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B. A. FROLOV

2,213,801

PROCESS FOR THE SWEETENING OF HYDROCARBON DISTILLATES

Filed Jan. 28, 1939

2 Sheets-Sheet 1

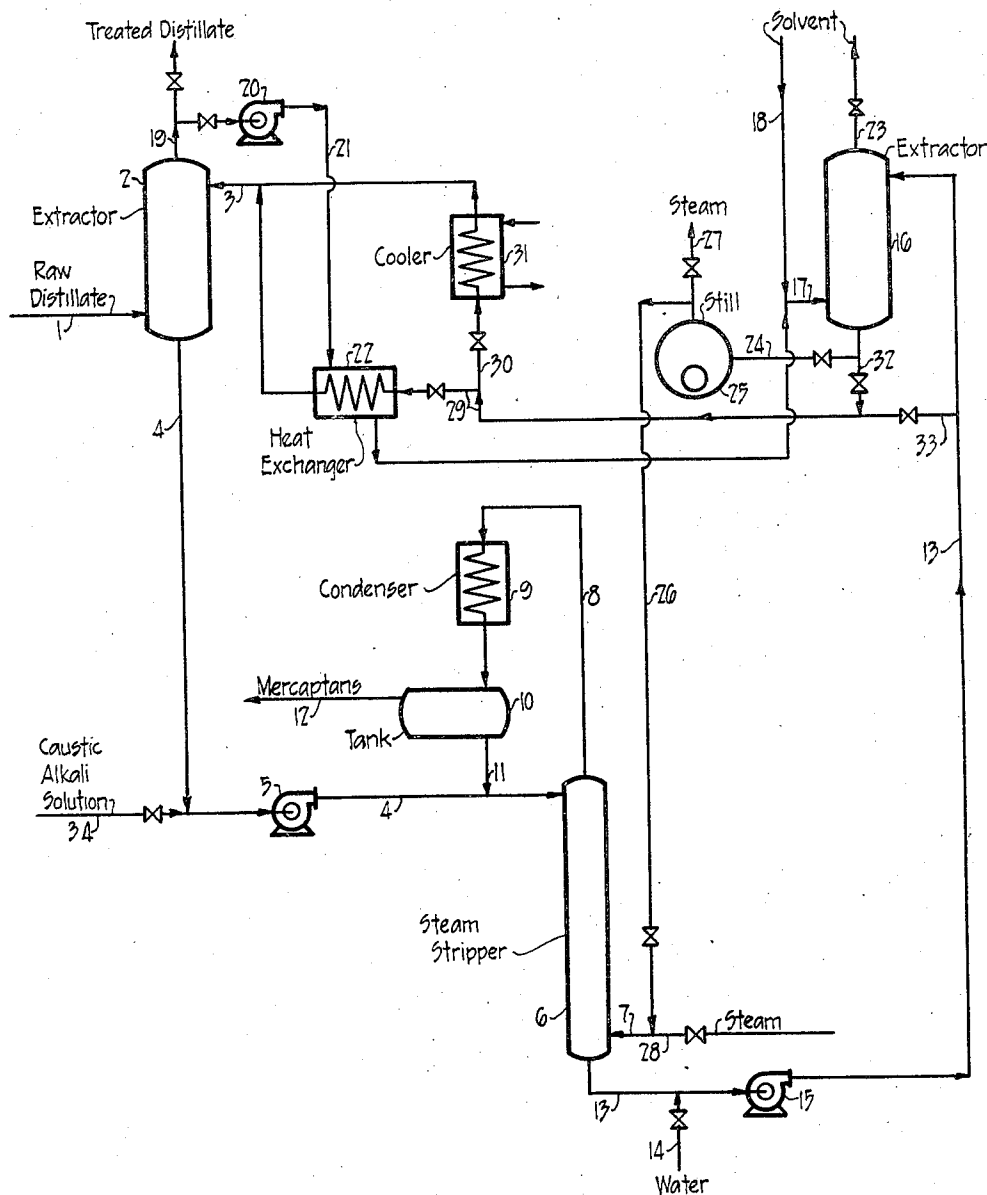


FIG. 1

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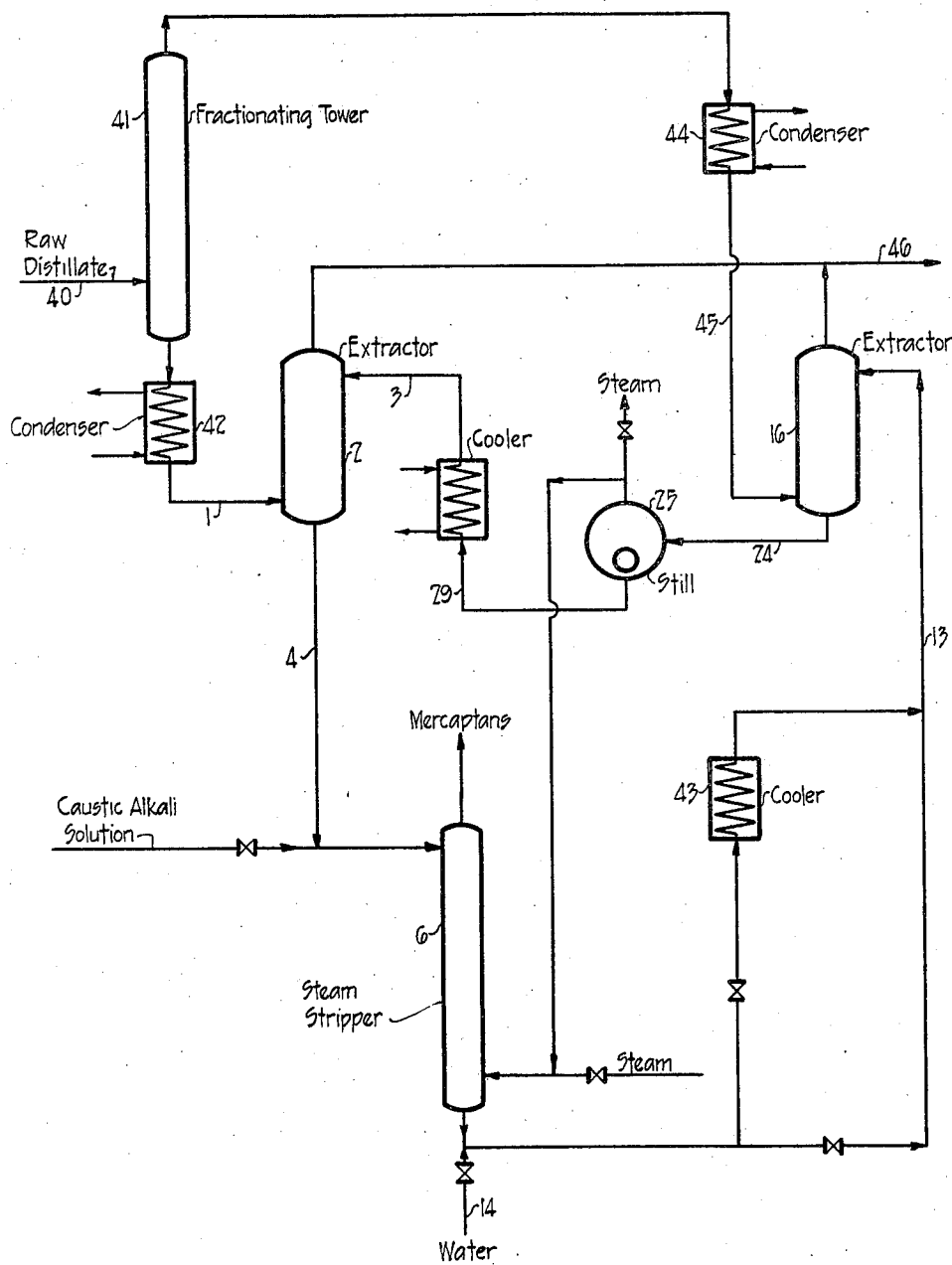


FIG. 2

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UNITED STATES PATENT OFFICE

2,213,801

PROCESS FOR THE SWEETENING OF
HYDROCARBON DISTILLATES

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Application January 28, 1939, Serial No. 253,357

11 Claims. (Cl. 260—609)

This invention relates to processes for the removal of weak organic acids from organic water-insoluble liquids by extraction with aqueous solutions of strong bases preferably containing substantial amounts of solubility promoters as solutizers for said acids, and more particularly deals with a method for controlling the compositions of these aqueous solutions.

It is known that weak organic acids, such as those having dissociation constants below about 10^{-5} , e. g., mercaptans, alkyl phenols, thiophenols, etc., are difficult to remove from their solutions in organic water-insoluble liquids by extraction with aqueous solutions of caustic alkali. It is further known that the extraction of these acids can be materially improved by adding to the aqueous solution substantial amounts of solubility promoters or solutizers for said organic acids. Suitable solutizers are organic compounds which are good solvents for the organic acids, are at least partially soluble in the aqueous solution of the base, are substantially insoluble in the organic water-insoluble solvent, and are physically and chemically inert to the action of caustic alkalis even at elevated temperatures of steam stripping. Thus, for example, the following compounds are known to be suitable solutizers of the type described: aliphatic alkanolamines and amino alkylamines in which the alkyl radicals contain two to three carbon atoms; diamino alcohols, glycols and amino glycols of three to five carbon atoms; alkyl glycerines in which the number of carbon atoms in the alkyl radicals is from one to four, diamino, di-hydroxy or amino hydroxy alkyl ethers or thioethers in which the alkyl radicals have from two to three carbon atoms; alkali metal and particularly potassium salts of fatty acids having from one to six carbon atoms, amino or hydroxy fatty acids having from two to seven carbon atoms, phenyl acetic acid, hydroxy or amino phenyl acetic acids, phenol, alkyl phenols; mixtures of the above, etc.

The amounts of solubility promoters dissolved in the aqueous base solution to be effective may vary between about 15% to 85%, and preferably 25% to 75%, although in some instances the maximum which may be added is less because of a limited solubility.

Strong bases applicable in the extraction are in particular the alkali metal hydroxides, the sodium and potassium hydroxides being preferred. However, other strong bases, such as alkali metal hydroxides, ammonia, quaternary ammonium bases, etc., may be useful.

It is further known that the organic solvents

from which the weak organic acids are to be removed, aside from being substantially insoluble in water, should also be inert to the action of the base under the conditions of the extraction, i. e., at about normal room temperature and for a period of, say, at least 10 minutes.

Extraction of weak organic acids with the aid of solutizers has its most important application in the refining, and more particularly, in the sweetening of sour gasolines, kerosenes, naphthas, generally referred to as hydrocarbon distillates, i. e., in the extraction of mercaptans and other weak organic acids, such as alkyl phenols, which may be contained in sour distillates. The extraction process is usually carried out by contacting the unrefined hydrocarbon distillate at a temperature between about 0° to 60° C. with the aqueous solution of the strong base containing solutizers, preferably in countercurrent in several stages or in a packed tower. The resulting treated distillate is separated from the spent aqueous solution containing absorbed organic acids, the treated distillate is water washed if necessary, to recover small amounts of solutizers which may have been dissolved in the distillate, and the resulting wash water may be combined with the spent aqueous solution if washing has been resorted to. The combined aqueous solution is then steam stripped to remove absorbed mercaptans. The stripped aqueous solution is returned to treat further amounts of unrefined distillate.

It has now been found that difficulty may be experienced in the above regenerative process when treating distillates containing in addition to mercaptans considerable amounts of alkyl phenols. Alkyl phenols are, on the average, somewhat more strongly acidic than mercaptans, and therefore are more difficult to remove from the aqueous base solution by steam stripping. As a result, there is a tendency to accumulate in the circulating aqueous base solution an amount of alkyl phenolates which may be harmful to the continued operation of the process. For example, excessive amounts of alkyl phenolates in the aqueous base solution may raise its viscosity to such an extent that incomplete separation between the distillate and the aqueous solution in the extraction is obtained; or they may precipitate at some point of the system where a low temperature is maintained a portion of the solutizer contained in the aqueous solution, precipitation often causing serious difficulties, particularly if the solutizer is a solid under the conditions of the extraction.

It is a purpose of this invention to prevent the building-up of alkyl phenolates above a certain desired maximum in the circulating aqueous base solutions, which solutions are used for extracting mercaptans from sour distillates containing alkyl phenols, and which are continuously regenerated by steam stripping to remove absorbed mercaptans. It is another purpose to return a portion of the extracted alkyl phenols to distillates from which they were derived without returning mercaptans. Other purposes and advantages will become apparent from the description below.

My process comprises the steps of extracting sour hydrocarbon distillate containing both mercaptans and alkyl phenols with an aqueous solution of a strong base capable of extracting at least a portion of the mercaptans. Preferably a sufficient amount of mercaptans should be removed to effect sweetening of the distillate. To be effective, the aqueous base solution should contain a substantial amount of a solutizer of the type hereinbefore described. Incidental to this mercaptan extraction, a major portion of the alkyl phenols are extracted simultaneously. The resulting spent base solution containing mercaptides and alkyl phenolates is steam stripped to regenerate it, whereby a relatively large portion of the mercaptans and a smaller portion of the alkyl phenols are expelled. In order that the regenerated solution may be used successfully for further sweetening, it is necessary to reduce its mercaptan content to a certain maximum level, which may be established experimentally in each individual case. Since, however, the steaming operation is relatively expensive, the minimum amount of steam is used which will barely strip mercaptans to this desired level. Under these conditions, a relatively large portion of the alkyl phenols is retained by the aqueous base solution. To remove this excess of retained alkyl phenols and to prevent its building up in the circulating aqueous solution, I now contact the stripped aqueous solution with a solvent for alkyl phenols under conditions unfavorable to the absorption of weak organic acids in aqueous caustic alkali. Such conditions are, for example, relatively high temperatures, low concentration of the solutizer in the aqueous solution, and/or of alkyl phenols in the solvent, etc. Thus, I may effect the contact of the aqueous alkyl phenolate solution with the solvent at a temperature substantially higher than that of the preceding extraction, for instance, at approximately the temperature of the steam stripping; or I may dilute the aqueous solution with water prior to contacting it; or both.

Solvents for the alkyl phenols useful for the removal of the latter from the aqueous base solution are, for example, hydrocarbon distillates, such as gasoline, kerosene, etc., benzene, toluene, xylene; alcohols preferably having 4 and more carbon atoms, as butyl, amyl, etc., alcohols; ketones, as acetone, methyl ethyl ketone, methyl propyl ketone, diethyl ketone, dipropyl ketone, etc.; ethers, as diethyl ether, diisopropyl ether, dibutyl ether, etc. While certain polar solvents, such as the diisopropyl ether, methyl ethyl ketone, amyl alcohols, etc., may be better solvents for the alkyl phenols than hydrocarbon distillates, and even may dissolve substantial amounts of the phenolate salts, I frequently prefer the use of hydrocarbon distillates which are free from mercaptans, particularly cracked distillates which, for reasons of gum stability, require the

addition of gum inhibitors. By contacting such distillates with a steam-stripped aqueous base solution under the conditions described, i. e., after pre-dilution or at elevated temperatures, or both, the double purpose of stabilizing these distillates and removing excess alkyl phenols from the base solution can be accomplished in a single operation. After the contact, the base solution may then be reconcentrated or cooled or both, as the case may require, and the resulting aqueous solution is ready for extracting further amounts of sour hydrocarbon distillates.

Figures 1 and 2 of the drawings represent flow diagrams of two possible variations of my process. In Fig. 1 is shown the general arrangement of a preferred form in which a sour hydrocarbon distillate containing mercaptans and alkyl phenols is extracted in an extraction zone with an aqueous solution of a caustic alkali. The resulting spent aqueous solution containing absorbed mercaptans and alkyl phenols is regenerated by steam stripping to expel mercaptans and thereafter scrubbed with the same distillate or a separate solvent for alkyl phenols to remove alkyl phenols. The regenerated aqueous solution is returned to the extraction zone. Fig. 2 discloses a special application of my process in which a hydrocarbon distillate containing both mercaptans and alkyl phenols is fractionally distilled to produce a light fraction containing light mercaptans but no alkyl phenols, and a heavier fraction containing the heavier mercaptans and all of the alkyl phenols. The heavier fraction is contacted with an aqueous caustic alkali solution to remove mercaptans and alkyl phenols, and the resulting spent aqueous solution is regenerated by steam stripping, whereby mercaptans are removed. The regenerated aqueous solution containing alkyl phenolates is now scrubbed with the light hydrocarbon fraction under conditions just sufficient to effect a transfer of the light mercaptans to the aqueous solution, thereby sweetening the light fraction. Since light mercaptans are relatively easily absorbed in aqueous caustic alkali, these conditions may be comparatively unfavorable for the extraction, which makes possible a simultaneous transfer of alkyl phenols in the opposite direction, i. e., from the aqueous alkaline solution to the light distillate. The treated light and heavy fractions may then be recombined to produce a sweet gasoline containing at least a substantial portion of the alkyl phenols originally contained therein.

Referring to Fig. 1, sour hydrocarbon distillate, such as a cracked gasoline distillate containing both mercaptans and alkyl phenols, is introduced through line 1 into extractor 2 from a source not shown. Aqueous solution of a caustic alkali, e. g., sodium or potassium hydroxide, preferably containing a substantial amount of one or several solutizers, such as sodium isobutyrate, diamino isopropanol, butylene glycol, is admitted through line 3 to the extractor 2 to flow in countercurrent to the distillate. The temperature in the extractor is preferably maintained between about 0° to 60° C. At temperatures below about 0° C., difficulties may arise because of excessive viscosity of the aqueous solution, partial or total solidification, etc., while at higher temperatures than 60 C. the extraction efficiency becomes so low as to make, in general, sweetening difficult, if not impossible. The spent aqueous solution which emerges from the extractor through line 4 contains dissolved a major portion of the mer-

captans and alkyl phenols originally contained in the distillate. This spent solution is conveyed by pump 5 to still or steam stripper 6 in which it is subjected to boiling or steam stripping, preferably in accordance with principles disclosed in the Yabroff and White application Serial No. 174,512, filed November 15, 1937. Stripping steam is injected into the stripper through line 7, and is removed together with liberated mercaptans and alkyl phenols through line 8 to be condensed in condenser 9. Condensate is accumulated in tank 10, where it forms two liquid layers, a lower water layer and a layer of organic acids. The water of condensation may be returned through line 11 to the spent caustic alkali solution passing through line 4 to pre-dilute the same and to facilitate its stripping. The layer of organic acids consisting predominantly of mercaptans is withdrawn from tank 10 through line 12.

Stripped aqueous caustic alkali solution which has retained a substantial portion of the alkyl phenols absorbed in the extractor 2, and which may be considerably diluted with water of condensation from tank 10, emerges from the bottom of stripper 6 through line 13. If further dilution is desired, additional water may be added through line 14. Pump 15 in line 13 conveys the solution to the top of the extractor 16, where it is further stripped of retained alkyl phenols by scrubbing with a suitable solvent for alkyl phenols. If desired, at least a portion of this stripped solutizer solution may be returned by pump 15 through lines 13, 33, 29 or 30, and 3 to the extractor 2 in order to maintain the desired concentration of alkyl phenols in the solutizer solution.

In the extractor-scrubber 16, conditions are maintained which are different from those in extractor 2. In extractor 2 a relatively low temperature ranging from about 0° to about 60° C. is maintained, and the caustic alkali solution passing through it is in a relatively concentrated state, having preferably a high content of solubility promoter. In the extractor-scrubber 16 a much higher temperature is usually maintained, preferably above 60° C. but below the boiling temperature of the lowest boiling substances entering it. If desired, considerable superatmospheric pressure of, say, 50 to 250 pounds or higher, may be maintained to enable operation at temperatures above the normal boiling temperature of the lowest boiling substance.

Solvent for the alkyl phenols is admitted to the extractor-scrubber 16 through line 17. This solvent may be supplied through line 18 from an outside source, not shown, or treated distillate leaving extractor 2 through line 19 may serve for this purpose. If treated distillate is used, all or a portion of it may be pumped by pump 20 in line 21 through heat exchanger 22, where its temperature is raised, preferably to 60° C. or above, and through line 17 to the extractor-scrubber 16. Solvent, containing alkyl phenols removed from the aqueous base solution, is withdrawn from the extractor-scrubber 16 through line 23.

Scrubbed aqueous caustic alkali solution now freed from mercaptans, as well as from excess of alkyl phenols, passes from extractor-scrubber 16 through line 32 and into extractor 2, if no further concentration is needed, or through line 24 to still 25, where it is concentrated by boiling. Steam so produced may be conveyed through line 26 to stripper 6 to be used in the steam

stripping operation. If preferred, however, it may be diverted through line 27 for some other purpose, and steam used for stripping may be introduced to stripper 6 through line 18 from an outside source not shown.

Reconcentrated aqueous caustic alkali solution is now returned to extractor 2 through lines 29 and 3 and heat exchanger 22, or through lines 30 and 3 and cooler 31, or both.

Make-up caustic alkali solution may be introduced into the cycle at some convenient point, for example, through line 34.

In Fig. 2, vapors of a gasoline distillate, e. g., a full range gasoline, containing both mercaptans and alkyl phenols, are admitted from a source not shown through line 40 to fractionating tower 41, in which they are separated by fractional distillation, into a light top fraction free from alkyl phenols containing light mercaptans, and a heavier bottom fraction containing all of the alkyl phenols and the heavier mercaptans. The heavier fraction passes through cooler 42 and line 1 to extractor 2, where it is extracted with aqueous caustic alkali solution admitted through line 3. The resulting spent aqueous solution containing heavier mercaptans and alkyl phenols passes through line 4 to steam stripper 6, where it is stripped of absorbed organic acids as described in connection with Fig. 1. The stripped solution may be diluted with water from line 14, and proceed through line 13 to extractor-scrubber 16. A portion or all of the solution may pass through cooler 43, while on its way to the extractor-scrubber 16.

The light fraction produced in fractionator 41 is condensed in condenser 44 situated in line 45, and thence enters extractor-scrubber 16 near its bottom. Conditions in the extractor-scrubber 16 are different from those in extractor 2 for the reasons stated in connection with Fig. 1. Since, in the instant case, however, it is desired to achieve a double purpose, i. e., not only of scrubbing alkyl phenols from the aqueous solution by means of the light distillate fraction, but also of simultaneously extracting light mercaptans from the latter in order to sweeten it, conditions may not usually be as favorable for scrubbing as formerly described. Obviously, the set of conditions which will result in optimum scrubbing of alkyl phenols from the aqueous caustic alkali solution with simultaneous production of sweetened light fraction will be chosen. What these conditions will be cannot be definitely stated, because they may vary over a wide range depending upon several factors. For example, if the light fraction contains very light mercaptans only, such as C₁—C₃ mercaptans, and is free from heavier mercaptans, more favorable scrubbing conditions, i. e., higher temperatures and/or greater degrees of dilution may be employed than if substantial amounts of heavy mercaptans were present. In other words, the boiling range and, more particularly, the end boiling point of the light fraction, has an important bearing as well as the degree of fractionation achieved in the fractional distillation. A well fractionated distillate is more easily sweetened than one containing high boiling portions. Likewise, much depends on the relative volumes of the two liquids countercurrently flowing through the extractor-scrubber 16: the higher the ratio of aqueous solution to distillate, the more favorable may be the scrubbing conditions. Other factors are concentration of both mercaptans and alkyl phenols in the regenerated aqueous solution entering the

extractor-scrubber 16, number of stages in the extractor-scrubber, etc.

Scrubbed aqueous solution free from excess of alkyl phenols but containing light mercaptans is transferred from the extractor-scrubber 16 through line 24 to still 25, where it is boiled in order to reconcentrate it. In the course of the boiling, a considerable portion of the mercaptans is driven off so that the resulting concentrated aqueous solution which is removed from the still 25 through line 29 is substantially regenerated and may be used for sweetening the heavier distillate fraction in extractor 29 described.

The two independently sweetened distillate fractions, that is, the heavier one from extractor 24 which has been substantially denuded of alkyl phenols, and the light fraction from extractor-scrubber 16, which has recaptured at least a portion of the alkyl phenols removed from the heavier fraction, may be joined in line 46 to produce a sweetened gasoline containing an adequate amount of natural gum inhibitors.

While in the foregoing I have described two flow diagrams of my process, it shall be understood that other variations are possible. In particular, the addition of pumps, by-passes, heat exchangers and other necessary equipment are considered to be within the skill of the designer for such equipment. Moreover, pieces of equipment described may be replaced by others known to be equivalent. For example, instead of using a steam stripper 6, I may employ a simple boiler.

I claim as my invention:

1. In a regenerative process of separating mercaptans from a hydrocarbon distillate containing both mercaptans and alkyl phenols by extraction with an aqueous solution of a strong base, the method of controlling the composition of said solution comprising the steps of treating said distillate with said aqueous solution under conditions to absorb mercaptans and alkyl phenols in the latter and to form two liquid layers, an aqueous layer containing absorbed mercaptans and alkyl phenols and a layer consisting essentially of treated distillate, separating the layers, subjecting the aqueous layer to a stripping to remove mercaptans and to produce a stripped solution retaining a substantial portion of the absorbed alkyl phenols, and scrubbing the stripped solution with a solvent for alkyl phenols.

2. The process of claim 1 in which the aqueous solution contains dissolved a substantial amount of a solubility promoter for mercaptans.

3. The process of claim 1 in which the stripped solution is scrubbed at a temperature which is higher than the temperature at which the distillate is treated.

4. The process of claim 1 in which the aqueous layer is diluted with water prior to the scrubbing.

5. In a regenerative process of separating mercaptans from a hydrocarbon distillate containing both mercaptans and alkyl phenols by extraction with an aqueous solution of a strong base, the method of controlling the composition of said solution comprising the steps of treating said distillate with said aqueous solution at a temperature between 0° and 60° C. to absorb mercaptans and alkyl phenols in the latter and to form two liquid layers, an aqueous layer containing absorbed mercaptans and alkyl phenols, and a layer consisting essentially of treated distillate, separating the layers, subjecting the aqueous layer to a stripping to remove mercaptans and to produce a stripped solution retaining a substantial portion of the absorbed alkyl phenols, and scrubbing the

stripped solution with a solvent for alkyl phenols at a temperature higher than that of treating said distillate but below the boiling temperature of the lowest boiling substance employed in said scrubbing.

6. The process of claim 5 in which the scrubbing is carried out under superatmospheric pressures.

7. In a regenerative process of separating mercaptans from a hydrocarbon distillate containing both mercaptans and alkyl phenols by extraction with an aqueous solution of a strong base, the method of controlling the composition of said solution comprising the steps of treating said distillate with said aqueous solution under conditions to absorb mercaptans and alkyl phenols in the latter and to form two liquid layers, an aqueous layer containing absorbed mercaptans and alkyl phenols, and a layer consisting essentially of treated distillate, separating the layers, subjecting the aqueous layer to a steam stripping to remove mercaptans and to produce a stripped solution retaining a substantial portion of the absorbed alkyl phenols, and scrubbing the stripped solution with said treated distillate at a temperature which is higher than the temperature of treating said distillate.

8. In a regenerative process of separating mercaptans from a hydrocarbon distillate containing both mercaptans and alkyl phenols by extraction with an aqueous solution of a strong base, the method of controlling the composition of said solution comprising the steps of treating said distillate with said aqueous solution in an extraction zone under conditions to absorb mercaptans and alkyl phenols in the latter and to form two liquid layers, an aqueous layer containing absorbed mercaptans and alkyl phenols and a layer consisting essentially of treated distillate, separating the layers, subjecting the aqueous layer to a stripping to remove mercaptans and to produce a stripped solution retaining a substantial portion of the absorbed alkyl phenols, diluting said solution with water at a point subsequent to the separation of said layers, thereby producing a dilute solution, scrubbing the dilute solution with a solvent for alkyl phenols, boiling the scrubbed solution to vaporize water of dilution, and returning the resulting reconcentrated solution to said extraction zone.

9. The process of claim 8 in which steam produced in the boiling of the stripped solution is used for stripping said aqueous layer.

10. In a regenerative process of separating mercaptans from a hydrocarbon distillate containing both mercaptans and alkyl phenols by extraction with an aqueous solution of a strong base, the method of controlling the composition of said solution comprising the steps of fractionally distilling said distillate to produce a low boiling fraction free from alkyl phenols and containing low mercaptans and higher boiling fraction containing alkyl phenols and higher mercaptans, treating said higher boiling fraction in a first extraction zone with said aqueous solution under conditions to absorb mercaptans and alkyl phenols in the latter and to form two liquid layers, a first aqueous layer containing absorbed heavy mercaptans and alkyl phenols and a layer consisting essentially of treated higher boiling distillate, separating the layers, subjecting the first aqueous layer to a steam stripping to remove mercaptan and to produce a stripped aqueous solution retaining a substantial portion of the absorbed alkyl phenols, treating the low boiling

fraction with the stripped solution in a second extraction zone at a temperature higher than that of the first extraction zone but sufficiently low to absorb at least a substantial portion of said low mercaptans in the stripped aqueous solution and to form two liquid layers, one comprising a second aqueous layer containing absorbed low mercaptans, and the other consisting essentially of treated low boiling fraction containing alkyl phenols, combining the treated low and higher boiling fractions and returning said second aqueous layer to said first extraction zone.

11. In a regenerative process of separating mercaptans from a hydrocarbon distillate containing both mercaptans and alkyl phenols by extraction with an aqueous solution of a strong base, the method of controlling the composition of said solution comprising the steps of fractionally distilling said distillate to produce a low boiling fraction free from alkyl phenols and containing low mercaptans, and higher boiling fraction containing alkyl phenols and higher mercaptans, treating said higher boiling fraction in a first extraction zone with said aqueous solution under conditions to absorb mercaptans and alkyl

phenols in the latter and to form two liquid layers, a first aqueous layer containing absorbed heavy mercaptans and alkyl phenols and a layer consisting essentially of treated higher boiling distillate, separating the layers, subjecting the first aqueous layer to a steam stripping to remove mercaptans and to produce a stripped aqueous solution retaining a substantial portion of the absorbed alkyl phenols, diluting said solution with water at a point subsequent to the separation of said layers, thereby producing a dilute solution, treating the low boiling fraction with the diluted stripped solution under conditions to absorb low mercaptans in the aqueous solution, to dissolve alkyl phenols in said low boiling fraction, and to form two liquid layers, one comprising a second aqueous layer containing absorbed mercaptans, and the other consisting essentially of the treated low boiling fraction containing alkyl phenols, combining the treated low and higher boiling fractions, boiling said second aqueous layer to vaporize water of dilution and returning the resulting reconcentrated aqueous solution to said first extraction zone.

BORIS A. FROLOV. 25