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REGENERATION OF SPENT AQUEOUS SOLUTIONS OF CAUSTIC ALKALI CONTAINING MERCAPTIDES

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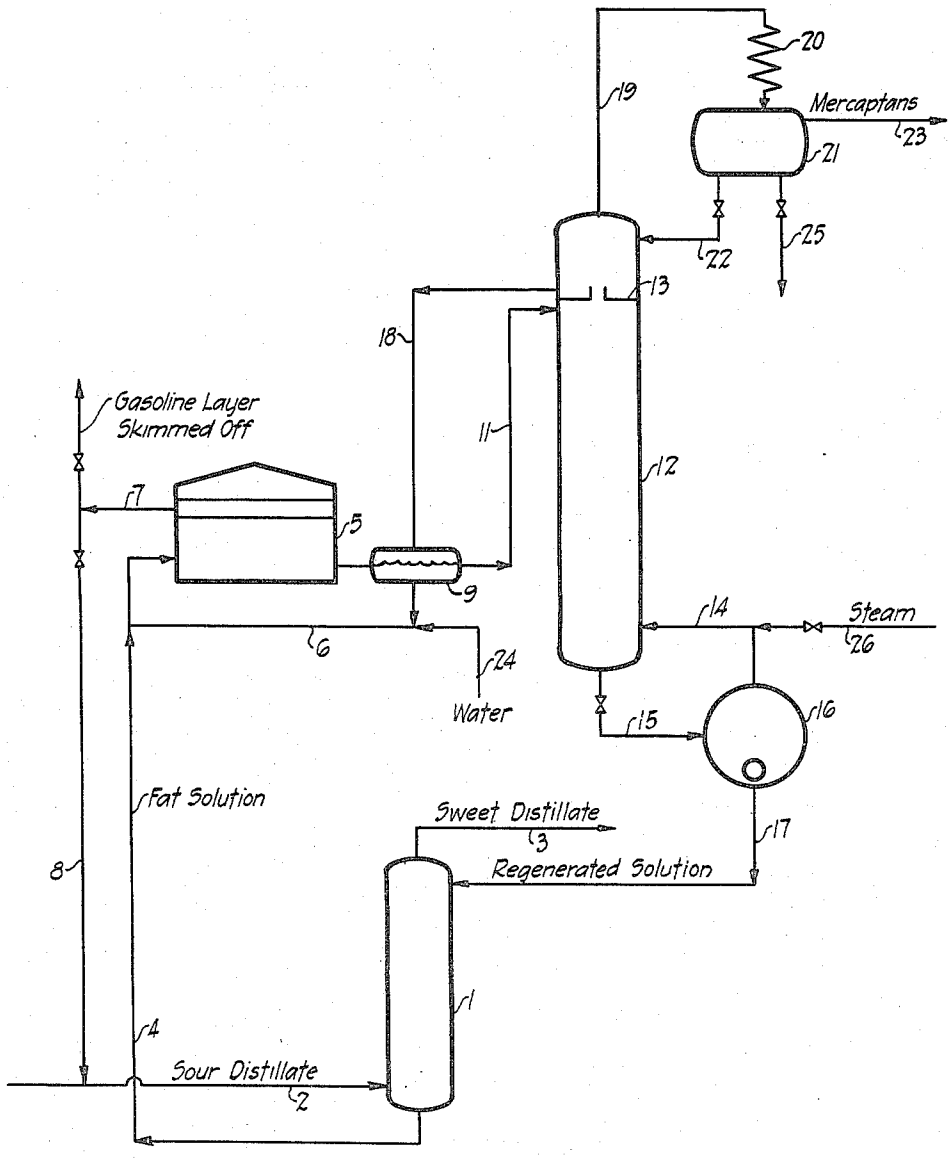

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REGENERATION OF SPENT AQUEOUS SOLUTIONS OF CAUSTIC ALKALI CONTAINING MERCAPTIDES

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6 Claims. (Cl. 260—609)

This invention relates to the regeneration of spent aqueous solutions of caustic alkali containing absorbed mercaptides and solutizers for mercaptans, and more particularly is concerned with a simple pretreating step preceding the regeneration proper.

It is known that sour hydrocarbon distillates and, more particularly, gasoline distillates can be sweetened by extracting mercaptans contained therein with aqueous solutions of alkali metal hydroxides containing solutizers. In this process, the role of the solutizer is to increase the solvent power of the aqueous solution for free mercaptans. Solutizers, therefore, are substances which are readily soluble in aqueous solutions of caustic alkali, are substantially insoluble in the hydrocarbon oil to be extracted, are good solvents for free mercaptans, are inert to the caustic alkali even at the elevated temperatures of steam stripping, and preferably have boiling temperatures substantially above that of water. To be effective, the solutizer must be present in an amount sufficient to materially raise the solvent power of the aqueous solution for mercaptans, e. g., normally in amounts in excess of about 15%.

Among the many substances having solutizing properties, the following are the most useful: Amino and hydroxy alkyl amines in which the alkyl radicals have 2 to 3 carbon atoms; glycols, amino glycols and diamino alcohols of 3 to 5 carbon atoms; diamino, dihydroxy or amino hydroxy dialkyl ethers or thioethers in which the alkyl radicals have 2 to 3 carbon atoms; alkali metal, and particularly potassium salts of fatty acids having from 3 to 5 carbon atoms, or of hydroxy or amino fatty acids having from 4 to 7 carbon atoms, or of phenyl acetic or hydroxy or amino phenyl acetic acids, or of alkyl phenols; or mixtures of the above.

More detailed information about the various solutizers and the amounts in which they are effective has been disclosed in U. S. Patents 2,152,720, 2,152,723, 2,152,166, 2,149,379, 2,149,380, 2,156,577, 2,152,722, 2,164,851 and Serial Nos. 255,100 (filed February 7, 1939) and 271,962 (filed May 5, 1939).

It has been found that even though the solutizers are substantially insoluble in hydrocarbon oils, their presence in caustic alkali solutions in amounts sufficient materially to raise the solvent power of these solutions for mercaptans causes dissolution of appreciable amounts of the hydrocarbon oils in the aqueous phase when extracting the oils with the solutized solution. Thereafter, when regenerating spent extracting solution containing mercaptides and the dissolved oil, as by steam stripping, hydrocarbon oil and mercaptans are expelled together. Upon condensation of the resulting overhead vapors, a condensate is obtained which segregates into two layers, a water layer and an oily mercaptan layer, the latter being highly contaminated with hydrocarbon oil.

Frequently it is desired to produce relatively pure mercaptans and the content of hydrocarbon oil in the mercaptan layer is, therefore, of distinct disadvantage. The mercaptans and hydrocarbons cannot be separated by distillation, since they usually have similar boiling ranges. Analyses of mercaptan layers have shown that they sometimes contain 80% and more hydrocarbons.

Now I have discovered that when diluting with water a spent aqueous solution containing an effective amount of solutizer, absorbed mercaptans and hydrocarbons, a portion of the oil is released and separates out, without a simultaneous release of a proportionate amount of the absorbed mercaptans. The separated oil may be removed as by settling, centrifuging or the like. While it is usually sour, its content of mercaptans is not normally much greater than that of the hydrocarbon oil from which it had been extracted. Hence, if desired, it may be returned to the sour distillate receiving treatment, or it may be used for any other desired purpose.

The diluted aqueous caustic alkali solution freed from a large portion of the absorbed hydrocarbon oil may then be regenerated by steam stripping in the usual way and preferably by the method described in the Yabroff-White Patent 2,152,724. Mercaptans thus recovered, though normally still containing a small amount of neutral oil, are of a much higher degree of purity than prior to the separating step described. Whereas prior to the separating step, contents of 80% and more neutral oil are the rule, after the separating step this content is frequently below 15% and occasionally even below 5%.

The percent of dissolved oil separated depends primarily on the degree of dilution. The following example shows the effect which dilution with various amounts of water may have on the solubility of hydrocarbons in the solutized aqueous caustic alkali solution.

A sour gasoline was extracted with an aqueous alkaline solution containing 6 gm. mol KOH and 3 gm. mol potassium isobutyrate per liter. The spent solution was analyzed for its hydrocarbon oil content, and was found to contain .45% by volume hydrocarbons. Upon the addition of wa-

ter, the content of hydrocarbon decreased as shown in the table below:

Volume water added per 100 vol. alkaline solution	Gasoline solubility percent by volume
None	.45
15	.15-.20
30	.05-.10

My process is further illustrated in the attached drawing which represents a simplified flow diagram of a preferred form of my process.

A sour gasoline distillate is introduced from a source not shown into extractor 1 through line 2, and is sweetened by extraction with an aqueous solution of a caustic alkali containing sufficient solutizer to enable the desired sweetening to take place. Sweet distillate emerges through line 3 and fat aqueous solution containing absorbed mercaptans and hydrocarbons passes through bottom line 4 to a surge or settling tank 5. Water recovered from the stripping operation in a manner presently to be described is added from line 6 to the fat solution in line 4. Immediately upon dilution, the fat solution releases a portion of its dissolved hydrocarbons, which in tank 5 is allowed to rise to the top and is withdrawn through line 7. If desired, the separated oil may be returned through line 8 to the sour distillate entering extractor 1.

The resulting lean solution, which still contains substantially all of the absorbed mercaptans passes from tank 5 through heat exchanger 9 in line 11, and the resulting hot solution enters steam stripper 12 at a point immediately below tray 13. Tray 13 divides the stripper 12 into an upper smaller reflux section and a lower large stripping section. The hot lean solution flows down through the stripper section in countercurrent to stripping steam which enters the stripper near its bottom through line 14. The stripped lean solution then passes from the stripper 12 through line 15 to reboiler 16, where the water of dilution, which had been added to the fat solution in line 4, is vaporized, and steam so produced is used for stripping, returning to the steam stripper through line 14.

Regenerated and reconcentrated caustic alkali solution returns to the top of extractor 1 through line 17 to sweeten further amounts of sour distillate.

The steam in stripper 12 rises through plate 13 into the upper reflux section in which a portion of the small amount of residual dissolved hydrocarbons, which have remained in the lean solution after dilution and which are expelled in the stripper, may be condensed and returned to tank 5 together with the water of dilution, through lines 18 and 6 and heat exchanger 9.

The small amount of mercaptans dissolved in the reflux added through line 22 to stripper 12 are steamed out in the reflux section (above plate 13) and the water of dilution flowing through line 18 is thus substantially free of mercaptan. This reflux also serves as a spray catcher.

The remaining vapors emerge from the reflux section of stripper 12 through line 19 and are condensed in condenser 20. The resulting condensate flows into receiving tank 21, where two liquid layers are formed, an upper relatively pure mercaptan layer which is withdrawn through line 23, and a lower water layer, containing small amounts of mercaptans, which layer is returned through line 22 to the stripping sections where it serves as reflux. In the course of the refluxing, the small amounts of mercaptans contained in the reflux water are revaporized so that the water withdrawn from plate 13 and used for dilution purposes in tank 5 is substantially free from mercaptans.

The amount of water available for dilution in tank 5, in a completely closed system as the one described above, is controlled by the amount of steam required to effect the regeneration. The more steam is used for stripping, the more water is available for diluting. Experience has shown that the amount of steam required varies between wide limits, depending not only on the nature of the hydrocarbon distillate to be sweetened, but also on the number of theoretical stages in both the extraction and stripping equipment available. Thus, the amount of water available for dilution may normally vary between about 5% to 200% by volume of the spent aqueous caustic alkali solution.

Even in a system which is not completely closed, i. e., in which water for dilution may be introduced into line 6 and tank 5 from an outside source through line 24, in which further excessive water of condensation in tank 21 may be disposed of through line 25, and in which steam for stripping may be introduced from an outside source through line 26, the amount of water of dilution may not exceed that which is removed by evaporation in the reboiler 16, otherwise the circulating solution would become more and more diluted and incapable of sweetening the sour distillate.

I claim as my invention:

1. In the process of regenerating by steam stripping a spent aqueous solution of caustic alkali which contains an amount of solutizer sufficient materially to raise the solvent power of the aqueous solution for mercaptans, which further contains mercaptans and dissolved hydrocarbon oil, and which has been used to extract mercaptans from sour hydrocarbon distillates, the improvement comprising diluting said spent solution with water, whereby at least a portion of said dissolved oil is precipitated to form a separate phase, separating the precipitated oil from the diluted solution and thereafter subjecting the latter to steam stripping to expel mercaptans.

2. In the process of regenerating by steam stripping a spent aqueous solution of caustic alkali which contains an amount of solutizer sufficient materially to raise the solvent power of the aqueous solution for mercaptans, which further contains mercaptans and dissolved hydrocarbon oil, and which has been used to extract mercaptans from sour hydrocarbon distillates, the improvement comprising diluting said spent solution with an amount by weight of water not greater than the amount by weight of steam required in the steam stripping, whereby at least a portion of said dissolved oil is precipitated to form a separate phase, separating the precipitated oil from the diluted solution, and thereafter stripping the latter with said amount of steam.

3. The process of claim 2 in which the amount of water of dilution is between 5% and 200% of the spent aqueous solution.

4. In the process of regenerating by steam stripping a spent aqueous solution of caustic alkali which contains an amount of solutizer sufficient materially to raise the solvent power of the aqueous solution for mercaptans, which

further contains mercaptans and dissolved hydrocarbon oil, and which has been used to extract mercaptans from sour hydrocarbon distillates, the improvement comprising diluting said spent solution with an amount by weight of water substantially equal to the amount by weight of steam required in the steam stripping, whereby at least a portion of said dissolved oil is precipitated to form a separate phase, separating the precipitated oil from the diluted solution, and thereafter stripping the latter with said amount of steam.

5. In the process of regenerating by steam stripping a spent aqueous solution of caustic alkali which contains an amount of solutizer sufficient materially to raise the solvent power of the aqueous solution for mercaptans, which further contains mercaptans and dissolved hydrocarbon oil, and which has been used to extract mercaptans from sour hydrocarbon distillates, the improvement comprising diluting said spent solution with water, whereby at least a portion of said dissolved oil is precipitated to form a separate phase, separating the precipitated oil from the diluted solution, stripping the latter with steam to remove mercaptans, thereby producing a foul steam containing mercaptans, condensing the foul steam to form a condensate which separates into two liquid layers, an upper mercaptan layer and a lower aqueous layer, separating the layers and using at least a portion of the condensed water for diluting said spent solution.

6. In the process of regenerating by steam stripping a spent aqueous solution of caustic alkali which contains an amount of solutizer sufficient materially to raise the solvent power of the aqueous solution for mercaptans, which further contains mercaptans and dissolved hydrocarbon oil, and which has been used to extract mercaptans from sour hydrocarbon distillates, the improvement comprising diluting said spent solution with water, whereby at least a portion of said dissolved oil is precipitated to form a separate phase, separating the precipitated oil from the diluted solution, stripping the latter with steam to remove mercaptans, thereby producing a foul steam containing mercaptans, refluxing said foul steam with water, condensing the refluxed foul steam to form a condensate which separates into two layers, an upper mercaptan layer and a lower water layer containing small amounts of mercaptans, separating the layers, using at least a portion of said water layer for said refluxing of said foul steam, whereby mercaptans dissolved in said portion are vaporized, and further using the resulting portion substantially free from mercaptans for diluting said spent solution.

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