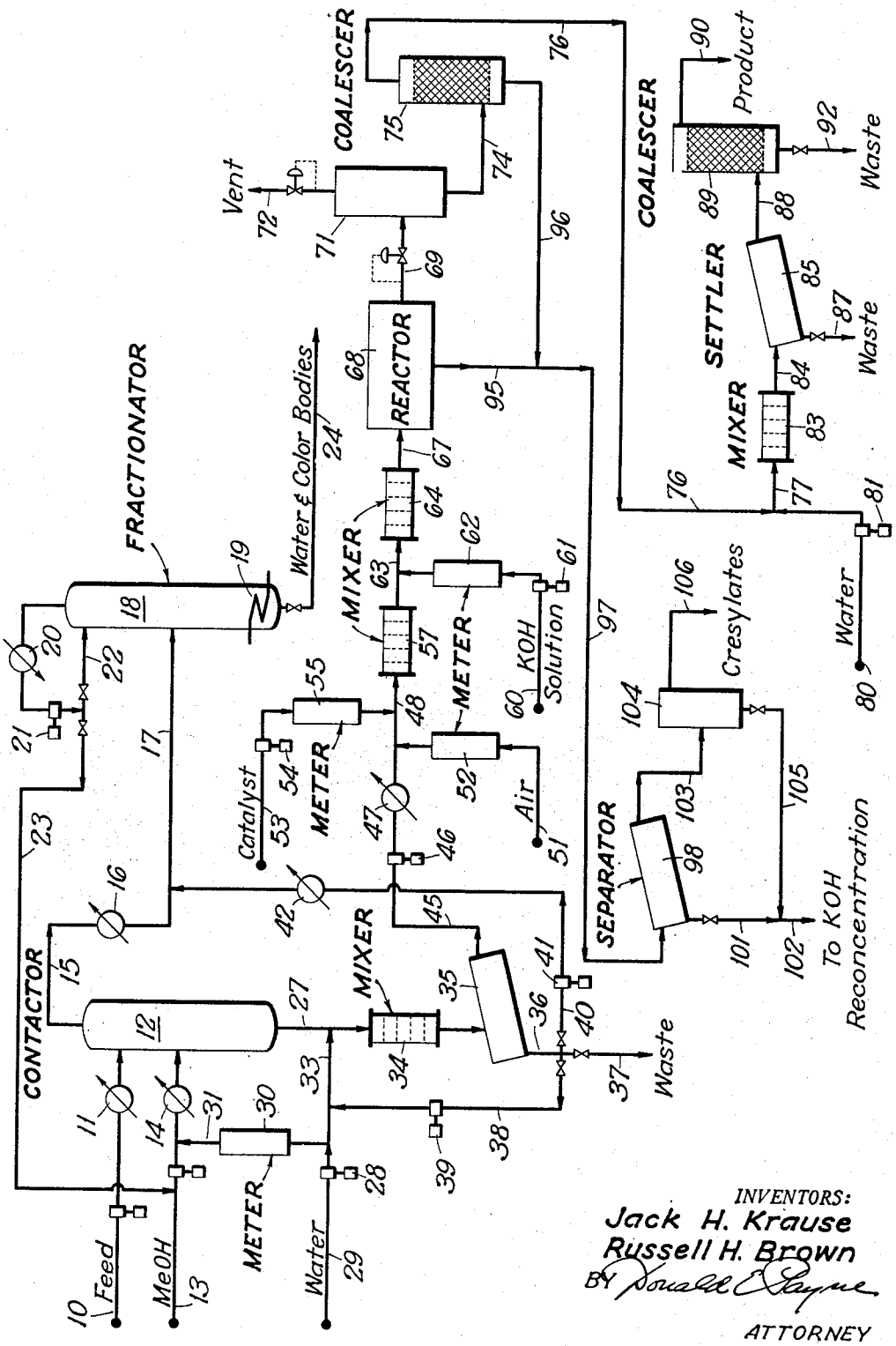
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REFINING SOUR HYDROCARBON OILS

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REFINING SOUR HYDROCARBON OILS

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This invention relates to the refining of sour hydrocarbon oils, such as heavy naphtha, kerosene, diesel oil, heater oil and furnace oil, which are derived from the distillation of crude oil or from cracking processes, either thermal or catalytic. More particularly the invention relates to a method of treating such stocks in order to remove mercaptans with little or no degradation of the color of the oil.

The removal of mercaptans from petroleum products because of their objectionable odor has been a problem of long standing with the petroleum refiners. Many methods are known for the removal of the mercaptans, as such, or for their conversion to the relatively non-odorous disulfides. Some of the more well known methods are: In the case of the light naphthas and gasolines, the mercaptans are removable by washing with an aqueous alkali solution; sometimes, so-called "solutizers" are added to increase the solubility of the mercaptans in the aqueous alkali solution. In the case of distillates boiling above the gasoline range, the mercaptans are less alkali soluble and their removal is much more difficult. The removal of the mercaptans has been accomplished by the use of solutized alkali or by extraction with caustic-methanol solutions. Another method has involved converting the mercaptans to disulfides by air oxidation in the presence of concentrated sodium hydroxide solution at elevated temperatures. The elevated temperature caustic solution process forms a considerable amount of color in the treated oil and supplementary color improvement procedures must be resorted to.

Krause-Tom application Ser. No. 141,391, filed January 31, 1950, now Patent No. 2,591,946, describes a novel sweetening process which comprises contacting the sour oil with air and a highly concentrated aqueous caustic solution in the presence of a copper catalyst. The invention described and claimed herein is an improvement on the process of said application.

An object of this invention is to remove mercaptans from sour hydrocarbon distillates with a minimum of color degradation. Another object is to convert the mercaptans in sour hydrocarbon distillates into disulfides with little or no formation of objectionable color bodies. Still another object is to treat sour hydrocarbon oils boiling above the gasoline boiling range to produce a substantially sweet oil with little or no color formation during the treating process. Yet another object is to prevent the formation of objectionable color in a sweetened oil during the sweetening process by extracting the color forming materials with methanol before the oil is sweetened.

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It has been discovered that sour hydrocarbon distillates and particularly those distillates boiling above the gasoline range, for example, heater oil which boils between 350 and 650° F., can be made substantially doctor sweet with little if any change in color by the following method of treating: The sour distillate is extracted with non-alkaline methanol which contains less than about 10 volume per cent of water in order to remove materials which appear to be color formers when the sour oil is contacted with air and concentrated caustic solution. The methanol solution containing said materials is separated from the oil and the extracted oil can be water washed to recover any methanol dissolved and entrained therein. The extracted oil, the mercaptan number of which has not changed appreciably, is then contacted with air and a highly concentrated aqueous caustic solution in the presence of a catalytically active copper compound to produce a substantially sweet oil of about the same color as the sour oil charged to the process.

The invention is illustrated by a drawing which forms a part of this specification and is a schematic diagram of an apparatus suitable for carrying out the process.

The cause of color formation during sweetening by air or free oxygen in the presence of caustic solution is not fully understood but is thought to be due to the oxidation of phenolic substances contained in high sulfur oils. These substances are present in only very small amounts; for example, extracting 100 volumes of sour heater oil with five treats of 10 volumes each of substantially anhydrous methanol removed only about 0.2 volume of oxygenated hydrocarbons believed to be alkyl phenols; the color of this extracted oil after sweetening with air in the presence of 55% KOH solution and a copper catalyst was better than the color of the sour oil.

The effect of these color formers at various oxidation temperatures is shown clearly by the following data. These data were obtained using a 500 cc. sample of a West Texas heater oil with a Saybolt color of +16 and a mercaptan number of 65; the treating reagent was a 55 weight per cent aqueous KOH solution containing 0.1 weight per cent of $CuSO_4.5H_2O$; the ratio of solution to oil was 1 per cent by volume and 4.85 cu. ft. of air per hour were bubbled through the mixture. The aeration was carried on until the oil was substantially sweet, i. e., about zero mercaptan number.

Temp., ° F.	Color, Saybolt	Time, Minutes
80	0	30
100	−2	23
120	−4	15
150	−16	8

The same West Texas heater oil was used in obtaining the following data. One hundred volumes of the sour oil was extracted at about 80° F. with five treats of methanol in amounts and containing volume percentages of water hereinafter indicated; the solvent was separated from the oil and the extracted oil water washed to remove the methanol dissolved and entrained therein. The extracted oil was then treated as described in the previous paragraph except that all the treats were at about 80° F., to obtain a sweet product.

Solvent Composition		Solvent, Vol. Percent Per Treat	Color, Saybolt Product Oil
MeOH	Water		
100	----------	10	+18
100	----------	5	+13
98	2	10	+15
95	5	10	+14
85	15	10	+1

These data indicate that the color of the sweet oil can be maintained substantially unchanged or even improved by extracting the sour oil with from about 5 to 100 volumes of solvent per 100 volumes of sour oil. The range of solvent usage should be from 5 to 200, preferably from about 25 to 100, volumes of solvent per 100 volumes of sour oil. The solvent composition can vary from substantially anhydrous methanol to about 90 volume per cent methanol and 10 volume per cent water. Preferably the water content should be less than 5% and for best results should be about 2%.

It has been found that the use of highly concentrated aqueous solutions of KOH are superior to NaOH solutions in that not only may lower temperatures be used to obtain a substantially sweet oil but also better colored products are obtained. Also it has been found that the addition of a copper compound to the caustic solution or preferably to the sour oil before the caustic solution is added very markedly increases the rate of sweetening and also decreases the rate of color formation. The best sweetening results are obtained with a substantially saturated—at the temperature of operation—aqueous caustic solution; a reaction temperature between 80 and 125° F.; a contact time of between 3 and 60 minutes, depending on the temperature, and from about 1% by volume to about 15% by volume of caustic solution. The copper catalyst can be any compound which is somewhat soluble in hot concentrated caustic solution or which can be dispersed in the form of a water solution in the sour oil before the caustic solution is added. In terms of weight per cent of caustic solution used, the copper compound added can vary from about 0.004 to about 0.3 weight per cent in terms of copper. The preferred copper compounds to be added are cupric chloride and cupric sulfate.

It was found that sour oils that had been extracted with caustic-methanol solutions and water washed did not sweeten when treated with air, caustic solution and copper catalyst. An oil of 65 mercaptan number was extracted with one

10 volume per cent treat of a solution consisting of 33 weight per cent, KOH; 29 weight per cent, methanol; and 38 weight per cent, water; the separated oil was water washed and then treated with 1 volume per cent of a 55% KOH solution containing 0.1 weight per cent of $CuSO_4.5H_2O$ and air at 80° F. for 30 minutes; the extracted oil was 28 mercaptan number and +15 color while the treated oil was 20 mercaptan number and +14 color. It is believed that the caustic-methanol removed not only the color forming bodies but also the natural oxidation accelerators present in the oil, which are thought to be somewhat acidic; the absence of the natural oxidation accelerators prevents the further removal of the mercaptans by the air-caustic process. The use of non-alkaline methanol appears to remove the materials that cause serious color degradation without also removing enough of the natural oxidation accelerators to impair the subsequent oxidation of the mercaptans.

While either caustic soda or caustic potash can be used in this process, caustic potash is preferred. Sour oils can be sweetened more quickly when concentrated, for example, 50–60 weight per cent, potassium hydroxide solutions are used in the sweetening step.

The odor of the oil obtained by this improved process has been found to be satisfactory and the color stability and burning qualities are excellent.

A fuller understanding of the treating process and the preferred conditions of operation will be obtained from the figure which is only one form of the many that the process can assume. Referring to the figure, the sour oil, which may be given a preliminary wash with a weak alkaline solution, for example 4.0 to 10.0% by weight of NaOH in water, to remove hydrogen sulfide if this is present in the oil, is introduced by line 10 and the temperature is suitably adjusted by heat exchanger 11, a preferred temperature is about 90° F. The sour oil passes into a contacting tower 12 near the top of the tower which may be filled with crushed rock, Raschig rings, or other suitable material or even may be of the bubble tray type. The solvent in this illustration is 95% by volume of methanol and 5% by volume of water; this ratio is chosen in order to reduce the miscibility of the methanol in the oil and reduce the losses of the solvent into the oil and the amount of wash water needed; the solvent is introduced by line 13 and passes through heat exchanger 14 where the temperature is adjusted to about 90° F. and then passes into tower 12 at about the vertical midpoint of the tower; about 50 volumes of solvent are added per 100 volumes of oil. While a packed tower is illustrated, the same degree of contacting can be obtained by using several stages of batch extraction with a portion of the solvent used in each stage; 4 to 6 stages are considered suitable. The solvent is added at the midpoint of the tower because its specific gravity is less than that of the oil and it will flow up against the descending oil stream.

The solvent, less that dissolved and entrained in the oil, passes out from the tower 12 through line 15 and passes through heater 16 where it is heated to about 150° F., about the boiling point of anhydrous methanol, and passes through line 17 into fractionator 18 about the vertical midpoint; fractionator 18 is suitably a bubble tower but may be a packed tower. If additional heat is needed in the fractionator, this can be supplied through the reboiler coil 19 shown in the bottom of the fractionator. Substantially anhydrous

methanol passes overhead from the fractionator and is condensed in heat exchanger 20; part of the condensate, suitably about 5–10% is used as reflux and returned to the fractionator by line 21 and pump 22; the remainder of the methanol passes through line 23 and is returned to the extraction step through line 13.

From the bottom of fractionator 18 water and the color bodies, 0.1–0.2% of the sour oil, extracted from the sour oil are withdrawn by line 24 and either thrown away or sent to further processing to separate the color bodies. These color bodies are believed to be alkylphenols which boil well above the boiling point of water and are somewhat soluble in the water.

From the bottom of contactor 12, the extracted oil and the solvent dissolved and entrained therein are withdrawn by line 27; if it is desired to recover the methanol carried in the extracted oil, the oil is water washed and this procedure is illustrated because the approximately 2% solubility of methanol in the oil represents a considerable loss. Wash water is introduced by pump 28 and line 29. A portion of this water is diverted through meter 30 and line 31 to line 13 where the incoming methanol is diluted to the previously defined solvent composition. The main portion of the water passes by line 33 and is mixed with the extracted oil in mixer 34, which may be of the orifice type, before passing into separator 35. A suitable amount of wash water is about 10–20% by volume of the extracted oil.

The water-methanol solution from separator 35 passes out through line 36 and may go to waste through valved line 37 or may be recycled through line 38 and pump 39 to line 33 to the water washing step in order to be used until its methanol content becomes too high for efficient contacting, or the solution can be sent by line 40 and pump 41 through heater 42 where it is heated to about 150° F. before passing into fractionator 18 where the methanol is recovered overhead.

The water washed extracted sour oil passes out of separator 35 through line 45 to pump 46. Pump 46 passes the oil through heater 47 where the oil is raised to a temperature of about 90° F., which is a suitable temperature for the sweetening process, and on into line 48. Air is introduced by line 51 and flows through meter 52 to line 48; the air should provide between 1.5 to 2.5 times the stoichiometric amount of oxygen needed to react with the mercaptan sulfur in the oil. The copper catalyst, preferably $CuSO_4.5H_2O$, in an amount of about 0.1 weight per cent of the KOH solution used in the process, is introduced in the form of a water solution, such as 10%, by line 53 and pump 54 through meter 55 into line 48 where the copper sulfate solution is finely dispersed throughout the sour oil by the mixer 57. An aqueous KOH solution of about 55 weight per cent concentration and in an amount equal to about 5 volume per cent of the sour oil is introduced by line 60 and pump 61 through meter 62 into line 63 where it joins the sour oil-air-catalyst mixture; the reactants are thoroughly mixed in mixer 64, a suitable residence time being about one minute. If desired the copper catalyst can be dissolved in the KOH solution and added to the oil as part of the KOH solution.

The resulting mixture flows by line 67 to reactor 68 where most of the KOH solution separates; a suitable contact time is 25 to 40 minutes. Oil and unused air pass by line 69 to separator 71 from which the air is vented by valved line 72. It is preferred to maintain the reactor 68 under

pressure, for example about 100 p. s. i. g., and to reduce the pressure to about atmospheric by valve 70 in order to facilitate the separation of air in separator 71. 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. When oxygen is used, superatmospheric pressure is not ordinarily required. From separator 71 the oil flows by line 74 to coalescer 75 which is packed with a fibrous or granular material such as glass wool, sand, gravel, etc. in order to provide an extensive surface for the removal of suspended KOH solution from the oil; by effecting a more rapid and complete removal of KOH, the coalescer 75 serves to arrest the development of color in the treated oil.

From coalescer 75 the treated oil flows by line 76 to line 77; water is introduced by line 80 and pump 81 into line 77 and passes into mixer 83 where the coalesced oil is thoroughly contacted with the water in order to remove any KOH remaining in the oil; a suitable amount of water is about 5–10% by volume of the oil. The water-oil mixture is conducted by line 84 to settler 85 from which waste water is withdrawn by line 87. The washed oil flows by line 88 to coalescer 89 and the finished oil product is discharged from the system by line 90. Waste water from coalescer 89 is discharged by line 92.

From reactor 68 spent KOH is withdrawn by lines 95 and 97 to separator 98; the KOH solution recovered from coalescer 75 passes by lines 96 and 97 to separator 98. In separator 98 the cresylates dissolved out of the oil by the KOH solution are allowed to collect as an upper layer. The separated KOH solution is withdrawn by line 101. The cresylate layer from separator 98 is conducted by line 103 to separator 104 which may be a storage tank providing an extended time for settling out entrained caustic. The recovered KOH is conducted by line 105 to the KOH line 102 where it joins the KOH stream from separator 98. This spent KOH may be sent to a conventional reconcentration system (not shown) where the water picked up in the mercaptan oxidation reaction is driven off and the regenerated KOH then conducted to line 60 for reuse in the process; or the spent KOH may be used in other refining processes and only fresh KOH used in the sweetening process. It has been found that the small amount of caustic insoluble copper compounds formed by reaction between the catalyst and some of the hydrocarbons in the sour oil when catalyst is added directly to the oil is preferentially soluble in the cresylates and passes out of the system with the cresylate layer from separator 98. The settled cresylates are discharged from the system by line 106.

The finished oil contains a trace of copper but not more than 1 part per million. The effect of this minute amount of copper on the color stability of the oil can be readily offset by the addition of a small amount of metal deactivator, for example, 0.001 to 0.01% of N,N' disalicylidine-1,2-diaminopropane.

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 copper oxide; such catalyst is preferably obtained by adding to the system a copper salt, such as copper sulfate, which has been found to give outstandingly good results.

We claim:

1. The process of removing mercaptans from a sour hydrocarbon distillate which is higher boiling than gasoline with a minimum of color

degradation which comprises contacting the sour distillate with about 5 to 200 per cent by volume of non-alkaline methanol solvent which contains not more than about 10 volume per cent of water, separating the solvent and dissolved color-forming bodies from the extracted oil, water washing the extracted oil to remove dissolved methanol solvent, treating the washed oil with about 1 to 15 per cent by volume of a concentrated aqueous caustic solution, introducing a free-oxygen containing gas into the mixture of oil and caustic solution, maintaining the temperature of treating at between about 80° to 125° F., said caustic solution also containing an effective amount of a copper compound which is active as an oxidation catalyst, and separating spent caustic solution and associated reaction products from the treated oil.

2. The process of claim 1 wherein the copper catalyst consists of from about 0.004 to 0.3 weight per cent as copper based on the caustic solution of a copper salt which forms a copper compound that is active as an oxidation catalyst when contacted with the caustic solution.

3. The process of removing mercaptans from a sour hydrocarbon distillate which is higher boiling than gasoline with a minimum of color degradation which comprises intimately contacting the sour distillate with about 25 to 100 volume per cent of a non-alkaline methanol solvent which comprises from about 5 volume per cent to substantially no water, separating the solvent and associated material removed from the sour oil, water washing the extracted sour oil to remove dissolved methanol solvent, intimately contacting the washed oil with about 5 to 10 volume per cent of concentrated aqueous caustic solution, introducing into the mixture oxygen in excess of the stoichiometric amount needed to react with the mercaptans present in the oil, maintaining said mixture at a temperature of about 80–125° F. wherein said caustic solution contains an active copper catalyst which is effective as an oxidation promoter in an amount of 0.004 to 0.3 weight per cent of copper based on the caustic solution present in said mixture, which active copper catalyst is in the form of a copper compound and not in the form of metallic copper, continuing the contacting until the oil is substantially sweet, and then separating spent caustic solution and associated reaction products from the treated oil.

4. The process of claim 3 wherein the time of contact between the extracted oil and the caustic-copper catalyst solution is about 3 to 60 minutes.

5. 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 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 a concentrated aqueous caustic solution at a temperature of about 80–125° F. for a contact time of between 5–60 minutes and wherein said caustic solution contains an active copper catalyst which is effective as an oxidation promoter in an amount of 0.004 to 0.3 weight per cent of copper based on caustic solution present in the contacting step, the improvement which comprises contacting the sour distillate before the sweetening step with about 25–100 volume per cent of non-alkaline methanol solvent containing less than about 10 volume per cent of water in order to remove bodies that cause color formation during the sweetening step and water washing the extracted oil to remove dissolved methanol solvent.

6. The process of claim 5 wherein the concentrated aqueous caustic solution is a 50–60 weight per cent potassium hydroxide solution.

7. The process of treating a sour heater oil distillate containing a large amount of mercaptan sulfur, which process comprises intimately contacting the distillate with about 50 volume per cent of a non-alkaline methanol solution containing about 2 volume per cent of water, separating the methanol solution from the distillate, water washing the extracted distillate to remove dissolved methanol solvent intimately contacting the extracted distillate with about 5 volume per cent of a solution containing a substantially saturated aqueous KOH solution and about 0.004 to 0.3 weight per cent, based on said solution, of copper in the form of a copper compound which is active as an oxidation promoter and which copper has been derived from copper sulfate, introducing sufficient oxygen to convert the mercaptans, maintaining the reaction mixture at a temperature of about 80–125° F. for a contact time sufficient to render the distillate substantially doctor sweet, and then separating the spent caustic solution and associated reaction products from the treated oil.

8. The process of claim 2 wherein said copper salt is copper sulfate.

9. The process of claim 2 wherein said copper salt is copper chloride.

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