Dec. 2, 1958 C. D. TEN HAVE ET AL 2,862,878

SWEETENING PROCESS AND METHOD FOR REMOVING WATER OF REACTION FROM THE SWEETENING REAGENT

Filed May 28, 1956

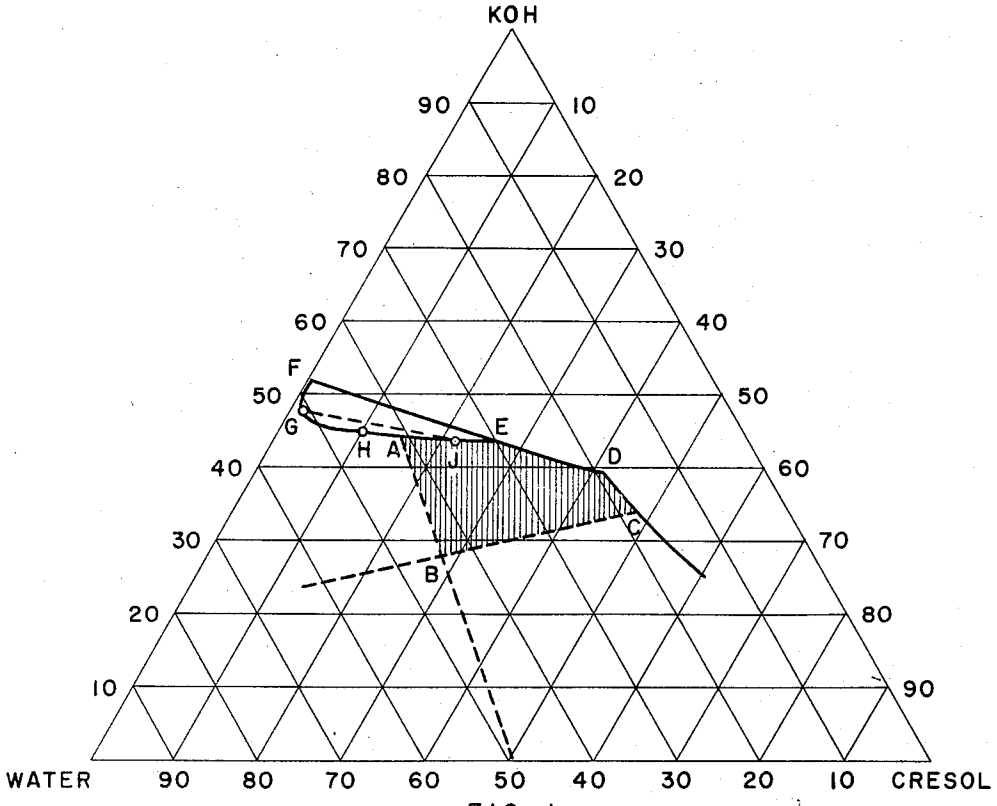


FIG. 1

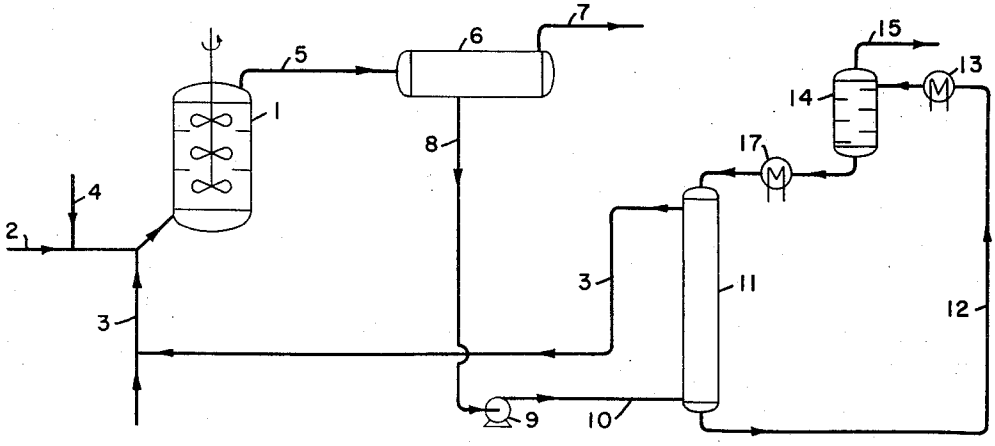


FIG. 2

INVENTORS

CORNELIS D. TEN HAVE

WILLEM J. PIETERS

BY James Todaro Inc

THEIR ATTORNEY

United States Patent Office 2,862,878 Patented Dec. 2, 1958

2,862,878

SWEETENING PROCESS AND METHOD FOR REMOVING WATER OF REACTION FROM THE SWEETENING REAGENT

Cornelis D. Ten Have and Willem J. Pieters, Amsterdam, Netherlands, assignors to Shell Development Company, New York, N. Y., a corporation of Delaware

Application May 28, 1956, Serial No. 587,532

Claims priority, application Netherlands May 31, 1955

6 Claims. (Cl. 208—234)

This invention relates to a method for the direct sweetening of hydrocarbon oils containing acidic sulfur compounds. More particularly, it relates to a method for converting acidic and malodorous mercaptans in petroleum hydrocarbon fractions into organic disulfides, and especially to such a method for the treatment of petroleum hydrocarbon fractions which contain a relatively small proportion of such undesirable sulfur compounds.

It is well known commercial practice to extract mercaptans from hydrocarbon oils by means of an aqueous solution of an alkali metal hydroxide and a "solutizer" such as an alkali metal phenolate and/or an alkali metal organic carboxylate, such as naphthenates, butyrates, and the like. The resulting spent caustic extraction solution is usually regenerated by stripping the mercaptans therefrom, as by steam stripping, or by oxidation with air, usually in the presence of an oxidation catalyst.

It is further known (cf. U. S. Patents 2,015,038 and 2,550,905) that the mercaptans present in hydrocarbon oils can be oxidized to disulfides if the hydrocarbon oil is brought into contact, in the presence of an oxidizing agent, for example, oxygen, with an alkali metal hydroxide solution containing a comparatively small amount of a special type of phenol which is active as oxidation catalyst, particularly a polyhydric phenol or aminophenol having the hydroxyl groups or the hydroxyl and amino groups in the ortho- or para-position with respect to each other. According to U. S. Patent 2,550,905, the aqueous alkali metal hydroxide solution may also contain cresols and xylenols which promote the solubility of mercaptans in the aqueous alkali metal hydroxide solution.

With methods by which mercaptans present in hydrocarbon oils, particularly in gasoline or kerosene, are oxidized to disulfides by contacting the oil with an aqueous alkali metal hydroxide solution in the presence of oxygen, the oxidation itself takes place in the aqueous alkali metal hydroxide solution. The mercaptans are first extracted from the hydrocarbon oil by the alkali metal hydroxide solution and in this solution, in which they are present as mercaptides, they are oxidized by the oxygen present to disulfides which then pass into the hydrocarbon oil. At the same time, the oxygen, being much more soluble in the oil than in the aqueous solution, is supplied to the aqueous solution for the oxidation primarily via the oil. However, the transfer of oxygen from the hydrocarbon oil to the aqueous alkali metal hydroxide solution proceeds with relative difficulty.

A method is described in a copending application, now Ten Have, U. S. 2,763,594, by which the oxidation of mercaptans to disulfides in processes of the type referred to in the preceding paragraph is effected much more rapidly. This method involves the use of aqueous alkali metal hydroxide solutions containing phenolates and having a water content not greater than 54% by volume. This method has been widely adopted in commercial practice because of its effectiveness and simplicity, especially in the sweetening of hydrocarbon fractions containing an amount of mercaptans which is not so great as to

justify the relatively expensive mercaptan extraction processes wherein a large volume of extraction solution must be applied to the hydrocarbon oil and subsequently treated or regenerated in a separate step for the removal of the extracted mercaptans.

In this previous process, the treating solution is gradually diluted with water of reaction formed during the oxidation of mercaptans to disulfides as well as by water which is usually present in small quantities in the hydrocarbon oil being treated. Thus, while the solution need not be subjected to the major stripping or regeneration steps necessary in mercaptan extraction processes for the removal of large quantities of mercaptans, nevertheless, the water of dilution must be removed continuously or intermittently to avoid dilution of the solution beyond the limit of 54 percent by volume whereupon the mercaptan oxidation reaction is drastically slowed. Heretofore, it has been necessary to vaporize the water with which the solution has been diluted, an expedient which is relatively expensive because it involves the heating of the entire treating solution to the vaporizing temperature and the use of stripping steam or the like. Also, in that process, the oxygen which is generally present during the regeneration, and the high temperatures involved, operate to convert some of the alkyl phenolate present to highly acidic oxidation products which irreversibly combine with some of the alkali metal hydroxide present, thus causing a loss of both alkali metal hydroxide and phenolate.

It is therefore a principal object of the present invention to provide an improved process for the sweetening of hydrocarbon oils. Another important object is to provide an improved process for the conversion of mercaptans to disulfides in an aqueous caustic solution. A further object is to provide an improved process for the conversion of mercaptans to disulfides by the use of an aqueous alkali metal hydroxide solution which can be easily and inexpensively regenerated. Other objects will be apparent in the description of the invention.

It has now been discovered that the foregoing objects are accomplished by contacting a light hydrocarbon oil containing mercaptans, in the presence of oxygen, with an aqueous treating solution of an alkali metal hydroxide and a phenolate, the initial composition of which is the same as that of an aqueous solution of an alkali metal hydroxide and a phenolate which can co-exist as a separate liquid phase in heterogeneous equilibrium with another alkali metal hydroxide solution containing less phenolate.

Further description of the invention will be made with reference in part to the accompanying drawing, wherein:

Figure I is the phase diagram of the ternary system water-potassium hydroxide-cresol at 20° C., and is exemplary of the water-alkali metal hydroxide-phenol systems suitably used in the practice of the invention. The figures along the axes of the diagram are the percentages by weight of the various components.

Figure II is a flow diagram schematic of a typical application of the process of the invention.

The definition of the treating solutions suitable in the practice of the invention means in effect that the process is carried out with solutions which constitute only an extremely small part of the ternary phase diagram for the water-alkali metal hydroxide-phenol system. For example, in Figure I, the area ABCDE represents solutions which can be used in the practice of the process of the copending application, now Ten Have, U. S. 2,763,594, referred to hereinbefore. However, in the practice of the present invention, for this particular system, only solutions are used in contacting the hydrocarbon oil which lie on the line AE, because only such solutions can co-exist as a separate liquid phase in heterogeneous equilibrium with potassium hydroxide solutions containing

less cresolate. The compositions of such solutions containing less cresolate lie on the line FH, as will be explained more fully hereinafter.

The process of the invention, whereby a mercaptan-containing light hydrocarbon oil is contacted in the presence of oxygen with a treating solution as defined above, is advantageous for several reasons. In the first place, the oxidation reaction by which mercaptans are converted to disulfides takes place in the aqueous treating solution. The speed of the reaction is thus determined by the rate the mercaptans are transferred into the treating solution and also by the rate the solution can absorb the oxygen required for the reaction. The treating solutions used in the process of the invention are superior to the more dilute solutions used heretofore because the distribution coefficient, i. e., the ratio of the equilibrium concentration of the mercaptan sulfur in the aqueous phase to that in the hydrocarbon oil phase, is much higher for the present solutions. Also, the rate of transfer of oxygen into such solutions is much higher. As a result, a smaller quantity of the treating solution is required for treating the same amount of hydrocarbon oil than was heretofore the case, for example, half or even less, so that with existing contacting equipment more hydrocarbon oil can be sweetened.

Still another advantage of the process of the invention is that the regenerating solution which may be used to remove excess water from the treating solution, will absorb negligible amounts of hydrocarbons, so that provision for hydrocarbon recovery in any evaporation step is not necessary as it usually is when the water of reaction is removed by direct evaporation of a treating solution according to prior processes.

More especially, however, the regeneration of the treating solutions of the invention is considerably simplified and less expensive. Instead of vaporizing excess water from the used treating solution, with the attendant high cost of supplying heat and the loss of alkali metal hydroxide and phenolate because of the oxidation of phenolates at the high regeneration temperatures, as was heretofore necessary, the used treating solution of the process of the invention is regenerated merely by contacting it with a second solution, which can co-exist as a separate liquid phase in heterogeneous equilibrium with a solution having a composition the same as the original treating solution. This second solution is aptly referred to as the regenerating solution, because by contacting the used treating solution with such a solution the treating solution reverts to its original composition, the excess water being removed therefrom by absorption into the regenerating solution.

This advantage will be better understood by referring to Figure I. A treating solution which in accordance with the invention has a composition on the line AE, for example, at point J, will be diluted with excess water during the treatment of the mercaptan-containing light hydrocarbon oil, as discussed above. The composition of the treating solution will thus shift from the point J to a point in the direction of the water apex of the phase diagram. However, when the used treating solution containing the excess water is contacted with a solution having the composition indicated by the point G, i. e., with a solution which can coexist as a separate liquid phase in heterogeneous equilibrium with a solution with the composition of the original treating solution (at point J), then the excess water is removed from the used treating solution and its composition again reverts to that of the original solution at point J. During this regeneration step the composition of the regenerating solution will of course, change in the direction of the water apex of the phase diagram. It is obvious from the description herein that minor variations from the optimum composition of the regenerated treating solution, which might arise from this dilution of the regenerating solution, can be simply compensated for, when desired, by the use of a slightly more concentrated regenerating solution.

As is evident from an inspection of Figure I, the regenerating solutions contain only very small concentrations of phenolate. This results in another important advantage of the invention since the excess water absorbed by the regenerating solution from the used treating solution can be readily removed by simple flash evaporation with little or none of the loss of phenolate or alkali metal hydroxide which would otherwise arise from the formation of strongly acidic oxidation products from the phenolate if it were present in substantial concentrations. For this reason, it is preferred that the treating solution have a composition such that the regenerating solution contains no more than about 5% by weight, and especially no more than about 2% by weight, phenol. In the particular case of the system: potassium hydroxide-water-cresol, as represented in Figure I, regenerating solutions containing no more than 2% by weight cresol are those the compositions of which lie on that portion of line FH from point F to point G.

The alkali metal hydroxide used in the process of the invention is preferably either sodium hydroxide or potassium hydroxide. Potassium hydroxide is particularly preferred because of the lower viscosity of solutions thereof at the concentrations required in the process.

The alkali metal phenolates (phenates) in the alkali metal hydroxide treating solution can be derived from unsubstituted phenol or from monohydric alkylphenols, such as phenol, o-, m- and p-cresols, the various xylenol isomers, the ethyl phenols, the propylphenols, and mixtures of any of these, the alkyl groups of which contain no more than three carbon atoms in total; these phenols are understood to be otherwise unsubstituted. Thus, the suitable phenolates are those monohydroxy phenolates which contain only alkali metal, carbon, hydrogen and oxygen atoms and which contain from 6 to 9 carbon atoms. Such individual phenolates and alkylphenolates and mixtures thereof are referred to throughout the description of the invention by the generic designation "phenolate." Of the suitable phenolates, the cresolates and xylenolates are preferred, especially the cresolates.

The ratio of the volume of the alkali phase to the volume of the hydrocarbon oil may vary within wide limits and usually lies between 0.03 and 3; a ratio of 0.03 to 0.3 is preferably used, particularly 0.05 to 0.1.

The oxidation step of the present process, i. e., the contacting of the mercaptan-containing hydrocarbon with the treating solution in the presence of air, is generally carried out at temperatures of 0° C. to 70° C., preferably 10° C. to 45° C.

The oxygen for the oxidation step may be supplied to the two-phase system to be treated either as such or in the form of a mixture of oxygen with another gas which is inert under the reaction conditions, e. g., in the form of air. Oxygen-yielding compounds such as ozone or peroxides may also be introduced into the two-phase system to be treated. Some of these possibilities may, of course, be combined.

If oxygen is used as such, it may either be dissolved in the hydrocarbon oil in advance, or be injected into the oil while the latter is being brought into contact with the aqueous solution of alkali metal hydroxide and phenolate. The oxygen is preferably present in an excess of 50% to 200%, particularly 75% to 125%, over the quantity of oxygen theoretically required for the conversion of the mercaptans in the hydrocarbon oil to disulfides. If peroxide is also used, for instance in a quantity of 10% to 40% of the stoichiometric quantity with respect to the mercaptans or mercaptides to be converted, in accordance with the process of Pieters, U. S. 2,744,054, the quantity of oxygen supplied as such can be considerably reduced. In this connection it should be noted that hydrogen peroxide is not readily soluble in hydrocarbon oils and rapidly decomposes in the aqueous alkali metal hy-

droxide solution. It is therefore preferably injected into the hydrocarbon oil in the form of a concentrated solution in water or mixed with the oil in the form of an alcoholic solution. Organic peroxides may frequently be directly dissolved in the hydrocarbon oil, while ozone mixed with oxygen or air may be supplied, for instance by first passing the oxygen or air through an ozonier.

If the process is used for removing mercaptans from gasoline or kerosene with a mercaptan sulfur content of not more than 0.04% to 0.05% by weight and if the gasoline or kerosene is in equilibrium with atmospheric air, the quantity of oxygen present in the gasoline or kerosene will generally be sufficient to effect the desired oxidation. However, the mercaptans are usually removed from the hydrocarbon oils shortly after the latter have been obtained from the crude oil and after any other pre-treatments have been carried out, with the result that they are not saturated with air. In this case, it is often necessary for air or another oxygen-containing gas to be dissolved in the hydrocarbon.

In general, the process is carried out at atmospheric pressure. If the process is used for removing mercaptans from hydrocarbon oils with a relatively high mercaptan sulfur content, e. g., more than 0.05% by weight, and air is used as the oxygen-containing gas, it may be advisable to operate at elevated pressure in order to dissolve a sufficient quantity of oxygen in the hydrocarbon oil. If peroxides are also used, the increase in pressure may be considerably less than when these compounds are not used.

In order to promote the transfer of the oxygen from the hydrocarbon oil to the aqueous alkali metal hydroxide solution containing the phenolate, care must be taken to effect an intense contact between the two phases. This contact may be brought about, for example, by means of a propeller mixer, a centrifugal mixer such as the so-called turbomixer (see John H. Perry, Chemical Engineers' Handbook, 1941, pp. 1554–1555), or a colloid mill, for instance the so-called Hurrell mill. The alkali metal hydroxide solution may also be sprayed very finely into the hydrocarbon oil under high pressure, for instance, by means of a spray nozzle, or the hydrocarbon oil may be sprayed in this way into the aqueous alkali metal hydroxide solution.

The various agents customarily employed in extractions for increasing the surface between the phase to be extracted and the extraction agent may also be used for the present purpose. Thus, the process may be carried out in a column provided with packing, projections or rotating discs. In this connection, it should, however, be borne in mind that sudden drops in temperature of the alkali metal hydroxide solution should be avoided, since in this case there is a risk of a second liquid alkali phase forming, or of solid components crystallizing out from the solution.

The process can be applied for removing mercaptans from light hydrocarbon oils, i. e., hydrocarbon oils with a boiling point or final boiling point of at most 370° C., particularly gasoline and kerosene, of different origin, including gasoline and kerosene obtained by straight-run distillation from crude oils, as well as gasoline and kerosene obtained from heavy basic materials by cracking. The so-called reformed gasoline may also be freed from mercaptans according to the present process. When using the process for hydrocarbon oils containing unsaturated components, especially cracked gasoline and reformed gasoline, it is preferred to add to the oil an anti-oxidant such as an aryl amine or an alkyl phenol, the alkyl groups of which contain a total of 4 or more carbon atoms, to prevent the formation of peroxides and gum from the unsaturated components of the oil. In general, a quantity of 0.0001% to 0.01% by weight of such an anti-oxidant is sufficient.

It is often desirable to remove from the hydrocarbon oils any acids present therein, such as hydrogen sulfide, which are stronger than the mercaptans by means of a dilute aqueous alkali metal hydroxide solution, before oxidizing the mercaptans according to the present process. Particularly with products obtained by catalytic cracking, a pre-treatment with dilute caustic alkali solution has the further advantage that aromatic mercaptans, which are more difficult to oxidize than aliphatic mercaptans, are removed at least to a considerable extent. It is preferable to carry out this pre-treatment before the cracked products come into contact with oxygen so as to prevent gum formation.

Since when applying the process for removing mercaptans from hydrocarbon oils the disulfides formed during oxidation pass again into the hydrocarbon oil, the process is primarily suitable for treating light hydrocarbon oils with a low mercaptan content, viz. lower than 0.05% by weight, and preferably lower than 0.02% by weight, calculated as mercaptan sulfur.

When gasoline or kerosene with a considerable mercaptan sulfur content, e. g., 0.05% by weight or more, is to be freed from mercaptans, the greater portion of the mercaptans, if desired together with other sulfur compounds, may be first removed by any of the hitherto usual methods, and then the remainder of the mercaptans oxidized according to the process of the invention. A more advantageous application of the invention to such high mercaptan-content oils is to use a two-step integrated process, the first step being a conventional mercaptan extraction with a relatively dilute extracting solution of an alkali metal hydroxide and an alkali metal phenolate whereby most of the mercaptans are removed and either stripped from or oxidized in the dilute solution, and the second step being the use of the concentrated solutions defined herein for the oxidation of the remaining mercaptans. In this embodiment of the invention the mercaptan-containing dilute solution from the first step is stripped or oxidized for the removal or conversion of the mercaptans; water is removed by then contacting the solution (and equilibrating it) with a regenerating solution as defined herein; the thus-reconcentrated solution is used in the second step oxidation of the remaining mercaptans; and finally the solution from the second step, which now contains excess water, is recycled to the first step and there used as the relatively dilute extracting solution.

The present process provides a very simple method by which light hydrocarbon oils can be freed from mercaptans in a short time, which in most cases varies between 2 and 20 minutes. If the hydrocarbon oil contains mercaptans which are difficult to oxidize, it may be necessary to keep the oil and the aqueous solution of the alkali metal hydroxide and phenolate in contact with each other in the manner described for a somewhat longer period. With a sufficiently intense contact between the hydrocarbon oil to be treated and the aqueous solution of alkali metal hydroxide and phenolate, it is, however, also possible in the latter case to free the hydrocarbon oil from mercaptans to such an extent that the oil has a negative "doctor test" within an hour.

The invention is further illustrated by the following example with reference to the accompanying Figure II.

Example

70 cu. m. gasoline with a mercaptan sulfur content of 0.02% by weight, 4 cu. m. of cresolate-containing potassium hydroxide treating solution with a composition as indicated by point J in Figure I, and 10 standard cu. m. of air are introduced continuously per hour via lines **2**, **3**, and **4**, respectively, into a three-stage turbo-mixer **1**, while stirring vigorously. During the residence time in the turbo-mixer, i. e., 6 minutes, the mercaptans are almost completely oxidized to disulfides. The mixture of gasoline and treating solution is drawn off continuously via line **5** into settling vessel **6**, from which the gasoline with a mercaptan sulfur content of less than 0.0005%

by weight is led via line **7** to storage or blending operations (not shown).

The used cresolate-containing potassium hydroxide solution, which is now diluted with water of reaction, is led from the bottom of the settling vessel **6** via line **8**, pump **9** and line **10** to the bottom part of a contact apparatus **11** and contacted counter-currently with a concentrated aqueous potassium hydroxide regenerating solution, the composition of which is indicated by point G in Figure I. The thus regenerated treating solution of cresolate and alkali, which now again has a composition indicated by point J in Figure I, leaves the contact apparatus **11** at the top and is again led to the turbo-mixer via line **3** for use in treating further amounts of mercaptan-containing gasoline. The water-diluted potassium hydroxide regenerating solution is led from the bottom of the contact apparatus via line **12** and heater **13** into a flash evaporator **14**, from which water vapor is drawn off at the top, and the thus reconditioned regenerating solution is led from the bottom of the flash evaporator to the contacting apparatus **11** via line **16** and cooler **17**, for further use in regenerating used treating solution as before.

We claim as our invention:

1. In a process for removing mercaptans from a light hydrocarbon oil wherein there occurs intimate liquid contacting of the oil in presence of oxygen with an aqueous treating solution of an alkali metal hydroxide and an alkali metal phenolate to effect an oxidation of the mercaptans to disulfides with an accompanying formation of water of reaction which causes an objectionable dilution of the treating solution, the improvement comprising utilizing in the process a treating solution of the foregoing description having an initial composition which permits its coexistence as a separate liquid phase in heterogeneous equilibrium with a second alkali metal hydroxide solution containing less of the alkali metal phenolate, recovering the water-diluted treating solution from the contacted light hydrocarbon oil and subjecting said treating solution to an intimate washing with said second alkali metal hydroxide solution, thereby regenerating the aqueous treating solution to substantially its original water content by transferring the water of reaction to said second solution, separating the regenerated treating solution and the second solution, and recycling said treating solution for contacting with additional amounts of said light hydrocarbon oil.

2. A process in accordance with claim 1, wherein the alkali metal is potassium.

3. A process in accordance with claim 2, wherein the light hydrocarbon oil has a boiling range within the boiling range of gasoline and kerosene, and, before it is contacted with said aqueous treating solution, has a mercaptan sulfur content not greater than 0.05% by weight.

4. A process in accordance with claim 3, wherein said light hydrocarbon oil is gasoline and is contacted with said aqueous treating solution at a temperature of from 0° C. to 70° C.

5. A process in accordance with claim 2, wherein the phenolate is a cresolate.

6. A process in accordance with claim 1, wherein the separated second solution is heated to remove sufficient water therefrom to adjust its composition back to the composition thereof before contacting with the used treating solution, and is recycled for further contacting with additional amounts of used treating solution.

References Cited in the file of this patent

UNITED STATES PATENTS

2,556,438	Parker et al.	June 12, 1951
2,645,602	Tom et al.	July 14, 1953
2,663,674	Krause et al.	Dec. 22, 1953