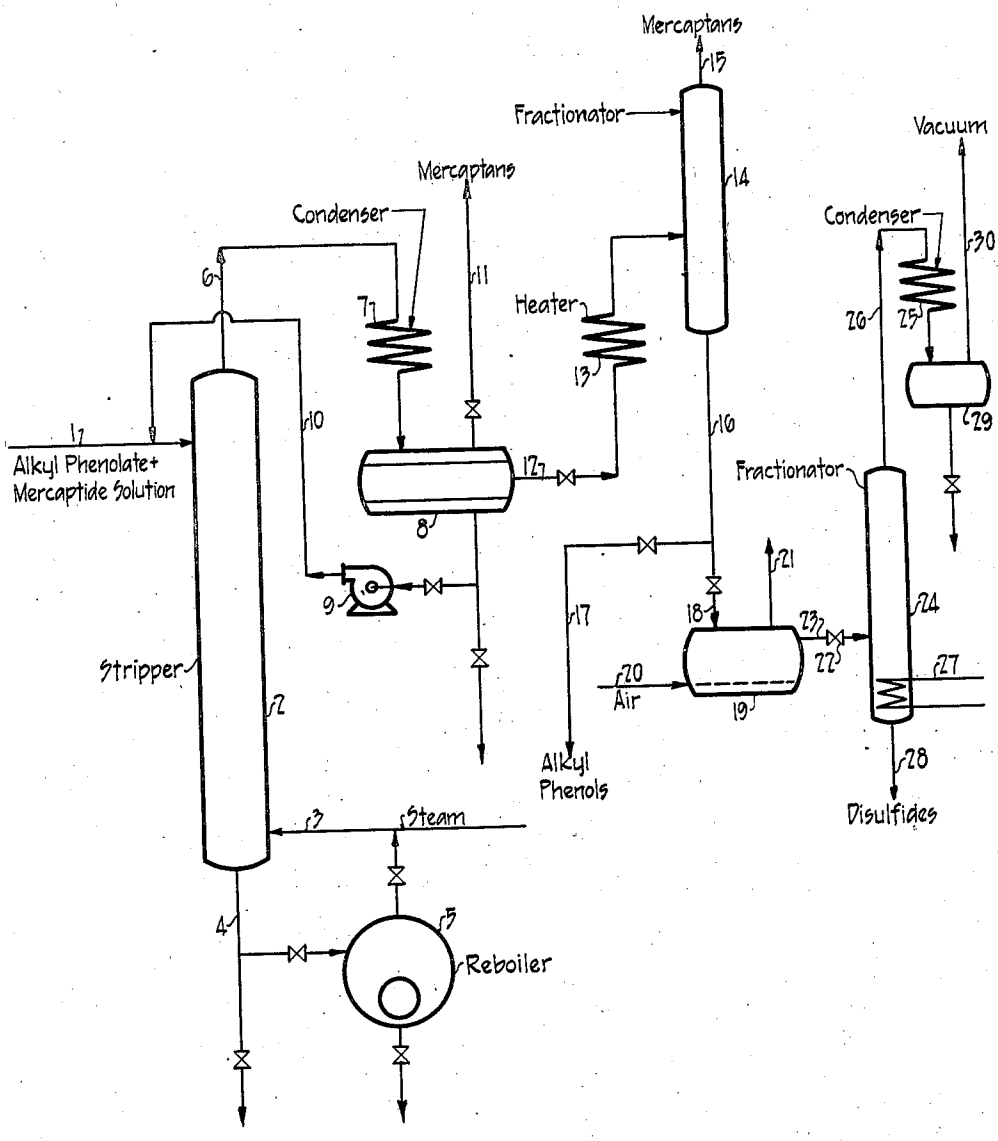
April 1, 1941. D. L. YABROFF ET AL 2,236,723

PROCESS FOR THE SEPARATION OF AZEOTROPIC MIXTURES

Filed March 4, 1939



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Patented Apr. 1, 1941

2,236,723

UNITED STATES PATENT OFFICE

2,236,723

PROCESS FOR THE SEPARATION OF AZEOTROPIC MIXTURES

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Application March 4, 1939, Serial No. 259,760

6 Claims. (Cl. 260—609)

This invention deals with the separation of three component azeotropic mixtures consisting essentially of mercaptans, alkyl phenols and water. Such mixtures are obtained when steam stripping aqueous solutions of caustic alkali containing substantial amounts of both mercaptides and alkyl phenolates.

It is known to extract mercaptans from sour distillates containing same by treating such distillates with strong aqueous solutions of a strong base, preferably an alkali metal hydroxide, in which is dissolved a substantial amount of a solubility promoter or solutizer for the mercaptans. The spent solutized caustic alkali solutions resulting from such extractions containing mercaptides are then regenerated, preferably by simple steam stripping, whereby the mercaptans are liberated and taken overhead together with the stripping steam.

Solutizers to be suitable in the extraction must have the following properties: They must be at least partially soluble in the aqueous base solution; they must be inert to the base even under conditions of steam stripping; they must boil higher than water, be insoluble in hydrocarbon distillates in the presence of 15% or less water and be good solvents for the mercaptans. Among the several compounds which are known to be suitable as solutizers, alkyl phenolates are particularly useful, especially in admixture with other solutizers such as alkali metal salts of hydrocarbon carboxylic acids, e. g., fatty acids, having from 1 to 8 carbon atoms, diamines or alkanolamines, the alkylene radicals of which contain 2 or 3 carbon atoms; glycols, amino glycols or diamino alcohols of 3 to 5 carbon atoms; dihydroxy, diamino, or amino hydroxy diethyl ethers, thioethers or imino ethers, etc. Reasons for the exceptional suitability of alkyl phenolates are explained in detail in our copending application Serial No. 255,684, filed February 10, 1939.

However, alkyl phenolates have the disadvantage of being partially decomposed during regeneration by steam stripping of spent alkaline solutions containing them, free alkyl phenols being taken overhead, together with the stripping steam and the mercaptans. We have found that the mixtures of steam, mercaptans and alkyl phenols thus produced form azeotropes which resist being separated by ordinary refluxing with condensate water, even though alkyl phenols in the mixture are normally much higher boiling than water or the mercaptans, the boiling temperature of phenol (mono hydroxy benzene), the lowest boiling hydroxy aromatic compound, being 182° C., and alkyl phenols except ortho-cresol boiling above 200° C.; while practically all mercaptans removed from hydrocarbon oils by solutized aqueous caustic alkali solutions in substantial amounts boil below about 180° or 200° C.

The alkyl phenols coming overhead in this manner are effectively lost, being discarded together with the mercaptans, unless special steps are taken to recover them. Since losses of alkyl phenols from this source materially raise the cost of the mercaptan extraction with solutized alkaline solutions, it is important that these alkyl phenols be recovered. One method in which the problem was solved has been described in our copending application Serial No. 235,572, filed October 18, 1938. According to this method, a small amount of a caustic alkali, i. e., from .5 to 5 mol equivalent of the alkyl phenols contained in the overhead stream, may be added to the latter to produce an aqueous layer containing alkyl phenolates and an oil layer consisting predominantly of mercaptans.

Now we have discovered a simple manner, not requiring the addition of an alkaline solution to the overhead mixture, in which to separate the azeotropes consisting essentially of steam, alkyl phenols and mercaptans. Our method comprises the steps of cooling the azeotropic mixture to condense the steam and to form hot water, simultaneously to condense the alkyl phenols and a portion of the mercaptans. The condensed mixture is then allowed to stand, whereupon three fluid layers are formed, two liquid layers and a vapor layer. The lower liquid layer consists essentially of water. The upper liquid layer being an oily layer consists essentially of mercaptans and alkyl phenols; and the vapor layer normally consists essentially of mercaptans boiling below the boiling point of water and also contains other non-condensible substances which, for instance, may have been introduced together with the steam. The three layers are withdrawn separately, and the middle oily layer is redistilled, preferably in the absence of added live steam. Fractionation may be so regulated to produce an overhead product substantially free from alkyl phenols having an end boiling point below the boiling temperature of the lowest boiling alkyl phenols present in the mixture and containing substantially all of the mercaptans boiling below the alkyl phenols, as well as small amounts of water which may have been dissolved in the mixture. The residual bottom fraction consisting predominantly of alkyl phenols may contain a small amount of relatively high boiling mercap-

tans. If desired, this bottom fraction may be further purified by oxidizing the mercaptans to disulfides, for example, by air blowing at temperatures between about 130° to 150° C., and thereafter redistilling the oxidized product, preferably under vacuum, to take the alkyl phenols overhead while leaving the disulfides in the second distillation residue.

Alkyl phenols so produced and purified are substantially free from mercaptans, and are excellent gum inhibitors for gasolines, having a greater inhibiting power than the average alkyl phenols recoverable from petroleum oils.

In the attached drawing is shown an illustrative flow diagram of one form of our process which may be used to carry out our invention.

An alkaline aqueous solution containing substantial amounts of alkyl phenolates and mercaptides such as may result from the sweetening of sour gasolines by extracting same with a solutized aqueous caustic alkali solution, is introduced preferably while hot, e. g., at a temperature near its boiling point, through line 1 into the upper part of steam stripper 2. The stripper may be of conventional design, and may contain baffles, bubble plates or a packing, etc. The hot solution flows downwardly through the stripper in countercurrent to steam introduced through line 3. Steam from an outside source not shown may be used, or it may be produced by boiling the stripped solution emerging from the stripper through line 4, in reboiler 5.

In the course of its upward path through the stripper and the counterflowing aqueous solution, the steam liberates a considerable portion of the mercaptans and alkyl phenols contained in the solution in the form of their salts. The resulting vaporous mixture of steam, mercaptans and alkyl phenols leaves the stripper through overhead line 6 and is cooled in condenser 7 to effect condensation of the steam to water. The condensing operation is advantageously controlled so that the condensate emerges from the condenser while hot, preferably as close to the boiling temperature of the water as is practical. The hot condensate is accumulated in tank 8 wherein 3 layers are formed: A lower liquid layer consisting essentially of water; an upper oily liquid layer consisting essentially of alkyl phenols and mercaptans boiling above the condensation temperature; and a vapor layer comprising mercaptans boiling below the condensation temperature.

Maintenance of the relatively high temperature in tank 8 is desirable to prevent dissolution of lighter mercaptans, particularly methyl mercaptan, in water, these lighter mercaptans being somewhat soluble in water. Water containing dissolved light mercaptans is obnoxious and is useless for most purposes. On the other hand, if the water is substantially free from mercaptans it may, for example, be returned, preferably while hot, by means of pump 9 through line 10, into line 1 for the purpose of diluting the incoming alkaline solution in order to facilitate its steam stripping in accordance with the principles disclosed in our copending application Serial No. 174,512, filed November 15, 1937. If desired, stripping may be conducted under considerable superatmospheric pressure.

The vaporous mercaptans are withdrawn from tank 8 through line 11 and may be utilized in any manner desired.

The oily liquid middle layer in tank 8 is taken through line 12 and heater 13 to be fractionally distilled in fractionator 14. In this distillation, it is usually possible to produce mercaptan fractions substantially free from alkyl phenols boiling up to 200° C. and even higher, by reason of the fact that the alkyl phenols which are taken overhead by the steam in the steam stripping of the strongly alkaline alkyl phenolate solutions are those which are relatively weakly acidic containing one or several alkyl radicals and having boiling temperatures above about 200° C.

The distillation is carried out in the absence of added steam or water to avoid as much as possible recurrence of the three component azeotropic mixtures, and is so controlled to produce an overhead fraction, removed through line 15, which fraction consists essentially of mercaptans and a small amount of water and which is substantially free from alkyl phenols. The distillation residue comprises the alkyl phenols and high boiling mercaptans boiling within the distillation range of the alkyl phenols, mercaptans, however, normally being present in small amounts only. This residue fraction emerges from fractionator 14 through line 16 and may go to storage through line 17 or through line 18 to tank 19.

In tank 19, the alkyl phenols may be air blown with air from line 20 to oxidize the residual mercaptans to disulfides, preferably at a temperature between about 130° to 150° C. This temperature may be controlled in any desired manner by means not shown. Waste air is vented through vent line 21.

The air blown alkyl phenols, while still hot, are then released through release valve 22 in line 23 into vacuum fractionating tower 2, where alkyl phenols are vaporized and are condensed in condenser 25 situated in line 26. Heat necessary for the distillation may be provided by heating coil 27. Disulfides are withdrawn through bottom line 28.

Condensed alkyl phenols substantially free from mercaptans are accumulated in receiver tank 29, line 30 connecting this tank with source of vacuum not shown.

While in the foregoing we have described a simplified flow diagram of our process, it is understood that other modifications are possible. In particular is the installation of additional pumps, heaters, coolers, condensers, heat exchangers, by-passes, tanks, etc., wherever necessary, considered within the skill of the average designer for such equipment.

We claim as our invention:

1. In the process of separating an azeotropic vapor mixture of steam, mercaptans and alkyl phenols, said mercaptans boiling above and below the boiling point of water, the steps comprising cooling said mixture to condense said steam and to produce hot water, simultaneously to condense said alkyl phenols and a portion of said mercaptans, thereby producing three fluid layers, a lower liquid layer consisting essentially of hot water free from dissolved light mercaptans normally soluble in water, an upper liquid oily layer comprising mercaptans and alkyl phenols, and a vaporous layer comprising uncondensed mercaptans, separately withdrawing the three layers, and fractionally distilling the oily layer substantially in the absence of added steam or water to produce an overhead mercaptan fraction having an end boiling point below the boiling temperature of the alkyl phenols present in the mixture and a residual alkyl phenol fraction.

2. The process of claim 1 in which the mer-

captan fraction has an end boiling point below 200° C.

3. A process for removing mercaptans from aqueous alkaline solutions containing mercaptides and alkyl phenolates comprising the steps of stripping said aqueous solution with live steam, thereby producing a vaporous azeotropic mixture of steam, mercaptans and alkyl phenols, separating said vaporous mixture from the aqueous solution, cooling the separated mixture to condense said steam and to produce hot water, simultaneously to condense said alkyl phenols and a portion of the mercaptans, thereby producing three fluid layers, a lower liquid layer consisting essentially of hot water free from dissolved light mercaptans normally soluble in water, an upper liquid oily layer comprising mercaptans and alkyl phenols, and a vaporous layer comprising uncondensed mercaptans, separately withdrawing the three layers and fractionally distilling the oily layer in the absence of added steam to produce an overhead mercaptan fraction having an end boiling point below the boiling temperature of the alkyl phenols present in said mixture and a residual alkyl phenol fraction.

4. A process for removing mercaptans from aqueous alkaline solutions containing mercaptides and alkyl phenolates comprising the steps of stripping said aqueous solution with live steam, thereby producing a vaporous azeotropic mixture of steam, mercaptans and alkyl phenols, separating said vaporous mixture from the aqueous solution, cooling the separated mixture to condense said steam and to produce hot water, simultaneously to condense said alkyl phenols and a portion of the mercaptans, thereby producing three fluid layers, a lower liquid layer consisting essentially of hot water free from dissolved light mercaptans normally soluble in water, an upper liquid oily layer comprising mercaptans and alkyl phenols, and a vaporous layer comprising uncondensed mercaptans, separately withdrawing the three layers, returning the condensed water to said aqueous solution, and fractionally distilling the oily layer in the absence of added steam to produce an overhead mercaptan fraction having an end boiling point below the boiling temperature of the alkyl phenol fraction.

5. In the process for the recovery of mercaptans which boil both above and below the boiling point of water and alkyl phenols from a spent aqueous solution obtained in this process which comprises extracting a sour hydrocarbon oil containing mercaptans and alkyl phenols with an aqueous solution of a caustic alkali containing a substantial amount of alkyl phenols to produce a spent solution containing mercaptides and alkyl phenolates, regenerating said spent solution by stripping with steam whereby a foul steam is produced containing mercaptans and alkyl phenols, the steps comprising cooling said foul steam to produce a vapor consisting predominantly of uncondensed mercaptans and two liquid layers, a lower layer consisting essentially of hot water free from dissolved light mercaptans normally soluble in water and an upper oily layer comprising mercaptans and alkyl phenols, separately withdrawing the two liquid layers, fractionally distilling the oily layer in the absence of added steam to produce an overhead mercaptan fraction having an end boiling point below the boiling temperature of the alkyl phenols present in the mixture and a residual alkyl phenol fraction.

6. In the process of separating an azeotropic vapor mixture of steam, mercaptans and alkyl phenols, said mercaptans boiling above and below water, the steps comprising cooling said mixture to condense said steam and to produce hot water of sufficiently high temperature to prevent dissolution of lighter mercaptans, simultaneously to condense said alkyl phenols and a portion of said mercaptans, thereby producing three fluid layers, a lower liquid layer consisting essentially of hot water free from dissolved light mercaptans normally soluble in water, an upper liquid oily layer comprising mercaptans and alkyl phenols, and a vaporous layer comprising uncondensed mercaptans, separately withdrawing the three layers, and fractionally distilling the oily layer substantially in the absence of added steam or water to produce an overhead mercaptan fraction having an end boiling point below the boiling temperature of the alkyl phenols present in the mixture and a residual alkyl phenol fraction.

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