

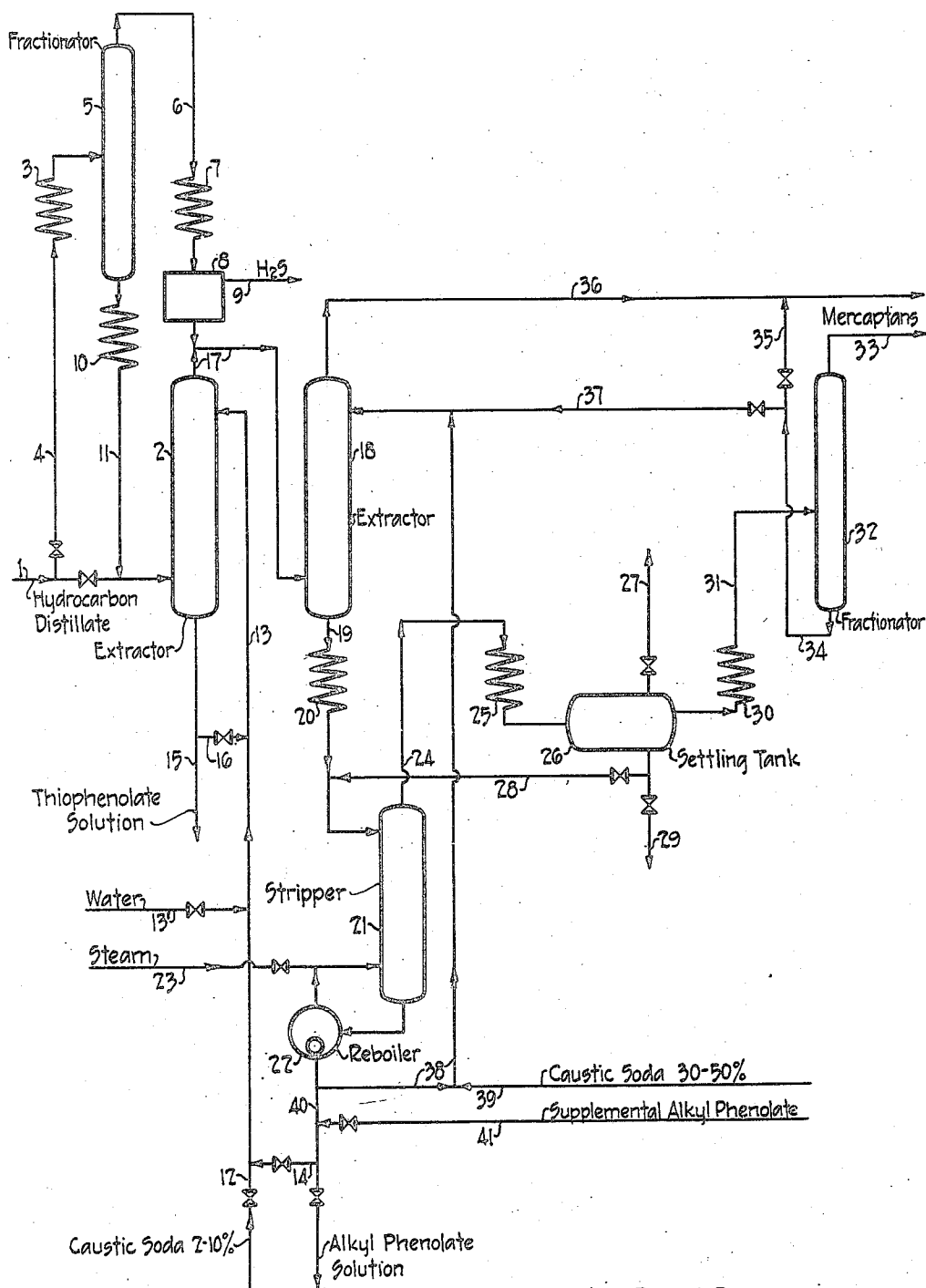
Jan. 7, 1941.

P. V. BROWER

2,228,028

PROCESS FOR THE REMOVAL OF MERCAPTANS FROM HYDROCARBON DISTILLATES

Filed June 19, 1939



Inventor: Paul V. Brower

By his Attorney: E. W. Zuber

UNITED STATES PATENT OFFICE

2,228,028

PROCESS FOR THE REMOVAL OF MERCAPTANS FROM HYDROCARBON DISTILLATES

Paul V. Brower, Edwardsville, Ill., assignor to
Shell Development Company, San Francisco,
Calif., a corporation of Delaware

Application June 19, 1939, Serial No. 279,817

7 Claims. (Cl. 196—30)

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 containing substantial

5 amounts of certain alkyl phenolates as solubility promoters for said acids, and more particularly deals with a method for utilizing the alkyl phenols contained in sour hydrocarbon distillates to be extracted as solubility promoters for mercaptans.

10 It is known that weak organic acids having dissociation constants below about 10^{-5} , e. g., mercaptans and alkyl phenols, 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 improved materially by adding to the aqueous solutions substantial amounts of solubility promoters or solutizers for said organic acids. Solutizers have been defined

20 as organic substances which are at least partially soluble in aqueous caustic alkali solutions, are insoluble in the organic water-immiscible solvent, are good solvents for the organic acid to be extracted and are inert to the action of the caustic

25 alkali even at elevated temperatures of steam stripping. In order to enable regeneration by steam stripping of spent solutized solutions containing absorbed mercaptans, without substantial loss of solutizers, it is desirable that the latter boil

30 considerably higher than water.

The most important application of solutizers lies in the removal of mercaptans from hydrocarbon distillates. It has been found in the past that, unfortunately, extraction with solutized

35 caustic alkali denudes hydrocarbon oils so thoroughly from alkyl phenols as well, that in general the extracted oils become very susceptible to oxidation, alkyl phenols being known to act as gum inhibitors. An exception has been found

40 when using alkyl phenolates such as alkali metal alkyl phenolates as solutizers. Apparently in this case a trace of alkyl phenols remains in the distillate sufficient to impart to it at least some degree of stability.

45 The term "alkyl phenols" as herein used refers to mixtures predominantly comprising alkyl hydroxy benzenes such as are obtained by extraction of cracked petroleum distillates or coal tar distillates with aqueous caustic alkali solutions, and acidification of the resulting extract. Raw

50 alkyl phenol mixtures so produced comprise mixtures of many different hydroxy aromatic compounds having different acidities, and invariably contain varying amounts of thiophenols, as is well

55 known. In order to obtain from the raw mixture, alkyl phenols which are substantially free from thiophenols, special desulfurization methods must be employed.

It is the purpose of this invention to make use of

60 alkyl phenols, particularly those contained in

cracked hydrocarbon distillates, for enhancing the solvent power of aqueous caustic alkali solutions for mercaptans, in a manner to produce more stable distillates than were heretofore obtainable by similar methods. It is another purpose to so

5 utilize the alkyl phenols that treated gasolines substantially free from mercaptans are obtained having relatively high oxidation stabilities. As an incident of the process, it is possible to produce as a by-product, alkyl phenols substantially

10 free from thiophenols. Other purposes and advantages will become apparent from the following.

According to my invention, I use as a solutizer for mercaptans an alkyl phenol mixture from

15 which all thiophenols have been removed. Together with the thiophenols a portion of the most strongly acidic alkyl phenols may also be removed. I have found that alkyl phenols free from thiophenols, and more particularly alkyl phenols, free from thiophenols, having average acidities substantially lower than those of raw alkyl phenol

20 mixtures, have definite advantages when used as solutizers for mercaptans. Their main advantage lies in the fact that hydrocarbon distillates extracted with aqueous caustic alkali solutions containing the refined and/or relatively weakly

25 acidic alkyl phenols are considerably more stable and possess better inhibitor susceptibilities towards commercial inhibitors than the same distillates extracted under identical conditions but

30 with raw alkyl phenol mixtures as solutizers.

As is well known, in the "solutizer process" the extraction is carried out at temperatures approximately between the limits of 0 to 60° C.

35

In order to take advantage of the above and to utilize alkyl phenols contained in hydrocarbon distillates from which mercaptans are to be removed, I may proceed as follows:

A cracked hydrocarbon distillate containing

40 aliphatic mercaptans, thiophenols and alkyl phenols is first treated to remove primarily thiophenols. The pretreated distillate is then further extracted with a circulating strongly alkaline alkyl phenolate solution which has been prepared by

45 extraction with aqueous caustic alkali of the alkyl phenols from the distillate itself. A small portion of fresh caustic alkali is continuously added to the circulating solution, and an equivalent amount of alkyl phenolate solution is continuously with-

50 drawn. In this manner, the concentration of alkyl phenols in the caustic alkali solution may be maintained within the proper limits at all times. In the course of its circulation, the alkyl phenolate solution, which, during its contact with the

55 sour distillate picks up mercaptans, is subjected to a steam stripping operation to expel the mercaptans therefrom, and to regenerate it and to make it fit for further extraction of mercaptans.

The preremoval of thiophenols can be accom-

60

plished in one of several ways. For example, I may treat the distillate containing the thiophenols, alkyl phenols and aliphatic mercaptans with an aqueous solution of an alkali metal hydroxide, for example, sodium hydroxide, having a concentration of about 2% to 10%, and preferably 3% to 5% by weight. The amount of the alkali metal hydroxide used in the treatment should be not less than 1 and preferably not more than 3 mol equivalents of the thiophenols contained in the distillate. I have found that under these conditions substantially all thiophenols are removed, usually together with some C₁—C₃ mercaptans and a small portion of the most strongly acidic phenols and carboxylic acids, if the latter are present. The resulting thiophenolate solution may, if desired, be acidified to recover the thiophenols.

Another method for removing the thiophenols without removing a large portion of the alkyl phenols comprises extracting the raw distillate with an amount of the alkaline alkyl phenolate solution produced in the process, which amount contains free alkali metal hydroxide less than, and a total content of available alkali metal, i. e., alkali metal not bound by acids stronger than thiophenol, equal to or greater than the equivalent of the thiophenols contained in the distillate. Thiophenols, being in general stronger acids than alkyl phenols, displace the latter from the aqueous solution and cause at least a portion of the latter to be redissolved in the distillate, while the thiophenols are effectively removed therefrom. Depending upon the magnitude of the excess of available total alkali metal over the thiophenol equivalent, a larger or smaller portion of the alkyl phenols is removed from the distillate with the thiophenols.

In consequence of the preremoval of the thiophenols, and, if desired, of a portion of the most strongly acidic oxy phenols, the circulating alkaline alkyl phenolate solution produced from the distillate is substantially free from thiophenols and contains accumulated therein primarily the more weakly acidic alkyl phenols only. An alkaline solution having this composition when used for extracting mercaptans from sour hydrocarbon distillates has the advantages pointed out over similar solutions containing raw alkyl phenols of a higher average acidity and/or not being contaminated with thiophenols.

As has already been stated, alkyl phenols have the one great advantage over other solutizers, that they produce demercaptanized distillates of relatively high oxidation stabilities. It has further been disclosed that the use of the more weakly acidic alkyl phenols only for this purpose further enhances the stability of demercaptanized distillates. The increase in the stability is considerably more than can be accounted for on the sole basis of larger amounts of alkyl phenols retained in the distillates due to the lower average acidities of the alkyl phenols in the treating solution. The improvement in the magnitude of the treated distillate can only be explained by assuming that the more weakly acidic alkyl phenols are the better oxidation inhibitors, and, moreover, that thiophenols actually interfere with the inhibiting action of the alkyl phenols.

Thus, for example, a cracked distillate which was treated with 2% by volume of 8.5 normal aqueous free sodium hydroxide solution containing 1.2 grams per liter mixed oxy and thiophenolates had an induction period by the oxygen bomb test of 2 hours. When the same dis-

tillate was treated under identical conditions with 8.5 normal free sodium hydroxide containing the same amount per liter of the same mixed phenolates from which, however, the thiophenolates and some of the most strongly acidic hydroxy phenolates had been removed, the induction period of the resulting distillate was 3½ hours.

In order to explain more fully my process, reference is had to the accompanying drawing which represents a simplified flow diagram of a preferred form of my process.

Sour hydrocarbon distillate, such as a cracked gasoline distillate containing alkyl phenols, thiophenols and aliphatic mercaptans enters the system through line 1 from a source not shown. The entire distillate may be introduced into the bottom of extractor 2, which may consist of one or several packed towers or mixing and settling stages. Or else, if desired, the distillate may first pass through heater 3 in line 4 to be fractionally distilled in fractionating tower 5, preferably under conditions to produce an overhead product substantially free from alkyl phenols and thiophenols, and a bottom product containing substantially all alkyl phenols and thiophenols originally contained in the distillate. The overhead fraction should have an end boiling point below 170° C., and preferably between about 125° to 160° C., thiophenol (phenyl mercaptan) boiling at 170° C. This overhead fraction is conducted through vapor line 6 and condenser 7, and if it contains hydrogen sulfide, may conveniently be treated in a conventional H₂S removal plant 8, hydrogen sulfide being expelled through line 9.

The residual bottom fraction in fractionator 5 comprising a concentrate of the phenols is conducted through cooler 10 in line 11 to the bottom of extractor 2.

In the extractor 2 the distillate or its bottom fraction described above, as the case may be, is extracted with an aqueous solution of a caustic alkali under conditions primarily to remove the thiophenols only. As hereinbefore explained, this may be accomplished in at least two ways. The extracting caustic alkali solution may consist of a 2% to 10% and preferably 3% to 5% aqueous solution of an alkali metal hydroxide, which may be admitted from a source not shown to the top of the extractor 2 through lines 12 and 13; or it may consist of an alkaline alkyl phenolate solution which is produced in a manner described later and is admitted through lines 14 and 13. In the latter case, it may be advantageous to dilute the alkyl phenolate solution with water from line 13' in order to avoid emulsion difficulties due to excessive viscosity of the extract emerging from the bottom of extractor 2.

As stated, the amounts of the respective solutions must be kept between certain limits depending primarily on the content of thiophenols in the hydrocarbon distillate passing through the extractor 2. Normally, these amounts are quite small in relation to the quantity of distillate treated, and in order to increase their volume, thereby to facilitate proper contact between the extracting and the extracted liquids, a portion of the thiophenolate extract emerging from the bottom of extractor 2 through line 15 may be recirculated to the top through lines 16 and 13.

Depending upon the conditions employed, the thiophenolate solution in line 15 may contain varying amounts of alkyl phenols. In general, when using in the extraction a 2% to 10% alkali metal hydroxide solution, a fairly clean separation between thiophenols and alkyl phenols takes

place, which separation is usually better than when employing the alkaline alkyl phenolate solution for the same purpose. However, the first method has the disadvantage of consuming larger amounts of alkali metal hydroxide, because not only is fresh hydroxide consumed to convert the thiophenols to their alkali metal salts, but also the free alkali contained in the alkaline alkyl phenolate solution is usually wasted when liberating the alkyl phenols therefrom by acidification. If desired, both methods may be combined, e. g., thiophenols only may be removed by extraction with a 2% to 10% aqueous solution of alkali metal hydroxide, and relatively strong acidic alkyl phenols are then extracted with a small amount of the alkyl phenolate solution from line 14. If this combination is resorted to, an additional extractor not shown in the flow diagram must be used. This combination has the advantage of utilizing the free caustic alkali in the alkyl phenolate solution, which alkali is otherwise wasted, as pointed out above. At the same time, advantages inherent in the pretreatment with the aqueous 2% to 10% soda solution are preserved.

The treated distillate substantially free from thiophenols but still containing aliphatic mercaptans and at least a portion of the alkyl phenols now passes through line 17 to the bottom of a second extractor 18 which may be of a design similar to that of extractor 2. If the original distillate has been fractionated in tower 5 as described before, the light fraction freed from H_2S , if H_2S was present, may conveniently be joined with the heavier one in line 17.

The extracting fluid which is admitted to the top of extractor 18 consists of a circulating strongly alkaline alkali metal alkyl phenolate solution. Its composition and quantity are controlled so that the free alkali metal hydroxide is considerably in excess of the equivalent of the alkyl phenols and mercaptans contained in the distillate. I prefer that the extract solution leaving the extractor 18 through line 19 contain at least 1 mol per liter of solution of free alkali metal hydroxide, and preferably between about 2 and 8 mols. At the same time, the concentration of the alkyl phenolates and mercaptides in this extract solution should not be in excess of their solubility limits, it being desirable in general that the extract be about 30% to 95%, and preferably 60% to 90%, saturated with respect to the alkyl phenolates. Occasionally, emulsion difficulties may arise due to excessive viscosity of the alkyl phenolate solution caused by too high a concentration of the alkyl phenolates. This difficulty has been described in the Yabroff and White application Serial No. 215,804, filed June 25, 1938, and may be remedied by reducing the concentration of the alkyl phenolates so that the viscosity of the solution in line 19 is not greater than 37½ centistokes at the treating temperature. The amount of extracting solution admitted to extractor 18 is normally about 5-100 volume percent of the distillate being extracted. However, larger or smaller amounts may be used.

The extract solution continues its passage from line 19 through heater 20 to a regeneration system comprising steam stripper 21 equipped with reboiler 22 wherein stripping steam may be produced by reboiling the stripped solution, an open steam line 23 to introduce, if desired, additional steam from an outside source not shown. Steam passes upward through the stripper in counterflow to the descending extract solution. In the course of the stripping operation, mercaptans and

a relatively small portion of the most weakly acidic alkyl phenols are liberated and are taken overhead together with the stripping steam through the vapor line 24. The vapor mixture is condensed in condenser 25 and condensate is accumulated in receiving tank 26. Residual vapors consisting essentially of low boiling mercaptans are withdrawn through vent line 27. The condensate forms two liquid layers, a lower aqueous layer which may be returned through line 28 to the top of the stripper 21, or be discarded through line 29; and an upper oily layer consisting essentially of mercaptans and alkyl phenols. The oily layer is conducted through heater 30 in line 31 and is further fractionally distilled in fractionator 32 in the absence of added steam, to produce a vapor fraction removed through overhead line 33 consisting essentially of mercaptans and some water, and a residual fraction consisting essentially of alkyl phenols normally containing little if any mercaptans or thiophenols. Occasionally this bottom fraction may contain small amounts of relatively high boiling mercaptans such as are contained in West Texas gasolines. In this case, the bottom fraction may, if desired, be subjected to a suitable desulfurization treatment not shown. The alkyl phenols so produced being excellent gum inhibitors may be returned through lines 34 and 35 directly to the extracted hydrocarbon distillate emerging from extractor 18 through line 36; or else they may be taken through line 37 to be recombined with the stripped alkyl phenolate solution returning from reboiler 22 through line 38 to the top of the extractor 18.

The extracted distillate in line 36 is frequently sweet, and has an oxidation stability far superior to gasolines sweetened by extraction with solutized aqueous caustic alkali solutions in which the solutizer consists, for instance, of potassium isobutyrate or full range alkyl phenolates or both. If the gasoline has not been completely sweetened, it may be subjected to a mild oxidation treatment to convert the small amount of residual mercaptans to disulfides.

In order to maintain a constant concentration of the alkyl phenolates in the circulating aqueous alkaline alkyl phenolate solution, I may introduce continuously or intermittently into the circuit through line 39 fresh alkali metal hydroxide, preferably having a concentration between about 30% to 50%, in an amount approximately equivalent to the alkyl phenols absorbed from the distillate, and withdrawing continuously or intermittently through line 40 an amount of the stripped alkyl phenolate solution in excess of that required to maintain the proper circulation. Further, if desired or if at times necessary, the alkyl phenolate solution produced within the process may be augmented with alkyl phenolate solution from line 41 from an outside source not shown, care being taken that the supplementary solution is free from thiophenols.

The withdrawn alkyl phenolate solution may either be taken outside the treating system to be utilized in a manner not affecting my process, for example, it may be acidified to recover alkyl phenols of low sulfur content, or at least a portion of this excess may be passed through lines 14 and 13 to the top of the extractor 2 to be utilized in the removal of the thiophenols as described before.

While in the foregoing I have described a certain simplified flow diagram of my process, it shall be understood that other modifications are possible and within the scope of my invention. In

particular is it considered that the installation of pumps, by-passes, heat exchangers, coolers, heaters, etc., not shown and wherever necessary is within the skill of the average designer for petroleum refinery equipment. Moreover, the substitution of one known type of equipment for another, such as the substitution of an ordinary boiler for the steam stripper, is also believed obvious where desirable.

I claim as my invention:

1. In the process of removing acidic components from hydrocarbon distillates containing aliphatic mercaptans, thiophenols and alkyl phenols to produce a desulfurized distillate of good oxidation stability, the steps comprising subjecting said distillate to a treatment to remove thiophenols without removing relatively weakly acidic alkyl phenols, further subjecting the treated distillate containing mercaptans and residual alkyl phenols to an extraction with an amount of an aqueous alkali metal alkyl phenolate solution having a content of free alkali metal hydroxide of not less than 1 mol per liter under conditions to absorb in said solution at least a major portion of said mercaptans and residual alkyl phenols and to form two liquid layers, one comprising an aqueous solution which is 30% to 95% saturated with alkyl phenolates and contains absorbed mercaptans, and the other consisting essentially of treated hydrocarbon distillate substantially free of thiophenols but containing a small fraction of the alkyl phenols originally contained therein, and separating the layers, at least a portion of said alkali metal alkyl phenolate solution having been produced by removing mercaptans from said aqueous layer.

2. The process of claim 1 in which the thiophenols are removed from the original distillate by treating same with an aqueous solution of an alkali metal hydroxide having a concentration of 2% to 10%.

3. The process of claim 1 in which the thiophenols are removed from the original distillate by treating same with an aqueous alkali metal hydroxide solution having a concentration of 2% to 10% in an amount so that the alkali metal hydroxide is between 1 to 3 mol equivalents of the thiophenols contained in said distillate.

4. In the process of separating acidic components from hydrocarbon distillates containing thiophenols and alkyl phenols, the steps comprising treating said distillate with an aqueous solution of an alkali metal hydroxide having a concentration of 2% to 10% in an amount so that the alkali metal hydroxide is between 1 to 3 mol equivalents of the thiophenols contained in said distillate, under conditions to form two liquid layers, an aqueous layer containing absorbed thiophenols and a hydrocarbon layer, and separating the layers.

5. In the process of separating acidic components from hydrocarbon distillates containing thiophenols and alkyl phenols, the steps comprising treating said distillate with an aqueous solution of an alkali metal hydroxide having a concentration of 3% to 5% in an amount so that the alkali metal hydroxide is between 1 to 3 mol equivalents of the thiophenols contained in said distillate, under conditions to form two liquid layers, an aqueous layer containing absorbed thiophenols and a hydrocarbon layer, and separating the layers.

6. In the process of removing acidic components from hydrocarbon distillates containing aliphatic mercaptans, thiophenols and alkyl phenols to produce a desulfurized distillate of good oxidation stability, the steps comprising subjecting said distillate to a treatment to remove thiophenols without removing relatively weakly acidic alkyl phenols, further subjecting the treated distillate containing mercaptans and residual alkyl phenols to an extraction with an amount of an aqueous alkali metal alkyl phenolate solution having a content of free alkali metal hydroxide of not less than 1 mol per liter under conditions to absorb in said solution at least a major portion of said mercaptans and residual alkyl phenols and to form two liquid layers, one comprising an aqueous solution which is 30% to 95% saturated with alkyl phenolates and contains absorbed mercaptans, and the other consisting essentially of treated hydrocarbon distillate substantially free of thiophenols but containing a minor fraction of the alkyl phenols originally contained therein, and separating the layers, at least a portion of said alkali metal alkyl phenolate solution having been produced by removing mercaptans from said aqueous layer and by continuously adding thereto aqueous alkali metal hydroxide having a concentration of 30% to 50% in an amount approximately equivalent to said absorbed residual alkyl phenols.

7. In the process of removing acidic components from hydrocarbon distillates containing aliphatic mercaptans, thiophenols and alkyl phenols to produce a desulfurized distillate of good oxidation stability, the steps comprising subjecting said distillate to a treatment to remove thiophenols without removing relatively weakly acidic alkyl phenols, further subjecting the treated distillate containing mercaptans and residual alkyl phenols to an extraction with an amount of a regenerated aqueous alkali metal alkyl phenolate solution having a content of free alkali metal hydroxide of not less than 1 mol per liter under conditions to absorb in said solution at least a major portion of said mercaptans and residual alkyl phenols and to form two liquid layers, one comprising an aqueous solution which is 30% to 95% saturated with alkyl phenolates and contains absorbed mercaptans, and the other consisting essentially of treated hydrocarbon distillate substantially free of thiophenols but containing a minor fraction of the alkyl phenols originally contained therein, separating the layers, said regenerated alkali metal alkyl phenolate solution having been produced by stripping mercaptans from the separated aqueous layer to produce a stripped solution and by continuously adding thereto aqueous alkali metal hydroxide having a concentration of 30% to 50% in an amount approximately equivalent to said absorbed residual alkyl phenols, continuously withdrawing an amount of the stripped solution which is in excess of that required to extract said treated distillate, said treatment of the original distillate to remove thiophenols being effected by contacting the same with at least a portion of said withdrawn stripped solution in an amount so that the free alkali metal hydroxide content is smaller, and the total content of total alkali metal not bound by acids stronger than the thiophenols is greater than the equivalent of the thiophenols contained in said original distillate.

PAUL V. BROWER.