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DRAWINGS ATTACHED

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(54) COMBINATION PROCESS FOR TREATMENT OF
 HYDROCARBON STREAMS CONTAINING A MERCAPTO
 COMPOUND

(71) We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of Ten UOP Plaza, Algonquin & Mount Prospect Roads, Des Plaines (formerly of No. 30, Algonquin Road, Des Plaines), Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The subject of the present invention is a combination process directed towards the simultaneous treatment of two hydrocarbon streams containing mercapto compounds, one stream having a relatively low boiling range, and the other a relatively high boiling range, to produce a first treated hydrocarbon stream which is substantially free of sulfur compounds and a second treated hydrocarbon stream which is substantially free of mercapto compounds. Mercapto compounds are compounds containing a sulfhydryl group such as alkyl and aryl mercaptans. More specifically, the present invention provides an efficient and economic solution to the problem of continuously treating, in a closed loop process, a hydrocarbon stream with an alkaline stream to remove mercapto compounds therefrom in the treated distillate. The solution involves a combination process wherein a second hydrocarbon stream containing mercapto compounds is first subjected to an extraction step and then is sweetened in a combination sweetening and disulfide extraction step which is designed to perform a final sweetening function on this second hydrocarbon stream while simultaneously extracting disulfide compounds from a partially regenerated alkaline stream to produce an alkaline stream which is substantially free of all sulfur compounds. This latter stream is subsequently used in the removal of mercapto compounds from the first hydrocarbon stream.

The concept of the present invention developed from efforts to solve a serious

hydrocarbon treatment problem. Attempts have been made to continuously utilize an alkaline stream to completely extract mercapto compounds from a relatively low boiling hydrocarbon stream without injecting sulfur compounds into the treated stream. In this type of process, an extraction step is coupled with a regeneration step and an alkaline stream is continuously recirculated therebetween. In the extraction step, the alkaline stream is used to extract mercapto compounds from the hydrocarbon stream, and the resulting "fat" alkaline stream is treated in the regeneration step to remove mercaptide compounds therefrom with continuous cycling of the alkaline stream between the extraction step and the regeneration step. The regeneration step is operated to produce disulfide compounds which are immiscible in the alkaline stream, and the major portion of which is separated therefrom in a settling step. In many cases, however, it is desired to remove substantially all disulfide compounds from the alkaline streams, whereas complete separation of disulfide compounds from the alkaline stream in a settling step is not feasible because of the high dispersion of these compounds throughout the alkaline solution. Accordingly, the art has resorted to a number of sophisticated techniques in order to coalesce the disulfide compounds and effect their removal from the regenerated alkaline stream. One technique that has been utilized involves the use of a coalescing agent such as steel wool in order to spring disulfides from the regenerated alkaline solution. Another technique which has been widely utilized involves the use of one or more stages of a naphtha wash in order to extract disulfide compounds from this alkaline solution. This latter technique has the disadvantage of requiring a separate train of vessels and separators with attendant piping and instrumentation, which adds a substantial increment of cost in the economics of the overall process.

As is well known to those skilled in the art, there are certain low-boiling-range hydro-

carbon streams for which it is essential that the amount of sulfur compounds contained therein be held to a very low level. In many cases, this requirement is expressed as a limitation on the total amount of sulfur that can be tolerated in the treated stream—typically, the requirement is for a sulfur content less than 50 wt. ppm. calculated as elemental sulfur, and, more frequently, the requirement is less than 10 wt. ppm. sulfur. Accordingly, when a mercapto compound extraction process of the type described above is designed to meet these stringent sulfur limitations it is essential that the amount of so-called re-entry sulfur, (which is the sulfur in the form of disulfide or mercaptide compounds contained in the regenerated alkaline solution) be held to an extremely low level in order to avoid contamination of the extracted stream with disulfide sulfur. For example, in the sweetening of a hydrocarbon stream containing C_3 and C_4 olefins and about 750 wt ppm mercaptan sulfur, an extraction process can easily be designed to produce a treated hydrocarbon distillate having about 5 wt ppm mercaptan sulfur; however, without special treatment of the regenerated alkaline solution utilized, by one of the techniques mentioned above, the total sulfur content of the treated hydrocarbon stream will be about 50 wt parts per million because of disulfide compounds which are returned to the extraction step via the alkaline stream where they are transferred to the treated hydrocarbon stream.

In general, the reasons why it is desired to produce treated hydrocarbon streams of extremely low sulfur content are well known to those skilled in the art. One example is commonly encountered in the treatment of C_3 , C_4 , and C_5 plus C_6 feedstocks for alkylation units wherein it has been determined that by desulfurizing these feedstocks to the lowest possible level, the quality and quantity of the alkylate yield is improved and the amount of acid consumed in the alkylation unit is sharply reduced. Similarly, in plants designed to polymerize light olefins, the principal effect of removing substantially all sulfur compounds from the feedstock is a dramatic increase in the stability of the polymerization catalyst. Other examples are associated with various petrochemical processes where the presence of sulfur in the feed stream to the process adversely affects the activity, selectivity, or stability of the catalyst utilized, where sulfur increases the amount of reagents utilized, or where sulfur causes corrosion problems. Regardless of the reason, it is clear that there is a substantial demand in the art for a simple and economic procedure designed not only to extract mercapto compounds from a relatively low boiling stream, but to insure that the amount of reentry sulfur acquired by the treated stream during the treatment procedure is held to an extremely low level.

In many refineries where hydrocarbon streams containing mercapto compounds are treated to remove mercapto compounds therefrom, there are a great number of hydrocarbon streams containing mercapto compounds of diverse boiling range which must be similarly treated. In general, it is only the relatively low boiling streams that are required to be substantially free of all sulfur compounds as explained above. For the relatively high boiling streams such as gasoline and kerosene fractions, the presence of disulfide compounds in the treated streams is not considered to be detrimental. In fact, these last streams are often sweetened by subjecting the stream to conditions resulting in the conversion of mercapto compounds to disulfided compounds which are allowed to remain in the treated hydrocarbon stream.

A convenient, simple, and economic solution has now been discovered to the problem of providing an extraction process using a continuously regenerated alkaline stream for a relatively low boiling hydrocarbon stream containing a mercapto compound where the amount of sulfur compounds (i.e., disulfide and mercaptides) carried into the extraction zone by the alkaline recycle stream is to be minimized. The solution involves combination process wherein both a relatively low boiling hydrocarbon stream and a relatively high boiling hydrocarbon stream are simultaneously treated in a series of interconnected and interdependent steps, and the high boiling stream is used to purify an alkaline recycle stream which is subsequently used to extract mercapto compounds from the low boiling stream. More specifically, the invention involves the use of the higher boiling hydrocarbon stream in a combination final sweetening and extraction step to sweeten this stream while simultaneously removing residual disulfide compounds and unreacted mercapto compounds from the alkaline stream used in the extraction step for the lower boiling hydrocarbon stream. Some of the broad advantages associated with this solution to the sulfur re-entry problem are: (1) it eliminates a separate purification step on the regenerated alkaline stream which is to be recycled to the extraction step to which the lower boiling stream is being charged; (2) it simplifies the resulting process by combining in a single zone an extraction step with a final sweetening step; and, (3) it minimizes the amount of unreacted mercaptides contained in the alkaline recycle stream charged to the extraction step operating on the lower boiling stream, thereby substantially increasing the efficiency of this extraction step.

It is, accordingly, an object of the present invention to provide a combination process for treating a first hydrocarbon liquid stream containing a mercapto compound and having a relatively low boiling range to produce a

first treated hydrocarbon liquid stream which is substantially free of sulfur compounds, and for simultaneously sweetening a second hydrocarbon liquid stream containing a mercapto compound and having a relatively high boiling range, said process comprising the steps of:

(1) contacting said first hydrocarbon liquid stream with a first alkaline liquid recycle stream which is substantially free of sulfur compounds, in a first extraction zone and withdrawing therefrom a treated hydrocarbon liquid stream and a first alkaline liquid extract stream containing a mercaptide compound;

(2) recovering from said treated hydrocarbon liquid stream a hydrocarbon stream substantially free of sulfur compounds;

(3) contacting said second hydrocarbon liquid stream with a second alkaline liquid recycle stream in a second extraction zone, and withdrawing therefrom a hydrocarbon liquid stream of reduced mercapto compound content and a second alkaline liquid extract stream containing a mercaptide compound;

(4) subjecting said first and second extract streams and a first air stream to contact with a first catalyst, effective to accelerate the oxidation of mercapto to compounds or mercaptides to disulfide compounds in a regeneration zone and withdrawing resulting effluent stream;

(5) separating from the effluent stream from step (4) a gas stream containing N_2 , a liquid stream containing disulfide compounds, and an alkaline liquid stream containing a minor amount of disulfide compounds;

(6) passing a portion of the alkaline liquid stream from step (5) to step (3) as said second alkaline liquid recycle stream;

(7) subjecting another portion of the alkaline liquid stream from step (5), the hydrocarbon liquid stream separated from the effluent from step (3) and a second air stream to contact with a second catalyst, effective to accelerate the oxidation of mercapto compounds, or mercaptides to disulfide compounds in a sweetening zone;

(8) withdrawing resultant effluent stream from step (7) and separating therefrom a gas stream containing N_2 , a hydrocarbon liquid product stream which is substantially free of mercapto compounds and contains a minor amount of disulfide compounds, and an alkaline liquid stream which is substantially free of mercaptides and disulfide compounds; and

(9) passing at least a portion of the alkaline liquid stream from step (8) to step (1) as the first alkaline liquid recycle stream.

Before considering in detail the various ramifications of the present invention, it is convenient to define several of the terms and phrases used herein. The term "sweetening" denotes the process of treating a hydrocarbon stream containing a mercapto compound with an oxidizing agent at conditions which effect

the oxidation of mercaptans to disulfides. The term "mercapto compound" is used here to describe compounds containing the sulfhydryl group such as the alkyl mercaptans and the aryl mercaptans. The term "mercaptide compound" denotes a metallic salt of a mercapto compound. The term "disulfide compound" denotes a compound having the structure



where R and R' are any suitable alkyl or aryl group. The expression "closed-loop" is used herein with reference to the alkaline streams which are continuously recirculated within the process is a closed circuit. The term "substantially from" denotes a content of less than 10 ppm.

The lower boiling hydrocarbon stream which is treated by the process of the present invention is preferably a hydrocarbon stream containing mercapto compounds that are highly soluble in common alkaline streams such as an aqueous solution of sodium hydroxide. For example, hydrocarbon streams containing C_3 , C_4 , and C_3+C_4 hydrocarbons are typical of the lower boiling hydrocarbon streams that can be treated by the method of the present invention. In general, the mercapto compounds contained in these hydrocarbon streams are soluble in common alkaline streams, and are present in an amount of 50 to 10,000 wt ppm of the stream, calculated as elemental sulfur. On the other hand, hydrocarbon streams boiling in the range of C_5 and higher, contain mercapto compounds that are not completely soluble in common alkaline streams, and, thus, these latter streams would rarely be used as the lower boiling hydrocarbon input stream.

The requirements for the high boiling hydrocarbons input stream for use in the present invention essentially involve its capability to dissolve disulfide compounds. In general, any hydrocarbon stream boiling in the gasoline range or above is suitable, and, this will include gasoline fractions, including cracked gasoline, straight-run gasoline, natural gasoline, or mixtures thereof, naphthas, jet fuels, and kerosenes. In most cases, the preferred higher boiling hydrocarbon input stream is a gasoline fraction, primarily because these are commonly available and because the presence of disulfide compounds therein is not detrimental. Typically, this hydrocarbon stream will contain 100 to 50,000 wt ppm of mercapto sulfur, calculated on an elemental sulfur basis.

The alkaline solution utilized in the present invention may comprise any alkaline reagent known to have the capability to extract lower molecular weight mercapto compounds from relatively low boiling hydrocarbon streams. A preferred alkaline solution generally comprises an aqueous solution of an

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alkali metal hydroxide, such as sodium hydroxide, or potassium hydroxide. Similarly, aqueous solutions of alkaline earth hydroxides may be utilized if desired. A particularly preferred alkaline solution for use in the present invention is an aqueous solution of 1 to 50% by weight of sodium hydroxide, with particularly good results obtained with aqueous solutions having 4 to 25 wt % sodium hydroxide. Suitable agents which increase of solubility of mercapto compounds, such as alcohols, alkylphenols, or dialkylsulfoxides, may be added to the alkaline solution if desired; however, excellent results are obtained without such agents.

The catalyst utilized in the regeneration step and the sweetening step of the present invention may be any catalyst which is effective to accelerate the oxidation of mercapto compounds or mercaptides to disulfide compounds. A particularly preferred catalyst for use in the present invention comprises a metal phthalocyanine. These include cobalt phthalocyanine, vanadium phthalocyanine, iron phthalocyanine, copper phthalocyanine, nickel phthalocyanine, and chromium phthalocyanine. The metal phthalocyanine *per se* is, in general, not highly active for the oxidation of mercapto compounds and, accordingly, it is generally a good practice to utilize a polar derivative thereof. Particularly preferred polar derivatives are the sulfonated derivatives such as the mono-sulfo derivative, the disulfo derivative, the tri-sulfo derivative, and the tetra-sulfo derivative. These derivatives may be obtained from any suitable source or may be prepared by one of two general methods: first, the metallic phthalocyanine compound can be reacted with a fuming sulfuric acid; or second, the phthalocyanine compound can be synthesized from a sulfo-substituted phthalic anhydride or equivalent thereof.

The preferred phthalocyanine catalyst can be used in the present invention in one of two modes. First, it can be utilized in a water soluble form or a form which is capable of forming a stable emulsion in water. Second, the phthalocyanine catalyst can be utilized as a combination of a phthalocyanine compound with a suitable carrier material. In the first mode (homogeneous mode), the catalyst is present as a dissolved or suspended solid in the alkaline stream which is charged to the regeneration step or to the final sweetening step. In this mode, the preferred catalyst is cobalt or vanadium phthalocyanine disulfonate which is utilized in an amount of 5 to 1,000 wt ppm of the alkaline stream. In the second mode of operation (heterogeneous mode), the catalyst is preferably utilized as a fixed bed of particles of a composite of the phthalocyanine compound with a suitable carrier material. The carrier material should be insoluble or substantially unaffected by the alkaline stream or hydrocarbon stream under

the conditions prevailing in the various steps of the process. Activated charcoals are particularly preferred because of their high adsorptivity under these conditions. The amount of the phthalocyanine compound combined with the carrier material is preferably 0.1 to 2.0 wt % of the final composite.

The catalyst must be utilized in the same mode for both the regeneration step and the sweetening step. That is, if the homogeneous mode of operation is used in the regeneration step, it must be used in the sweetening; similarly, if the heterogeneous catalyst mode is used, it must be used in both steps.

A specific embodiment of the invention will be further described with reference to the attached drawing, given in schematic outline.

Referring to the drawing, a first hydrocarbon stream having a relatively low boiling range enters the process via line 1 and is charged to the lower region of first extraction zone 2. This first hydrocarbon stream is, in a pretreatment step, given a pre-wash with a dilute solution of sodium hydroxide in order to remove hydrogen sulfide. A typical example of a first hydrocarbon stream is an LPG (liquefied petroleum gas) stream having a specific gravity of 0.57 at 15.6°C and a mercapto compound content of 510 wt ppm, calculated as elemental sulfur. Extraction zone 2 is typically a vertically positioned tower containing suitable contacting means such as baffles pans, trays and Raschig Rings, designed to effect intimate contact between the two liquid streams charged thereto. Also charged to extraction zone 2 is a first alkaline recycle stream which is substantially free of sulfur compounds and which enters the upper region of zone 2 via line 6. As explained hereinbefore, this stream is preferably an aqueous solution of sodium hydroxide containing from 5 to 40 weight % sodium hydroxide, with excellent results obtained with about a 15 wt % solution. The origin of this first alkaline recycle stream and the procedure by which mercaptide and disulfide compounds are removed therefrom will be explained below. The function of extraction zone 2 is to achieve intimate contact between the descending alkaline stream and the ascending first hydrocarbon stream. This zone is preferably operated at -4 to 93°C (25 to 200°F) with excellent results obtained at 38 to 66°C (100 to 150°F). Likewise, the pressure utilized within zone 2 is generally selected to maintain the first hydrocarbon stream in liquid phase, and may range from ambient up to 2.14 atm (300 psig). For an LPG stream the pressure is preferably 10.5 to 12.9 atm (140 to 175 psig). The volume of the alkaline stream is preferably 1 to 30% of the volume of the first hydrocarbon stream, with excellent results obtained for an LPG type stream when the alkaline stream is introduced into zone 2 in an amount of about 5% by volume of the hydrocarbon stream.

A treated hydrocarbon stream is withdrawn from the upper region of zone 2 via line 3 passed to a first separating zone 4 which is preferably maintained at conditions corresponding to those used in zone 2. A first alkaline extract stream containing mercaptide compounds is withdrawn from zone 2 via line 7 and passed to regeneration zone 9. In first separating zone 4, any entrained alkaline solution that is present in the treated first hydrocarbon stream is separated therefrom, and a treated hydrocarbon stream is withdrawn via line 5. For the LPG stream given as an example, the treated hydrocarbon stream withdrawn via line 5 will typically have a mercapto sulfur content of about 5 parts per million and, because of the minimization of the sulfur compound content of the alkaline stream utilized in zone 2 by the present invention, the total sulfur content of this stream will be less than 10 parts per million. The entrained alkaline solution which is separated in zone 4 is withdrawn therefrom via line 6 and returned to extraction zone 2.

A second hydrocarbon stream enters the process via line 25 and is charged to the lower region of second extraction zone 16. This stream will also be typically prewashed with a dilute caustic solution in order to remove H_2S therefrom. As explained hereinbefore, this stream may be any relatively high boiling hydrocarbon stream such as a gasoline fraction or a kerosene fraction. An example of a suitable second hydrocarbon stream is a straight-run naphtha having a boiling range of 79 to 149°C (175 to 300°F), a specific gravity of 0.78 to 15.6°C and a mercapto compound sulfur content of about 300 parts per million. Also charged to zone 16 is a second alkaline recycle stream which enters the zone via line 15 and the source of which is explained below. This stream preferably contains the same wt % sodium hydroxide as the first alkaline recycle stream mentioned above. Zone 16 contains suitable means for achieving intimate contact between the ascending hydrocarbon stream and the descending alkaline stream. It is preferably at approximately the same temperature and pressure conditions as disclosed above for zone 2. In general, for the higher boiling hydrocarbon streams it is preferred to use a slightly higher volume ratio of alkaline stream to hydrocarbon stream in zone 16 relative to that used in zone 2. For instance, for the LPG stream given as a specific example in the discussion of zone 2, a 5% ratio gives excellent results, whereas for the straight-run naphtha, given as an example here, excellent results are obtained with a 20% volume ratio. Because the mercapto compounds contained in the higher boiling hydrocarbon stream are not completely soluble in the alkaline stream, the treated hydrocarbon stream withdrawn from the top of zone 16 via line 18 will generally not be

sweet—that is, it will generally contain about 10 to 100 ppm of residual mercapto compound sulfur. Accordingly, it is necessary to give this partly treated stream a final sweetening treatment, and the partially treated hydrocarbon stream withdrawn from zone 16 via line 18 passed to sweetening zone 19.

A second alkaline extract stream containing mercaptide compounds is withdrawn from the lower region of zone 16 via line 17, and commingled with the first alkaline extract stream at the junction of line 17 with line 7. The resulting mixture is typically passed to a heating means not shown in the attached drawing wherein its temperature is raised 6 to 28°C (10 to 50°F). For example, when the extraction zones 2 and 16 are run at 38 to 49°C (100 to 120°F), the resulting mixture will be heated to about 54°C (130°F). The resulting heated mixture is then combined with a first air stream at the junction of line 8 with the 7. The amount of air commingled with the heated mixture at this point is ordinarily at least the stoichiometric amount necessary to oxidize mercaptides contained in this combined stream to disulfide compounds. That is to say, the amount of air will be sufficient to react about 0.25 moles of O_2 per mole of mercaptide compound contained in the combined alkaline stream. In general, it is a good practice to operate with sufficient excess air to insure that the reaction goes to completion. The resulting mixture of air and alkaline solution is passed via line 7 to regeneration zone 9. The function of zone 9 is to regenerate the alkaline solution by oxidizing the mercaptide compounds to disulfides; as pointed out hereinbefore this regeneration step is preferably performed in the presence of a phthalocyanine catalyst which may be present as a solution or emulsion in the alkaline stream or as a fixed bed of phthalocyanine compound combined with a carrier material. When the catalyst is present in zone 9 as a solution or emulsion in the alkaline stream, a suitable packing material will be utilized in order to effect intimate contact between the catalyst, the mercaptides, and oxygen—a particularly preferred contacting means is carbon Raschig Rings. On the other hand, in the other mode of operation, zone 9 will preferably contain a fixed bed of 0.55 to 1.68 mm (10–30 mesh) particles comprising a combination of cobalt phthalocyanine monosulfonate with activated carbon.

Zone 9 is preferably operated at a temperature corresponding to the entering rich alkaline solution which is typically in the range of 38 to 66°C (100 to 150°F). The pressure used in zone 9 is generally substantially less than that utilized in the extraction zone. For instance, in a typical embodiment wherein extraction zone 2 is run at 11.5 atm (155 psig) and extraction zone 16 at 8.5 atm (110 psig), zone 9 is preferably operated at about

4.4 atm (50 psig). For the preferred catalyst, the residence time within oxidizing zone 9 is ordinarily relatively short, for example, in the homogeneous mode of operation a residence time of about 5 to about 20 minutes ordinarily gives excellent results, and in the heterogeneous mode of operation with the fixed bed of catalyst, a liquid hourly space velocity of 0.5 to 10 is satisfactory.

Regardless of which mode zone 9 is operated in, an effluent stream containing N_2 , disulfide compounds, and alkaline solution is withdrawn therefrom via line 10 and passed to third separating zone 11 which is preferably operated at the conditions used in zone 9. In many cases, this effluent stream will also contain unreacted oxygen and a very minor amount of unreacted mercaptide compounds. In zone 11 the effluent stream is allowed to separate into a gas phase which is withdrawn via line 12 and discharged from the process, a disulfide phase which is substantially immiscible with the alkaline phase and is withdrawn from the process via line 13, and an alkaline phase which is withdrawn via line 14. In general, the complete coalescence of the disulfide compound into a separate phase is extremely difficult to achieve without the aid of suitable coalescing agents such as a bed of steel wool, sand, or glass. In addition, a relatively high residence time of 0.5 to 2 hours is typically used within zone 11 in order to further facilitate this phase separation. Despite these precautions, the regenerated alkaline stream which is withdrawn via line 14 inevitably contains minor amounts of disulfide compounds and mercaptide compounds. In fact, the amount of sulfur present in this regenerated stream is ordinarily in the range of 25 to 200 ppm, calculated as elemental sulfur. It is, of course, understood that these numbers refer to equilibrium levels of disulfide compounds which can build up in this alkaline stream during the course of a prolonged recycle operation.

In accordance with the present invention, the regenerated alkaline solution is divided into two portions at the junction of line 15 with line 14. The first portion is returned via line 15 to second extraction zone 16 as the second alkaline recycle stream which was referred to hereinbefore. The remaining portion of the regenerated alkaline stream is passed via line 14 to the junction with line 18 wherein it is commingled with the partially treated hydrocarbon stream withdrawn from zone 16 via line 18. The resulting mixture is then admixed with a second air stream at the junction of line 27 with line 18. The amount of air injected at this point is selected to provide oxygen in substantial excess of heat required to oxidize the residual mercapto compounds contained in the hydrocarbon stream from zone 16, to disulfide compounds.

The resulting mixture is then passed via line 18 into sweetening zone 19.

Sweetening zone 19 will contain a fixed bed of suitable packing material such as carbon Raschig Rings when the preferred catalyst is utilized in the form of a suspension or solution in the alkaline stream. In the heterogeneous mode of operation of sweetening zone 19, it will preferably contain a fixed bed of 0.55 to 1.68 mm (10 to 30 mesh) particles comprising a combination of phthalocyanine compound with a carrier material. A particularly preferred catalyst for this latter mode of operation is cobalt phthalocyanine monosulfonate combined with 0.55 to 1.68 mm activated carbon carrier material in an amount such that the catalyst contains about 1.0 wt % of the phthalocyanine compound. Regardless of which mode the catalyst is used in, sweetening zone 19 is preferably operated at a temperature and pressure corresponding to that utilized within zone 16. The time of contact in zone 19 between the liquid stream and the catalyst is generally adjusted to reduce the mercapto compound content of the treated stream to the desired low level. For the homogeneous catalyst mode of operation, a contact time of 0.05 to 1 hour is generally preferred. Likewise, for the heterogeneous mode of operation, a liquid hourly space velocity of 0.5 to 10 is preferred.

The functioning of sweetening zone 19 is not only to oxidize residual mercaptide compounds contained in the hydrocarbon stream from zone 16, but also to oxidize any residual mercaptide compounds contained in the regenerated alkaline stream from zone 11 and to extract disulfide compounds from this last alkaline stream. Accordingly, this zone is preferably operated so that intimate contact between the hydrocarbon stream and the alkaline stream charged thereto is achieved therein. Pursuant to this end, any suitable mixing means may be used on the mixture of alkaline solution with the hydrocarbon stream either before, during, or after passage of the combined stream through zone 19.

An effluent stream comprising nitrogen disulfide compounds, alkaline solution, and treated hydrocarbon is thereafter withdrawn from zone 19 and passed via line 20 to second separating zone 21. The function of zone 21 is to separate this effluent stream into three phases: a gas phase containing nitrogen and unreacted oxygen which is removed from the system via line 22, a hydrocarbon phase containing a minor amount of disulfide compound but which typically contains less than 5 ppm of mercapto compound sulfur which is withdrawn via line 26 as a sweetened hydrocarbon stream, and an alkaline stream which is substantially free of both mercaptide and disulfide compounds which is withdrawn via line 23. This last alkaline stream will typically contain less than 10 ppm of sulfur compounds,

calculated as elemental sulfur, and is consequently substantially free of sulfur compounds.

5 In accordance with the present invention at least a portion of this last alkaline stream is passed via lines 23, 24, and 26 to extraction zone 2 as the first alkaline recycle stream. Moreover, a second portion may be passed
10 via lines 23, 14, and 18 back to zone 19, if desired, in order to adjust the amount of disulfide compounds injected into this zone.

Accordingly, the process is operated in the manner described for a substantial period of time, and it is determined to provide an efficient and simple solution to the problem of
15 minimization of re-entry sulfur injected into zone 2 via the first alkaline recycle stream.

WHAT WE CLAIM IS:—

20 1. A combination process for treating a first hydrocarbon liquid stream containing a mercapto compound and having a relatively low boiling range to produce a first treated hydrocarbon liquid stream which is substantially free of sulfur compounds, and for simultaneously sweetening a second hydrocarbon
25 liquid stream containing a mercapto compound and having a relatively high boiling range, said process comprising the steps of:

30 (1) contacting said first hydrocarbon liquid stream with a first alkaline liquid recycle stream which is substantially free of sulfur compounds, in a first extraction zone and withdrawing therefrom a treated hydrocarbon liquid stream and a first alkaline liquid extract
35 stream containing a mercaptide compound;

(2) recovering from said treated hydrocarbon liquid stream a hydrocarbon liquid stream substantially free of sulfur compounds;

40 (3) contacting said second hydrocarbon liquid stream with a second alkaline liquid recycle stream in a second extraction zone, and withdrawing therefrom a hydrocarbon liquid stream of reduced mercapto compound content and a second alkaline liquid extract
45 stream containing a mercaptide compound;

50 (4) subjecting said first and second extract streams and a first air stream to contact with a first catalyst, effective to accelerate the oxidation of mercapto compounds or mercaptides to disulfide compounds, in a regeneration zone and withdrawing resulting effluent
55 stream;

(5) separating from the effluent stream from step (4) a gas stream containing N_2 , a liquid stream containing disulfide compounds, and an alkaline liquid stream containing a minor amount of disulfide compounds;

60 (6) passing a portion of the alkaline liquid stream from step (5) to step (3) as said second alkaline liquid recycle stream;

(7) subjecting another portion of the alkaline liquid stream from step (5), the hydrocarbon liquid stream separated from the effluent from step (3) and a second air stream to con-

65 tact with a second catalyst, effective to accelerate the oxidation of mercapto compounds or mercaptides to disulfide compounds, in a sweetening zone;

(8) withdrawing resultant effluent stream from step (7) and separating therefrom a gas stream containing N_2 , a hydrocarbon liquid product stream which is substantially free of mercapto compounds and contains a minor amount of disulfide compounds, and an alkaline liquid stream which is substantially free of mercaptides and disulfide compounds; and
70 (9) passing at least a portion of the alkaline liquid stream from step (8) to step (1) as the first alkaline liquid recycle stream.

2. A combination process as claimed in Claim 1 wherein the first hydrocarbon liquid stream is a C_3 stream, a C_4 stream, or a stream containing C_3 and C_4 .

3. A combination process as claimed in Claim 1 or 2 wherein the second hydrocarbon liquid stream boils in the gasoline range.

4. A combination process as claimed in any of Claims 1 to 3 wherein the first and second alkaline liquid recycle streams are aqueous solutions of an alkali metal hydroxide.

5. A combination process as claimed in any of Claims 1 to 4 wherein the first and second catalysts are phthalocyanine catalysts.

6. A combination process as claimed in Claim 5 wherein the first and second catalysts are each a metallic phthalocyanine bisulfonate.

7. A combination process as claimed in Claim 5 wherein the first and second catalysts are each sulfo-substituted cobalt phthalocyanine.

8. A combination process as claimed in any of Claims 1 to 6 wherein the first and second catalysts each comprise a phthalocyanine compound combined with a carrier material to form fixed beds of solid particles.

9. A combination process as claimed in Claim 8 wherein the first and second catalysts each comprise cobalt phthalocyanine monosulfonate combined with an activated carbon carrier material to form fixed beds of solid particles.

10. A combination process as claimed in any of Claims 1 to 9 wherein the first extraction zone is maintained at a temperature of from -4 to 93°C (25 to 200°F), a pressure of from atmospheric to 21.4 atm (300 psig), and wherein the volume of the first alkaline recycle stream is from 1 to 30% of the volume of the first hydrocarbon stream.

11. A combination process as defined in any of Claims 1 to 10 wherein the first extraction zone is maintained at a temperature of from 38 to 66°C , a pressure of from 10.5 to 12.9 atm, and wherein the volume of the first alkaline recycle stream is about 5% of the volume of the first hydrocarbon stream.

12. A combination process as claimed in Claim 10 or 11 wherein the second extraction zone is maintained at substantially the tem-



calculated as elemental sulfur, and is consequently substantially free of sulfur compounds.

5 In accordance with the present invention at least a portion of this last alkaline stream is passed via lines 23, 24, and 26 to extraction zone 2 as the first alkaline recycle stream. Moreover, a second portion may be passed via lines 23, 14, and 18 back to zone 19, if
10 desired, in order to adjust the amount of disulfide compounds injected into this zone.

Accordingly, the process is operated in the manner described for a substantial period of time, and it is determined to provide an efficient and simple solution to the problem of
15 minimization of re-entry sulfur injected into zone 2 via the first alkaline recycle stream.

WHAT WE CLAIM IS:—

20 1. A combination process for treating a first hydrocarbon liquid stream containing a mercapto compound and having a relatively low boiling range to produce a first treated hydrocarbon liquid stream which is substantially free of sulfur compounds, and for simultaneously sweetening a second hydrocarbon
25 liquid stream containing a mercapto compound and having a relatively high boiling range, said process comprising the steps of:

30 (1) contacting said first hydrocarbon liquid stream with a first alkaline liquid recycle stream which is substantially free of sulfur compounds, in a first extraction zone and withdrawing therefrom a treated hydrocarbon liquid stream and a first alkaline liquid extract stream containing a mercaptide compound;
35 (2) recovering from said treated hydrocarbon liquid stream a hydrocarbon liquid stream substantially free of sulfur compounds;

40 (3) contacting said second hydrocarbon liquid stream with a second alkaline liquid recycle stream in a second extraction zone, and withdrawing therefrom a hydrocarbon liquid stream of reduced mercapto compound content and a second alkaline liquid extract stream containing a mercaptide compound;
45 (4) subjecting said first and second extract streams and a first air stream to contact with a first catalyst, effective to accelerate the oxidation of mercapto compounds or mercaptides to disulfide compounds, in a regeneration zone and withdrawing resulting effluent stream;

50 (5) separating from the effluent stream from step (4) a gas stream containing N_2 , a liquid stream containing disulfide compounds, and an alkaline liquid stream containing a minor amount of disulfide compounds;
55 (6) passing a portion of the alkaline liquid stream from step (5) to step (3) as said second alkaline liquid recycle stream;

60 (7) subjecting another portion of the alkaline liquid stream from step (5), the hydrocarbon liquid stream separated from the effluent from step (3) and a second air stream to con-

65 tact with a second catalyst, effective to accelerate the oxidation of mercapto compounds or mercaptides to disulfide compounds, in a sweetening zone;

(8) withdrawing resultant effluent stream from step (7) and separating therefrom a gas stream containing N_2 , a hydrocarbon liquid product stream which is substantially free of mercapto compounds and contains a minor amount of disulfide compounds, and an alkaline liquid stream which is substantially free of mercaptides and disulfide compounds; and
75 (9) passing at least a portion of the alkaline liquid stream from step (8) to step (1) as the first alkaline liquid recycle stream.

2. A combination process as claimed in Claim 1 wherein the first hydrocarbon liquid stream is a C_3 stream, a C_4 stream, or a stream containing C_3 and C_4 .
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3. A combination process as claimed in Claim 1 or 2 wherein the second hydrocarbon liquid stream boils in the gasoline range.
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4. A combination process as claimed in any of Claims 1 to 3 wherein the first and second alkaline liquid recycle streams are aqueous solutions of an alkali metal hydroxide.
90

5. A combination process as claimed in any of Claims 1 to 4 wherein the first and second catalysts are phthalocyanine catalysts.

6. A combination process as claimed in Claim 5 wherein the first and second catalysts are each a metallic phthalocyanine bisulfonate.
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7. A combination process as claimed in Claim 5 wherein the first and second catalysts are each sulfo-substituted cobalt phthalocyanine.
100

8. A combination process as claimed in any of Claims 1 to 6 wherein the first and second catalysts each comprise a phthalocyanine compound combined with a carrier material to form fixed beds of solid particles.
105

9. A combination process as claimed in Claim 8 wherein the first and second catalysts each comprise cobalt phthalocyanine monosulfonate combined with an activated carbon carrier material to form fixed beds of solid particles.
110

10. A combination process as claimed in any of Claims 1 to 9 wherein the first extraction zone is maintained at a temperature of from -4 to 93°C (25 to 200°F), a pressure of from atmospheric to 21.4 atm (300 psig), and wherein the volume of the first alkaline recycle stream is from 1 to 30% of the volume of the first hydrocarbon stream.
115

11. A combination process as defined in any of Claims 1 to 10 wherein the first extraction zone is maintained at a temperature of from 38 to 66°C , a pressure of from 10.5 to 12.9 atm, and wherein the volume of the first alkaline recycle stream is about 5% of the volume of the first hydrocarbon stream.
125

12. A combination process as claimed in Claim 10 or 11 wherein the second extraction zone is maintained at substantially the tem-

- perature and pressure of the first extraction zone, and wherein the volume of the second alkaline recycle stream is about 20% of the volume of the second hydrocarbon stream.
- 5 13. A combination process as claimed in any of Claims 1 to 12 wherein the regeneration zone is maintained at a temperature of from 38 to 66°C, a pressure of from about atmospheric to a pressure below that of the
- 10 first and second extraction zones, and wherein at least sufficient oxygen is supplied to oxidize mercaptides contained in the material supplied to the regeneration zone to disulfide compounds.
- 15 14. A combination process as claimed in any of Claims 1 to 13 wherein the sweetening zone is maintained at substantially the temperature and pressure of the second extraction zone.
15. A combination process for treating 20 hydrocarbon streams according to claim 1 and substantially as hereinbefore described.
16. A hydrocarbon product substantially free of sulfur compounds when produced by a process according to any of claims 1 to 15. 25
17. A hydrocarbon product substantially free of mercapto compounds when produced by a process according to any of claims 1 to 15.

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