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SWEETENING HIGH-BOILING PETROLEUM DISTILLATES

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3 Sheets-Sheet 2

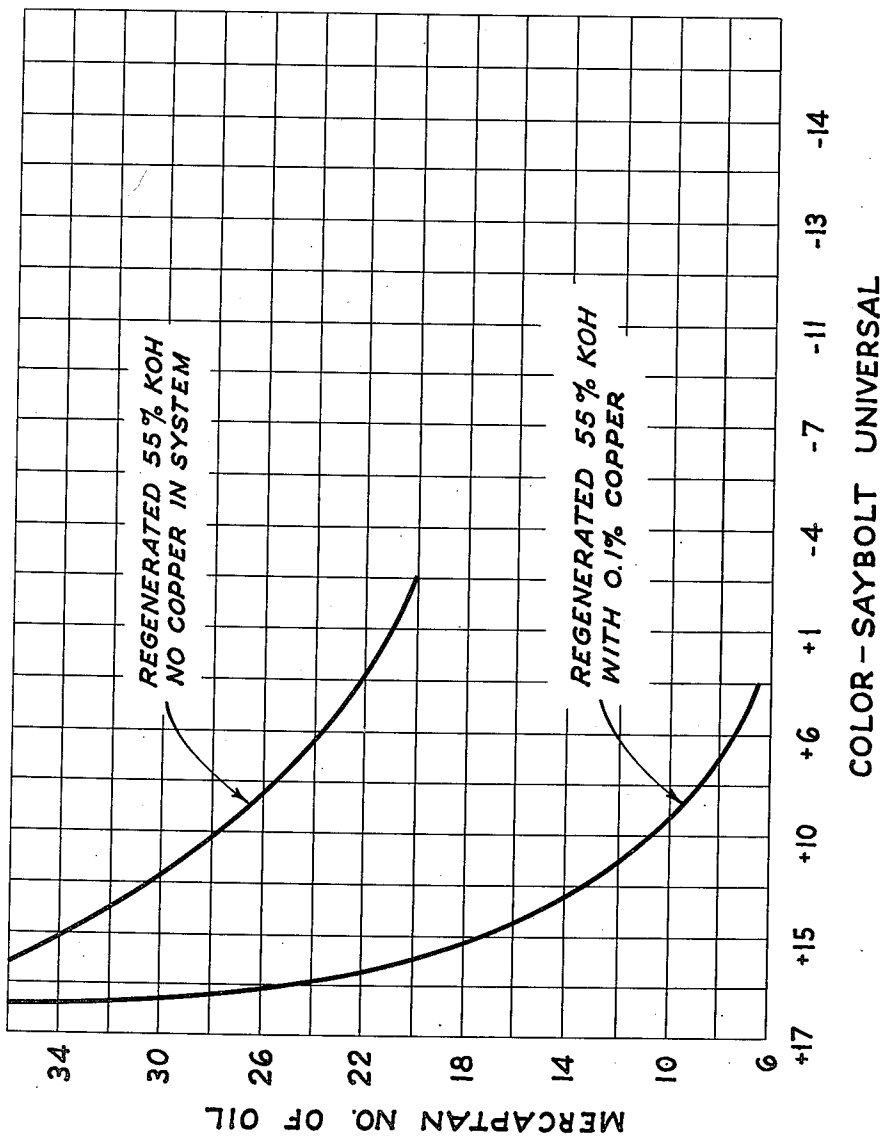


Fig. 2

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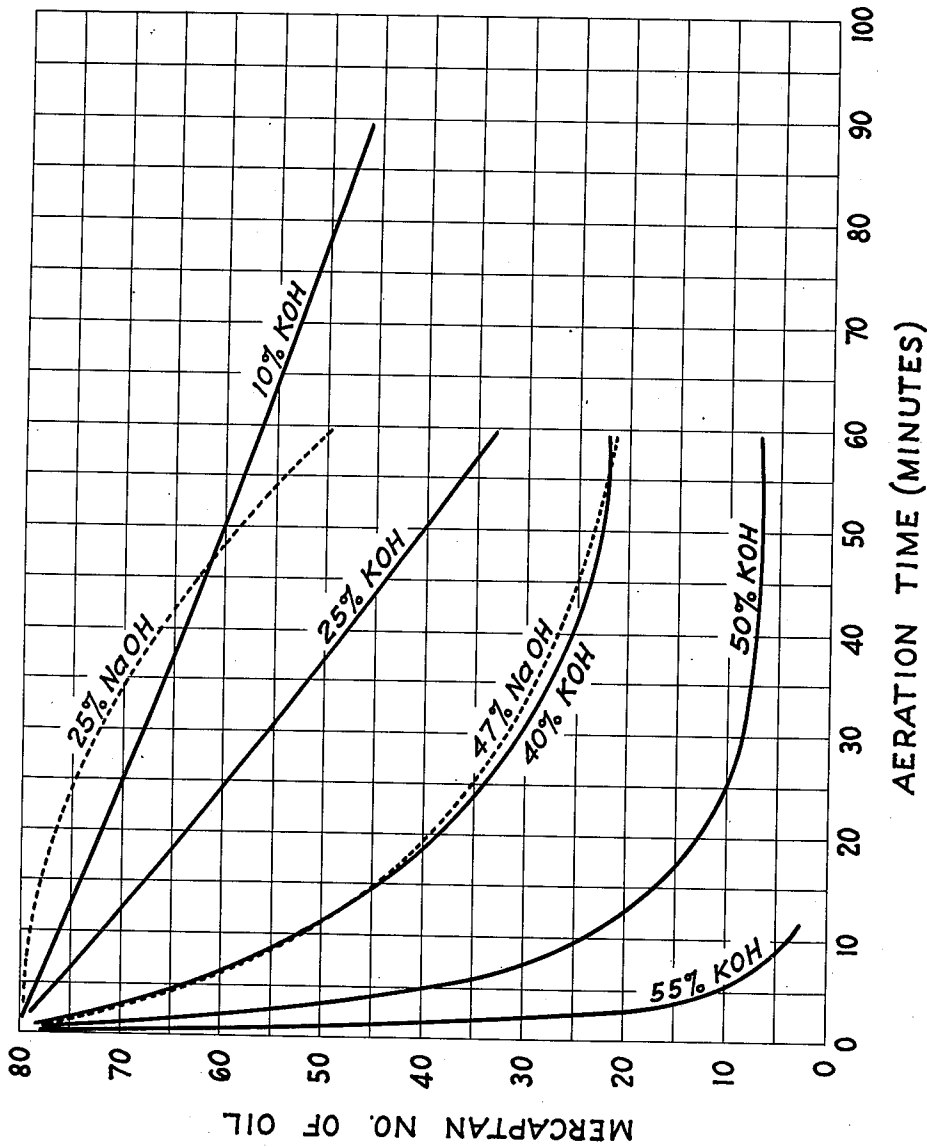


Fig. 3

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UNITED STATES PATENT OFFICE

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SWEETENING HIGH-BOILING PETROLEUM
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10 Claims. (Cl. 196—29)

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This invention relates to the refining of hydrocarbon distillates and more particularly to the refining of heavy naphthas, kerosene, heater oil and furnace oils derived from straight-run crude distillation or from cracking processes, either thermal or catalytic. Still more particularly the invention relates to a method of treating such stocks with concentrated caustic alkali solutions to remove mercaptans therefrom while avoiding undesirable color degradation or formation of oil-soluble color bodies.

It has heretofore been the practice to treat sour mercaptan-containing hydrocarbon distillates with alkaline solutions of various sorts to remove the mercaptans. Where low molecular weight mercaptans are involved as in the case of low-boiling distillates such as light naphthas, removal of mercaptans can be effected by simply washing with caustic alkali, e. g. caustic soda or caustic potash. For this purpose it is usually the practice to employ a caustic soda solution of about 10 to 20 per cent concentration. The caustic solution can be regenerated by steaming or air blowing to distil off the mercaptans or convert them to insoluble disulfides which can be separated from the caustic solution.

In the case of higher boiling stocks, particularly kerosene and heater oils, the removal of the mercaptans is much more difficult because of their increased oil solubility or higher oil-water partition coefficient due to their higher molecular weight. Numerous methods have been proposed and practiced for removing heavy mercaptans of the type found in these higher boiling distillates. Alkaline solutions containing organic solvents or so-called "solutizers" have been employed. Caustic-methanol solutions have a similar action. Chemical reagents which oxidize the mercaptans to disulfides in the presence of the oil have also been extensively employed. Among these are the familiar alkaline sodium plumbite or doctor solution, alkaline hypochlorite solutions, etc. Some attempts have been made to remove mercaptans from petroleum distillates by treating with anhydrous caustic in the form of a dry powder or in solution or suspension in an organic solvent such as methanol. When operating in this way, however, serious color formation has resulted especially where the treatment was conducted at elevated temperature, for example 150° F. and upwards. It has been found that to prevent color formation under these conditions it has been necessary to carefully exclude oxygen or air.

We have now discovered that mercaptans can be removed from sour hydrocarbon distillates, even of the heater oil distillate boiling range, without serious color formation by treating with a controlled amount of air or oxygen in the presence of an aqueous potassium hydroxide

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solution having a concentration in the range of about 50 to 60 per cent by weight at a temperature of about 80 to 125° F. (but high enough to prevent solidification of caustic), at atmospheric or superatmospheric pressure and in the presence of a particular type of copper catalyst. Under these conditions we have discovered that the mercaptans are converted to odorless disulfides without the formation of objectionable color bodies. The oil refined in this manner has also been found to be satisfactory from the standpoint of its burning characteristics when employed in sleeve-type burners. The amount of oxygen employed either as air or commercial oxygen is preferably about one and one-half to two and one-half times that theoretically required for converting the mercaptans present to disulfides.

We have found that the treating reaction is greatly facilitated by the presence of a small amount of copper, e. g. about .004 to 0.1 per cent by weight based on the potassium hydroxide solution in the form of a catalytically active copper compound or copper complex such as colloidal copper oxide. This corresponds to about 0.01 to 0.3 per cent of copper chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. With some catalysts larger amounts of copper may be used, e. g. up to .5 per cent by weight based on KOH, but usually it is not necessary to exceed .1 per cent. It is preferred to add the copper in the form of an aqueous solution of a copper salt such as copper chloride, sulfate, nitrate or acetate. The copper salt solution may be added directly to the potassium hydroxide solution if the latter is hot enough to avoid formation of a black precipitate. When added in this way, for example to boiling potassium hydroxide solution, a blue complex forms which appears to be a colloidal copper compound; in this form and concentration the copper remains in active condition and does not precipitate from the potassium hydroxide treating reagent.

The copper catalyst can also be added to an intimate reaction mixture of KOH solution and oil, the oil in this case forming the continuous phase of an emulsion so that when the copper salt is introduced it is also dispersed and results in the formation of active catalyst instead of inactive black precipitate. When operating in this way the solution of KOH is mixed with the oil, for example in a continuous mixer, during or after which a solution of a water-soluble copper salt is introduced. The oil and treating agent is then passed to another mixer into which air or oxygen is introduced. If desired, however, air may be introduced into the oil and KOH before adding the copper catalyst, the air, oil, KOH and catalyst being all maintained in intimate contact until mercaptans are substantially eliminated.

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The invention is illustrated by the drawings which form a part of this specification and which show diagrammatically in Figure 1 an apparatus suitable for carrying out the process. Figures 2 and 3 are graphs of data illustrating the results obtained in the process.

The following data illustrate the effect of concentration of copper catalyst on the rate of mercaptan oxidation reactions and the color of the oil. The oil used in these experiments was a straight-run west Texas heater oil having a color of about 17 Saybolt Universal and a mercaptan number of 69. The treats were carried out at about 80° F. with air and 1% by volume of an aqueous KOH solution of 55% concentration. The data follow:

CuCl ₂ ·2H ₂ O	Contact Time Minutes	Mercaptan Number	Color Saybolt Universal
0.3	6	13.1	+13
	8	10.6	12
	10	9.0	11
0.2	15	6.4	8
	5	13.8	12
	8	9.9	12
0.1	10	7.4	12
	15	4.5	9
	5	13.1	12
0.05	8	10.3	12
	10	8.3	12
	15	3.2	9
0.01	8	17.3	12
	10	13.5	11
	15	10.3	9
0.01	8	23.7	10
	10	19.6	9
	15	13.1	7

A fuller understanding of the treating process will be obtained from Figure 1 of the drawing in which the principal reaction vessel is indicated by A and the used KOH reconcentrator by B. Coalescers C and D are provided for more complete removal of caustic from the oil and E is a settler for removing wash water from the treated oil. Referring to the drawing, the sour oil is introduced by line 10 and the temperature is adjusted by heater 11 to a satisfactory point, e. g. 90° F. After flowing thru meter 12 the oil passes thru mixer 13 which is indicated to be of the orifice type. Air introduced by line 14 flows thru meter 15 and is mixed with the oil in mixer 13, a suitable residence time being about 35 seconds. If H₂S is present in the oil charged by line 10, it may be given a preliminary wash with an alkaline solution, e. g. sodium hydroxide or carbonate, to remove H₂S.

An aqueous KOH solution of 55 per cent concentration is introduced by line 16 into the stream of air and oil entering mixer 13. The resulting mixture flows by line 17 to reactor A where partial separation of KOH solution takes place.

Oil and unused air pass by line 18 to air separator 19 from which the air is discharged by line 20. It is preferred to maintain the reactor A under pressure, for example about 100 p. s. i. g., reducing the pressure by valve 21 to about 15 p. s. i. g. to facilitate separation of air in separator 19. The use of pressure with air increases the rate of oxidation, and pressures in the range of 25 to 200 p. s. i. g. are satisfactory. Where oxygen is used, pressure is not ordinarily required. From 19 the oil flows by line 22 to coalescer C which is packed with a fibrous or finely granular material such as glass wool, rock wool, sand, etc., providing an extensive surface for the removal of colloiddally

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suspended KOH solution from the oil. The coalescer may be a horizontal drum packed with glass wool, as indicated, connected with settling chamber 23, or it may be a packed vertical drum, preferably arranged for downflow of oil thru the packing with a separating chamber at the bottom. By effecting a more rapid and complete removal of KOH, the coalescer serves to arrest the development of color in the presence of the KOH solution.

From coalescer C the oil flows by line 24 to a second stage coalescer D. The residence time of the oil in the coalescers is suitably about 5 to 10 minutes. From coalescer D the oil flows by line 25 to water mixer 26, water being introduced into the oil stream by line 27. Mixer 26 of the orifice type is shown, altho any suitable efficient mechanical mixer may be substituted therefor. The amount of water introduced may suitably be about 5 to 10 per cent of the volume of the oil. The water-oil mixture is conducted by line 28 to water settler E from which waste water is withdrawn by line 29. Washed oil flows by line 30 to water coalescer 31, the finished oil being discharged from the system by line 32. Waste water from the coalescer is discharged by line 33. If desired, a preliminary water wash may be given the oil in advance of contactor 26 for the purpose of recovering KOH entrained in the oil.

From reactor A, spent KOH is withdrawn by line 34 to settler 35 where potassium cresylates are allowed to collect as an upper layer. The separated KOH is withdrawn by line 36 and pump 37 and thence flows by line 38 to reconcentrator B where it is heated by submerged steam coil 39 to drive off water which tends to accumulate in the system, particularly as a by-product of the sweetening reaction. In usual practice, the concentration may be increased in B from about 51 per cent to 55 per cent. Water eliminated as vapor is passed by line 40 to condenser 41 and is discharged from the system by line 42. The reconcentrated KOH flows by line 43 to cooler 44 and thence by line 45 to KOH solution filters 46 which remove potassium carbonate and any other insoluble products which may collect in the reagent. The KOH solution then flows by line 47 and pump 48 back to mixer 13 by line 16. Makeup KOH is supplied to the system from time to time by line 49 as needed. By operating reconcentrator B under reduced pressure, e. g. 5 p. s. i. g., the temperature can be held below about 280° F. thereby largely avoiding decomposition of mercaptides to K₂S which is undesirable because it separates and clogs the system. It also represents a loss of KOH.

From the coalescers C and D, separated KOH solution is conducted by line 50 to separator 35. The cresylate layer from separator 35 is conducted by line 51 to separator 52 which may be a storage tank providing an extended time for settling out aqueous KOH. This recovered KOH is conducted periodically by line 53 to the KOH line 36. If desired, separator 52 can be provided with suitable means for raising the temperature of the cresylates, thereby facilitating the separation of KOH. The settled potassium cresylates are discharged from the system by line 54.

Copper solution is introduced by line 55 and pump 56. For this purpose we may use a 10 per cent solution of copper chloride or sulfate. The copper catalyst solution can be introduced at

various points in the system but we prefer to add it directly to the hot KOH in concentrator B. Some of the added copper is precipitated from the caustic solution as insoluble copper sulfide, CuS. The treated oil contains a trace of copper but not more than 1 part per million. The effect of this minute amount of copper on color stability of the oil can be readily offset by addition of a small amount of a metal deactivator, e. g. .001 to .01 percent N,N'-disalicylidine-1,2-diaminopropane.

In the operation of our process, it is important to control the temperature within the range of about 80 to 125° F. if a product of satisfactory color is to be obtained. Higher temperatures have been found to increase color formation. We have found that use of the copper catalyst tends to prevent color formation, apparently by directing the oxidation reaction toward the conversion of mercaptans to disulfides. The cause of color formation is not fully understood but it is thought to be due in part to the oxidation of phenolic substances contained in high sulfur oils. This effect is apparent from the data shown graphically in Figure 2 obtained by treating a sour west Texas heater oil with 1% by volume of KOH solution at 120° F. and air at the rate of 4.85 cubic feet per hour. The upper curve shows rapid formation of color, i. e. decrease in Saybolt Universal color values as the mercaptan number of the oil is reduced when treated with air and regenerated 55 percent KOH. The lower curve illustrates the improved results obtained with the same KOH solution containing 0.1 percent by weight of $CuCl_2 \cdot 2H_2O$.

It is to be noted that the maximum oxidation rate occurred with a copper concentration of about 0.1 to 0.2 percent $CuCl_2 \cdot 2H_2O$. It is also to be noted that the oil obtained under these conditions showed an improved color.

The following data show the effect of temperature on the reaction, particularly with respect to mercaptan number and color. The treats were made by using straight-run west Texas heater oil having a +15 Saybolt color and a mercaptan number of 65. The treating reagent was a 55 percent aqueous KOH solution containing 0.1 percent $CuCl_2 \cdot 2H_2O$, the ratio of solution to oil being 1 percent by volume. The oil and solution were vigorously agitated in the presence of air. The following results were obtained:

Temp. ° F.	Mercaptan No.	Color, Saybolt	Time, Minutes
80	3.2	+9	15
100	3.8	+9	15
120	3.5	+9	5
150	0	-16	8
150 ¹	3	0	3

¹ Data interpolated.

It is desirable to separate the oil from the caustic solution after a contact time of about 25 to 40 minutes in order to avoid color formation and a contact time greater than one hour has been found to decrease the Saybolt color value from 16 to 5 or lower. Usually a contact time of 5 to 30 minutes is sufficient, depending largely on the temperature.

The ratio of caustic solution to oil may be varied over a range from 1 percent by volume to 10 or 15 percent by volume, altho about 5 percent by volume has been found to give best results in the case of heater oil from west Texas crude. When employing only 1 percent KOH

solution, the problem of separating the spent KOH solution from the oil is more difficult than when larger volumes of solution are used. The effect of coalescing the treated oil is particularly valuable in the case of low KOH-oil ratios as will be observed from the following table:

Heater oil treated with 55% KOH and air in presence of copper catalyst

	Color—Saybolt Universal
Untreated oil	17
Settled to remove spent KOH solution	9
Coalesced	13
Coalesced and washed with water	16

When recharging a coalescer with fresh glass wool or other packing material, it has been found that maximum efficiency in removal of color is not obtained until after operating for several hours. This initial operating period of low efficiency can be shortened by pre-wetting the coalescer packing with the strong KOH solution. When two coalescers are employed in series they can be renewed alternately thereby largely mitigating this unfavorable action at starting.

Attempts to use the cheaper caustic soda instead of KOH for sweetening fuel oil distillates were unsuccessful. In comparison with NaOH solution, KOH gave a faster reaction and a sweet product before color formation developed. The KOH solution also separates from the oil more readily whereas the NaOH becomes emulsified or dissolved in the heavy oil and is difficult to remove, even in the subsequent water washing operation.

Figure 3 illustrates the superior action of KOH in comparison with NaOH solutions. Note that the aeration time for reduction in mercaptan number is considerably greater for NaOH solution of the same concentration. Thus the aeration time required to reduce the mercaptan number from 80 to 60 was approximately 48 minutes with 25 percent NaOH and only 24 minutes with KOH solution of the same concentration.

Figure 3 also shows the effect of concentration on rate of mercaptan oxidation and it will be noted that there is a tendency for the oxidation to cease entirely or level off at a given mercaptan number depending on the concentration. Thus 40 per cent KOH leveled off at a mercaptan number of about 22, whereas 50 per cent KOH permitted the mercaptan number to be reduced to about 7. These data were obtained with a West Texas heater oil having a mercaptan number of 80, contacted with air and 1 per cent by volume of the caustic solution containing 0.1 percent $CuCl_2 \cdot 2H_2O$. The temperature of contacting was 85° F. and the rate of air input was 4.85 cubic feet per hour.

The odor of the oil treated by our KOH-air oxidation process has been found to be satisfactory for marketing requirements if the oxidation is carried to a point where the mercaptan number is below 5. (The mercaptan number is the number of milligrams of mercaptan sulfur per 100 cc. of oil, usually determined by titration with a standardized copper solution.) By employing about 5 volume per cent of caustic solution (55% concentration and containing about .02 weight per cent of copper in the form of active colloidal copper complex but introduced as aqueous copper sulfate) based on oil treated, mercaptan numbers have been reduced to about 1 or practically zero and treated products of good odor have been obtained with a Saybolt color of

15 to 17 and with good color stability and excellent burning qualities.

While a particular system for using the invention has been described in considerable detail, many modifications and alternative procedures and conditions will be apparent from the above description to those skilled in the art. For example, the used caustic may be withdrawn thru line 36a and only fresh make-up caustic introduced into heater B; this will avoid precipitation of a part of the copper by materials contained in the used caustic. The amounts of catalyst specified in the accompanying claims refer to copper in the form of an active compound or complex believed to be colloidal oxide and usually characterized by a blue color; such catalyst is preferably prepared in the manners herein described using, for example, copper sulfate, which has been found to give outstandingly good results.

We claim:

1. The process of removing mercaptans from a sour hydrocarbon fuel oil distillate without formation of excessive color therein, which comprises intimately contacting said distillate with about 1 to 15 percent by volume of an aqueous solution of KOH having a concentration of about 50 to 60 per cent, said solution containing about .004 to 0.1 per cent by weight of copper in the form of an active copper compound which is active as an oxidation catalyst, introducing a free oxygen containing gas in an amount about stoichiometrically equivalent to the amount of mercaptans present in said distillate into the mixture of distillate and KOH, maintaining the temperature of contacting at about 80 to 125° F. and separating spent KOH solution and associated reaction products from the treated oil.

2. The process of sweetening a sour hydrocarbon fuel oil distillate without formation of excessive color therein which comprises intimately contacting said distillate with about 5 to 10 per cent by volume of an aqueous solution of KOH having a concentration of about 50 to 60 per cent and containing about .004 to 0.1 per cent of copper in the form of an active copper compound which is active as an oxidation catalyst, introducing into the reaction mixture air containing an amount of oxygen stoichiometrically equivalent to about one and one-half to two and one-half times the amount of mercaptans present in said distillate, maintaining said reaction mixture highly agitated and at a temperature of about 80 to 125° F. until the mercaptan number of said distillate is reduced below about 5, then separating spent KOH solution and associated reaction products from the treated oil.

3. The process of claim 2 wherein said oil is washed by intimately contacting with water immediately after separation from said KOH solution.

4. The process of claim 2 wherein the time of contact between said distillate and said KOH solution is about 5 to 60 minutes.

5. The process of claim 2 wherein the spent KOH solution separated from the treated distillate is regenerated by subjecting to distillation at subatmospheric pressure and a temperature not exceeding about 300° F., and the resulting regenerated KOH solution is employed for the treatment of additional quantities of sour fuel oil distillate.

6. In a process for treating a sour hydrocarbon distillate which is higher boiling than gasoline and which contains a large amount of mercaptan

sulfur, in which process the hydrocarbon distillate is intimately contacted with an amount of oxygen stoichiometrically equivalent to about one and one-half to two and one-half times the amount of mercaptans present in the distillate and in which process the contacting is effected in the presence of concentrated aqueous potassium hydroxide of about 50 to 60 per cent concentration at a temperature in the range of about 80 to 125° F. and under a pressure in the range of about atmospheric to 200 pounds per square inch for a time of contact in the range of about 5 to 60 minutes, the improvement which comprises effecting said contacting also in the presence of an active copper catalyst which is active as an oxidation promoter in an amount of .004 to .1 per cent by weight of copper based on potassium hydroxide present in the contacting step, said active copper catalyst being in the form of a copper compound and not in the form of metallic copper.

7. The process of claim 6 wherein the copper compound is a blue colloidal copper oxide.

8. The process of claim 6 wherein the copper compound is formed by adding a copper salt to a solution of concentrated potassium hydroxide under conditions for avoiding the formation of appreciable amounts of black precipitate.

9. The method of claim 8 wherein the copper compound is formed by adding copper sulfate to concentrated aqueous potassium hydroxide at a temperature sufficiently high to avoid appreciable formation of black precipitate.

10. The process of treating a sour virgin heater oil distillate containing a large amount of mercaptan sulfur, which process comprises intimately contacting said distillate with about 5 per cent by volume of a concentrated potassium hydroxide solution of about 50 to 60 per cent concentration in the presence of a catalytic amount of an active copper compound which is active as an oxidation catalyst and with added oxygen in an amount stoichiometrically equivalent to about one and one-half to two and one-half times the amount of mercaptans present in said distillate, continuing said contacting at a temperature in the range of about 80 to 125° F. under a pressure in the range of atmospheric to 200 pounds per square inch for a time sufficient to obtain a low mercaptan number of said distillate without materially impairing the color and color stability thereof, then separating spent potassium hydroxide solution with reaction products contained therein from the treated oil, separating potassium cresylates from the withdrawn solution, then subjecting the solution to distillation at low pressure and at a temperature not exceeding about 300° F. for removing water therefrom, cooling the concentrated caustic solution and returning said cooled solution for contacting with additional amounts of said distillate.

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