there is formed an upper mercaptan layer and a lower methanol-water layer. Traces of gasoline which may have been carried over will settle in the mercaptan layer, and this layer is removed from separator 33 through line 34 containing valve 35. Separator 33 is also provided with conventional vent line 36 containing valve 37.

In accordance with the present invention, the methanol-water fraction, comprising about 20% methanol and 80% water and containing a minute quantity of mercaptans, is withdrawn from separator 33 through line 38 and valve 39 to pump 40, by means of which it is directed through line 41 and valve 42 into methanol purifying zone 43. Zone 43 may comprise any suitable contacting zone, preferably containing a suitable packing material which advantageously comprises carbon Raschig rings, and the aqueous methanol fraction passes downwardly therein countercurrently to an upwardly flowing stream of gasoline. While the case here illustrated comprises a countercurrent flow operation, it is understood that concurrent flow may be used. The gasoline may suitably comprise a portion of the untreated gasoline charging stock which may be diverted from line 4 through line 44 and is directed through valve 45 and line 46 into the lower portion of zone 43. As an alternative method of operation, a portion of the treated gasoline withdrawn from zone 6 may be utilized for this purpose and this may be accomplished by passing a portion of the treated gasoline from line 13 through line 47, valve 48 and line 46 to zone 43.

It is a particular feature of the present invention that the aqueous methanol fraction is subjected to purification in a separate zone out of the presence of the total mercaptans separated in the process. By this method of treatment, the minute quantity of mercaptans in the aqueous methanol fraction is substantially transferred

from the methanol phase to the gasoline phase and the mercaptan content of the aqueous methanol fraction is thereby considerably reduced. On the other hand, if the purification of the aqueous methanol fraction was endeavored in the presence of the total mercaptans separated from the process, as for example, by so treating the composition prevailing in separator 33, the percentage of mercaptans removed from the aqueous methanol layer would be considerably less due to equilibrium considerations unless an excessively large quantity of gasoline, which theoretically would be an infinite amount, was used. If such a large quantity of gasoline was used, it would then become contaminated with the mercaptans and would have to be discarded from the process, at the same time discarding whatever methanol was also dissolved in the gasoline. It could not be recycled to the extraction zone since this would then mean that the mercaptans removed at one place in the process were being returned back to the process, without any net removal of mercaptans.

The gasoline containing absorbed mercaptans is removed from zone 43 through line 49 and valve 50 to pump 51, by means of which it is directed through line 52 and valve 53 into line 4, to be supplied therefrom into zone 6 for treatment therein in the manner hereinbefore set forth. The purified aqueous methanol fraction is withdrawn from zone 43 through line 54 and is directed through valve 55 into fractionating zone 56. In zone 56 the aqueous methanol fraction is subjected to heating and distillation by any suitable means, such as steam introduced through line 57 and valve 58 through a suitable spray device indicated at 59. In fractionator 56 the methanol is separated from the water, and the latter is removed through line 60 and valve 61 to disposal as desired. It is understood that the water so recovered may be reused within the process if desired. Methanol is removed from the upper portion of zone 56 through line 62 and is directed through valve 63, condenser 64, line 65 and valve 66 into receiver 67. When required makeup methanol, to replace methanol lost or removed from the system, may be introduced to the process through line 68 and valve 69 into receiver 67. Receiver 67 is provided with conventional vent line 70 containing valve 71. The condensate in receiver 67 is removed therefrom through line 72 and valve 73 to pump 74, by means of which a portion thereof is directed through line 75, line 76 and valve 77 to the upper portion of fractionating zone 56 to serve as a cooling and recycling medium therein, while the remaining portion of the methanol is directed through line 11 and may be removed from the system through valve 78, but in accordance with the invention, at least a portion thereof is recycled by way of line 11 and valve 12 to zone 6 for further use therein in the manner hereinbefore set forth.

The increased solubility of mercaptans in caustic-methanol solutions as contrasted to a caustic-water solution has been shown in the prior art. However, the caustic-methanol process is limited in its inability to produce a doctor sweet gasoline in many cases. The present invention affords a ready and convenient improvement to the caustic-methanol process whereby the treated gasoline will be sweet to the doctor test.

The following example is introduced for the purpose of further illustrating the novelty and utility of the present invention but not with the intention of unduly limiting the same.

A cracked gasoline containing 0.065% of mer-

captan sulphur is introduced at a flow rate of 20 gallons per minute into the lower portion of an extraction zone, to which 0.2 gallon per minute of methanol containing 0.03% by weight of mercaptans is introduced at a mid-portion thereof and 0.5 gallon per minute of an aqueous solution of sodium hydroxide of 48° Bé. is introduced to the upper portion thereof. The extraction zone is maintained at a temperature of about 100° F. and a pressure of 75 pounds per square inch. The spent treating solution is removed from the bottom of the extraction zone, is heated to a temperature of 210° F. by indirect heat exchange, and is introduced to the stripping zone wherein it is contacted with steam superheated to a temperature of 750° F. The bottom temperature of the stripping zone is 285° F. and the top temperature is 230° F. The regenerated caustic solution is recycled to the upper portion of the extraction zone, while the vaporized mercaptans, methanol and water are removed from the top of the stripping zone, are cooled to a temperature of about 100° F. and are allowed to settle and stratify in a separating zone. The mercaptan layer is removed from the separating zone, while the methanol-water layer is withdrawn from the separator and is supplied to the upper portion of the methanol purifying zone. The methanol purifying zone is operated at a pressure of about 15 pounds per square inch. The aqueous methanol fraction is introduced to the purifying column at a flow rate of about one gallon per minute and contains about 0.6% of mercaptans. A portion of the untreated gasoline charging stock at a flow rate of two gallons per minute is supplied to the lower portion of the purifying zone and therein passes countercurrently to the descending aqueous methanol fraction. By this method 98% or more of the mercaptans contained in the methanol fraction will be absorbed by the gasoline fraction, and the gasoline fraction containing the absorbed mercaptans is returned to the extraction zone for treatment therein. The methanol fraction is removed from the purifying zone and is subjected to fractionation, utilizing a bottom temperature of about 227° F. and a top temperature of about 165° F. and atmospheric pressure. A purified and concentrated methanol fraction is withdrawn from the upper portion of the fractionating zone and is subjected to cooling and condensation. The condensate will contain about 0.03% by weight of mercaptans and is recycled to the extraction zone for use therein in the manner heretofore set forth.

The treated gasoline from the process as hereinbefore recited will contain less than 0.0004% of mercaptans and will be sweet to the doctor test. As compared to an operation not employing the features of the present invention, the methanol being recycled in the prior art processes may contain about 3% by weight of mercaptans, and the treated gasoline may contain between about 0.001 and 0.0006% of mercaptan sulphur and will not be sweet to the doctor test.

We claim as our invention:

1. In the refining of hydrocarbon oil containing mercaptans by treatment thereof with a solution comprising an alkali and an organic solvent selected from the group consisting of methanol, ethanol, propanol, acetone, ethylene glycol, and glycol ethers, the method which comprises separating said solution from the treated oil and distilling the same to vaporize mercaptans and organic solvent from the alkali, condensing the vapors to form a mercaptan layer and a solvent

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layer containing a small amount of mercaptans, separating said solvent layer from the mercaptan layer, contacting the separated solvent layer in the absence of said mercaptan layer with hydrocarbon liquid to reduce the mercaptan content of the solvent layer, and separating the solvent of reduced mercaptan content from said hydrocarbon liquid.

2. In the refining of gasoline containing mercaptans by treatment thereof with caustic-methanol solution, the method which comprises separating said solution from the treated gasoline and distilling the same to vaporize mercaptans and methanol from the caustic, condensing the vapors to form a mercaptan layer and a methanol layer containing a small amount of mercaptans, separating said methanol layer from the mercaptan layer, contacting the separated methanol layer in the absence of said mercaptan layer with hydrocarbon liquid to reduce the mercaptan content of the methanol layer, and separating the methanol of reduced mercaptan content from said hydrocarbon liquid.

3. The method as defined in claim 2 further characterized in that said hydrocarbon liquid comprises gasoline.

4. The method as defined in claim 2 further characterized in that said hydrocarbon liquid comprises a portion of said treated gasoline.

5. In the refining of hydrocarbon oil containing mercaptans by treatment thereof with an aqueous solution comprising an alkali and an organic solvent selected from the group consisting of methanol, ethanol, propanol, acetone, ethylene glycol, and glycol ethers, the method which comprises separating said solution from the treated oil and distilling the same to vaporize mercaptans, water and organic solvent from the alkali, condensing the vapors to form a mercaptan layer and an aqueous layer containing a small amount

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of mercaptans, separating said solvent layer from the mercaptan layer, contacting the separated solvent layer in the absence of said mercaptan layer with hydrocarbon liquid to reduce the mercaptan content of the solvent layer, and separating the solvent of reduced mercaptan content from said hydrocarbon liquid.

6. In the refining of gasoline containing mercaptans by treatment thereof with an aqueous caustic-methanol solution, the method which comprises separating said solution from the treated gasoline and distilling the same to vaporize mercaptans, water and methanol from the caustic, condensing the vapors to form a mercaptan layer and an aqueous methanol layer containing a small amount of mercaptans, separating said methanol layer from the mercaptan layer, contacting the separated methanol layer in the absence of said mercaptan layer with hydrocarbon liquid to reduce the mercaptan content of the methanol layer, and separating the methanol of reduced mercaptan content from said hydrocarbon liquid.

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