

SPECIFICATION

Process for Treating Sour Petroleum Distillates

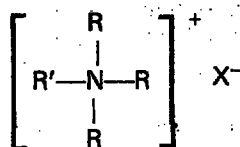
Processes for treating sour petroleum distillates wherein the distillate is contacted with a supported mercaptan oxidation catalyst at oxidation conditions in the presence of an alkaline reagent, have become well known and widely practiced in the petroleum refining industry. One such process is described in U.S. Patent No. 2,988,500. The process is typically designed to effect the oxidation of offensive mercaptans contained in a sour petroleum distillate with the formation of innocuous disulfides—a process commonly referred to as sweetening. The oxidizing agent is most often air admixed with the sour petroleum distillate to be treated, and the alkaline reagent is most often sodium hydroxide in aqueous solution, the aqueous caustic solution being charged continuously to the process, or intermittently as required.

Depending on the source of the petroleum from which the distillate was derived, the boiling range of the distillate, itself, and possibly the method of processing the petroleum to produce the distillate, the distillates will vary widely with respect to the concentration as well as the complexity of the mercaptans contained therein. In general, the lower boiling petroleum distillates, including natural, straight run and cracked gasoline, contain the lower boiling, less complex mercaptans and are more readily treated in the sweetening process.

Petroleum distillates boiling in excess of 135°C., for example kerosene, jet fuel, fuel oil or naphtha, generally contain the more difficultly oxidizable mercaptans, i.e. the highly hindered branched chain and aromatic thiols—especially the higher molecular weight tertiary and polyfunctional mercaptans.

The present invention seeks to provide a novel process for treating a sour petroleum distillate and effecting improved oxidation of the mercaptans contained therein, more especially a process which is particularly adapted to the treating of higher boiling petroleum distillates containing difficultly oxidizable mercaptans.

According to the present invention there is provided a process for treating a mercaptan-containing sour petroleum distillate which comprises contacting the sour distillate with a supported mercaptan oxidation catalyst at oxidation conditions in the presence of an alkaline reagent and a substituted ammonium halide of the general formula



where each R independently is an alkyl, cycloalkyl, aryl, aralkyl or alkaryl radical of up to 20 carbon atoms, R' is a substantially straight

chain alkyl radical of from 5 to 20 carbon atoms, and X⁻ the chloride, bromide, fluoride or iodide ion.

As will become apparent with reference to the examples appended hereto, the improvement derived from the practice of this invention is particularly notable when treating the described higher boiling sour petroleum distillates.

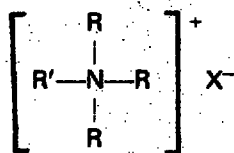
In one embodiment, the features of which are preferred singly and in combination, the sour distillate is contacted with a charcoal-supported metal phthalocyanine catalyst at oxidation conditions in the presence of a caustic solution and a dimethylbenzylalkylammonium chloride in which the alkyl substituent is a substantially straight chain alkyl radical containing from 5 to 20 carbon atoms.

A process according to this invention of which the features are particularly preferred singly and in combination comprises contacting the sour distillate admixed with air with a charcoal-supported cobalt phthalocyanine monosulfonate catalyst, and maintaining the sour distillate in contact with the catalyst for a period of time equivalent to a liquid hourly space velocity of from 0.1 to 10 in the presence of a dimethylbenzylalkylammonium chloride commingled with sodium hydroxide in aqueous solution in a mole ratio of from 0.001:1 to 1:1, the alkyl substituent of the dimethylbenzylalkylammonium chloride being a substantially straight chain alkyl radical of from 12 to 18 carbon atoms.

In the process of sweetening a sour petroleum distillate, it has heretofore been the practice to oxidize the mercaptans contained therein in the presence of an alkaline reagent. The supported mercaptan oxidation catalyst is typically initially saturated with the alkaline reagent, and the alkaline reagent thereafter passed in contact with the catalyst bed, continuously or intermittently as required, admixed with the sour petroleum distillate. Any convenient alkaline reagent may be employed. An alkali metal hydroxide in aqueous solution, e.g. sodium hydroxide in aqueous solution, is most often employed. The solution may additionally contain a solubilizer to promote mercaptan solubility, e.g. an alcohol, especially methanol, ethanol, n-propanol or isopropanol, or a phenol or cresol. A particularly preferred alkaline reagent is a caustic solution containing from 2 to 30 wt.% sodium hydroxide. The solubilizer, when employed, is preferably methanol, and the alkaline solution suitably contains from 2 to 100 vol.% thereof. While sodium hydroxide and potassium hydroxide constitute the preferred alkaline reagents, others, e.g. lithium hydroxide, rubidium hydroxide and cesium hydroxide, may also be employed.

Pursuant to the present invention, a substituted ammonium halide is used in conjunction with the alkaline reagent to provide improved oxidation and conversion of mercaptans to disulfides. The substituted ammonium halide, preferably a dimethylbenzylalkylammonium

chloride, is suitably employed in a molar ratio of from 0.001:1 to 1:1 with the alkali metal hydroxide or other alkaline reagent. The substituted ammonium halides herein contemplated are represented by the general formula



where each R independently is an alkyl, cycloalkyl, aryl, aralkyl or alkaryl radical of up to 20 carbon atoms, R' is a substantially straight chain alkyl radical of from 5 to 20 carbon atoms, and X⁻ is a chloride, bromide, fluoride or iodide ion. Suitable substituted ammonium halides thus include

- 10 dialkylphenylpentylammonium chloride,
- 15 dialkylphenylhexylammonium chloride, dialkylphenyloctylammonium chloride, dialkylphenyldodecylammonium chloride, dialkylphenyltetradecylammonium chloride,
- 20 dialkylphenylhexadecylammonium chloride, dialkylphenyloctadecylammonium chloride, dialkylphenyleicosylammonium chloride, dialkylbenzylpentylammonium chloride, dialkylbenzylhexylammonium chloride,
- 25 dialkylbenzylheptylammonium chloride, dialkylbenzyldecylammonium chloride, dialkylbenzylododecylammonium chloride, dialkylbenzyltetradecylammonium chloride, dialkylbenzylhexadecylammonium chloride,
- 30 dialkylbenzylododecylammonium chloride, dialkylbenzyleicosylammonium chloride, dialkyltolylpentylammonium chloride, dialkyltolylhexylammonium chloride, dialkyltolylododecylammonium chloride,
- 35 dialkyltolyldecylammonium chloride, dialkyltolylododecylammonium chloride, dialkyltolyltetradecylammonium chloride, dialkyltolylhexadecylammonium chloride, dialkyltolylododecylammonium chloride,
- 40 dialkyltolyleicosylammonium chloride, dialkylcyclohexyloctylammonium chloride, dialkylcyclohexyldodecylammonium chloride, dialkylcyclohexyltetradecyl ammonium chloride,
- 45 dialkylcyclohexylhexadecylammonium chloride, dialkylcyclohexyloctadecylammonium chloride and trialkyloctylammonium chloride, where the alkyl radicals in each case are independently selected from methyl, ethyl and propyl, it being understood that the C₅ to C₂₀ alkyl radicals in the above compounds are substantially straight chain. Mixtures of two or more such substituted ammonium chlorides may be used.

- 55 The preferred dimethylbenzylalkylammonium chlorides are commercially available from the Mason Chemical Company under the tradename Maquats. However, said dimethylbenzylammonium chlorides can be prepared by initially reacting ammonia and a C₁₂—C₁₈

- 60 carboxylic acid in contact with silica gel at about 500°C. to form a C₁₂—C₁₈ nitrile. The nitrile is then reduced with hydrogen in contact with a nickel catalyst at about 140°C. The resulting C₁₂—C₁₈ amine is separated from the reaction mixture and reacted with 2 molar proportions of methyl chloride. After neutralization of the reaction mixture, the amine is further reacted with 1 molar proportion of benzylchloride to yield the desired
- 65 dimethylbenzylalkylammonium chloride. The methyl chloride as well as the benzylchloride, is suitably reacted with the amine in methanolic solution at a temperature of about 150°C. The product can be used as is or further treated over activated charcoal to remove impurities.

- 75 The catalyst employed in the practice of this invention can be any of the various catalysts known to the treating art as effective to catalyze the oxidation of mercaptans contained in a sour petroleum distillate with the formation of polysulfide oxidation products. Said catalysts include the metal compounds of tetrapyridinoporphyrazine described in U.S. Patent No. 3,980,582, e.g. cobalt
- 80 tetrapyridinoporphyrazine; porphyrin and metaloporphyrin catalysts as described in U.S. Patent No. 2,966,453, e.g. cobalt tetraphenylporphyrine sulfonate; corrinoid catalysts as described in U.S. Patent No. 3,252,892, e.g. cobalt corrin sulfonate; and chelate organometallic catalysts such as described in U.S. Patent No. 2,918,426, e.g., the condensation product of an aminophenol and a metal of Group VIII. Metal phthalocyanines are a preferred class of mercaptan oxidation catalysts.

- 95 The metal phthalocyanines which may be employed to catalyze the oxidation of mercaptans contained in sour petroleum distillates include magnesium phthalocyanine, titanium
- 100 phthalocyanine, hafnium phthalocyanine, vanadium phthalocyanine, tantalum phthalocyanine, molybdenum phthalocyanine, manganese phthalocyanine, iron phthalocyanine, cobalt phthalocyanine, nickel phthalocyanine,
- 105 platinum phthalocyanine, palladium phthalocyanine, copper phthalocyanine, silver phthalocyanine, zinc phthalocyanine and tin phthalocyanine. Cobalt phthalocyanine and vanadium phthalocyanine are particularly preferred. The metal phthalocyanine is most frequently employed as a derivative thereof, the commercially available sulfonated derivatives, e.g. cobalt phthalocyanine monosulfonate, cobalt phthalocyanine disulfonate or a mixture thereof,
- 115 being particularly preferred. The sulfonated derivatives may be prepared, for example, by reacting cobalt, vanadium or other metal phthalocyanine with fuming sulfuric acid. While the sulfonated derivatives are preferred, it is to be understood that other derivatives, particularly the carboxylated derivatives, may also be employed. The carboxylated derivatives are readily prepared by the action of trichloroacetic acid on metal phthalocyanine.
- 120

For use in the fixed bed treating operation, the metal phthalocyanine catalyst can be adsorbed or impregnated on a solid adsorbent support in any conventional or otherwise convenient manner. In general, the support or carrier material, in the form of spheres, pills, pellets, granules or other particles of uniform or irregular shape and size, is dipped, soaked, suspended or otherwise immersed in an aqueous or alcoholic solution and/or dispersion of the metal phthalocyanine catalyst, or the aqueous or alcoholic solution and/or dispersion may be sprayed onto, poured over, or otherwise contacted with the adsorbent support. In any case, the aqueous solution and/or dispersion is separated, and the resulting composite is allowed to dry under ambient temperature conditions, or dried at an elevated temperature in an oven or in a flow of hot gases, or in any other suitable manner.

In general, up to 25 wt.% metal phthalocyanine can be adsorbed on the solid adsorbent support or carrier material and still form a stable catalytic composite. A lesser amount in the range of from 0.1 to 10 wt.% generally forms a suitably active catalytic composite; although the activity advantage heretofore derived from metal phthalocyanine concentrations in excess of about 2 wt.% has not warranted the use of higher concentrations. However, in view of the significant activity increase derived from the use of the substituted ammonium halides of this invention in conjunction with minimal metal phthalocyanine concentrations, it is contemplated that the higher concentrations will become effective to promote a further increase in the rate of mercaptan oxidation, particularly with regard to the hard to treat sour petroleum distillates.

One suitable and convenient method for adsorbing the metal phthalocyanine catalyst in a solid adsorbent support or carrier material comprises predisposing the support or carrier material in the distillate treating zone or chamber as a fixed bed, and passing the metal phthalocyanine solution and/or dispersion through the bed in order to form the catalytic composite in situ. This method allows the solution and/or dispersion to be recycled one or more times to achieve a desired concentration of the metal phthalocyanine on the adsorbent support. In still another method, the adsorbent support may be predisposed in said treating chamber and the chamber thereafter filled with the metal phthalocyanine solution and/or dispersion to soak the support for a predetermined period, thereby forming the catalytic composite in situ.

The metal phthalocyanine catalyst can be adsorbed or impregnated on any of the well-known solid adsorbent materials generally utilized as a catalyst support. Preferred adsorbent materials include the various charcoals produced by the destructive distillation of wood, peat, lignite, nutshells, bones, and other carbonaceous matter, and preferably such charcoals as have been heat treated or chemically treated or both, to form a highly porous particle structure of

increased adsorbent capacity and generally defined as activated carbon or charcoal. Said adsorbent materials also include the naturally occurring clays and silicates, e.g. diatomaceous earth, fuller's earth, Kieselguhr, attapulugus clay, feldspar, montmorillonite, halloysite and kaolin, and also the naturally occurring or synthetically prepared refractory inorganic oxides such as alumina, silica, zirconia, thorium borate, or combinations thereof like silica-alumina, silica-zirconia and alumina-zirconia. Any particular solid adsorbent material is selected with regard to its ability under conditions of its intended use. For example, in the treatment of a sour petroleum distillate heretofore described, the solid adsorbent carrier material should be insoluble in, and otherwise inert to, the petroleum distillate at the alkaline reaction conditions existing in the treating zone. In the latter case, charcoal, and particularly activated charcoal, is preferred because of its capacity for metal phthalocyanine, and because of its stability under treating conditions.

The process of this invention can be effected in accordance with prior art treating conditions. The process is usually effected at ambient temperature conditions, although higher temperatures up to about 105°C are suitably employed. Pressures of at least up to 69 atmospheres are usable, although atmospheric or substantially atmospheric pressures are entirely suitable. Contact times equivalent to a liquid hourly space velocity of from 0.1 to 10 are particularly effective to achieve a desired reduction in the mercaptan content of a sour petroleum distillate, an optimum contact time being dependent on the size of the treating zone, the quantity of catalyst contained therein, and the character of the distillate being treated.

As previously stated, sweetening of the sour petroleum distillate is effected by oxidizing the mercaptan content thereof to disulfides. Accordingly, the process is effected under oxidation conditions. Air is preferably employed as oxidizing agent although pure oxygen or other oxygen-containing gas may be employed. The sour petroleum distillate may be passed upwardly or downwardly through the catalyst bed. The sour petroleum distillate may contain sufficient entrained air, but generally added air is admixed with the distillate and charged to the treating zone concurrently therewith. In some case, it may be of advantage to charge the air separately to the treating zone and countercurrent to the distillate separately charged thereto.

The following Example II illustrates this invention whereas Example I is comparative. The examples should be read in conjunction with the accompanying drawing which is a graph of the mercaptan sulfur content of treated gasoline against the number of hours on stream.

Example I (Comparative)

The sour petroleum distillate treated in this and the subsequent example was a kerosene fraction

boiling in the 178 to 218°C range at 742 mm Hg. The kerosene had a specific gravity of 0.8081 and contained 448 ppm by weight mercaptan sulfur.

- 5 The kerosene was charged downflow through 100 cc of a charcoal supported cobalt phthalocyanine monosulfonate catalyst disposed as fixed bed in a vertical tubular reactor. The catalyst bed consisted of 1 wt.% cobalt phthalocyanine monosulfonate adsorbed on 10—
10 30 mesh (Tyler) activated charcoal particles. The kerosene was charged at a liquid hourly space velocity of 0.5 under 4 atmospheres of air—sufficient to provide about twice the stoichiometric amount of oxygen required to
15 oxidise the mercaptans contained in the kerosene. In this Example, carried out according to prior art practice, the catalyst bed was initially wetted with about 10 cc of an 8% aqueous sodium hydroxide solution, 10 cc of said solution being
20 subsequently charged to the catalyst bed at 12 hour intervals admixed with the kerosene charged thereto. The treated kerosene was analyzed periodically for mercaptan sulfur. In the accompanying drawing the change in the mercaptan sulfur content of the treated kerosene
25 with increasing number of hours on stream is shown by the broken line.

Example II

- 30 In this Example the described mercaptan-containing kerosene fraction was treated substantially as described in Example I except that a dimethylbenzyl-*n*-alkylammonium chloride was commingled with the aqueous sodium hydroxide solution, in accordance with the present
35 invention, to provide a 0.01 molar dimethylbenzyl-*n*-alkylammonium chloride solution. The dimethylbenzyl-*n*-alkylammonium chloride comprised:

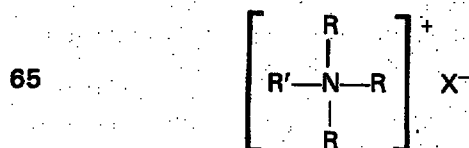
- 40 dimethylbenzyl dodecylammonium chloride (61%)
dimethylbenzyl tetradecylammonium chloride (23%)
dimethylbenzyl hexadecylammonium chloride (11%)
45 dimethylbenzyl octadecylammonium chloride (5%)

- The treated kerosene was again analyzed periodically for mercaptan sulfur. The accompanying drawing shows that mercaptan
50 sulfur content of the treated kerosene (solid line), plotted against the number of hours on stream, was lower than in Example I and remained invariate for a considerable period. It thus gives evidence of the substantial activity improvement
55 and exceptional activity stability resulting from the practice of this invention.

Claims

- 60 1. A process for treating a mercaptan-containing sour petroleum distillate which comprises contacting the sour distillate with a supported mercaptan oxidation catalyst at oxidation conditions in the presence of an alkaline

reagent and a substituted ammonium halide of the general formula



- where each R independently is an alkyl, cycloalkyl, aryl, aralkyl or alkaryl radical of up to 20 carbon atoms, R' is a substantially straight-chain alkyl radical of from 5 to 20 carbon atoms, and X⁻ is the chloride, fluoride, bromide or iodide ion.

- 70 2. A process as claimed in claim 1 wherein the alkaline reagent is sodium hydroxide in a from 2 to 30 wt.% aqueous solution.

- 75 3. A process as claimed in claim 1 or 2 wherein the substituted ammonium halide is employed in a molar ratio of from 0.001:1 to 1:1 with the alkaline reagent.

- 80 4. A process as claimed in any of claims 1 to 3 wherein the catalyst is a supported metal phthalocyanine catalyst.

5. A process as claimed in claim 4 wherein the supported mercaptan oxidation catalyst is a charcoal-supported cobalt phthalocyanine monosulfonate.

- 85 6. A process as claimed in any of claims 1 to 5 wherein the sour distillate is maintained in contact with the catalyst for a period of time equivalent to a liquid hourly space velocity of from 0.1 to 10.

- 90 7. A process as claimed in any of claims 1 to 6 wherein the substituted ammonium halide is a substituted ammonium chloride.

8. A process as claimed in any of claims 1 to 7 wherein the substituted ammonium halide is a dimethylbenzylalkylammonium halide in which the alkyl substituent is a substantially straight chain alkyl of from 12 to 18 carbon atoms.

- 95 9. A process as claimed in claim 8 wherein the substituted ammonium halide is selected from dimethylbenzyl dodecylammonium chloride, dimethylbenzyl tetradecylammonium chloride, dimethylbenzyl hexadecylammonium chloride and dimethylbenzyl octadecylammonium chloride.

- 100 10. A process as claimed in any of claims 1 to 9 wherein the sour petroleum distillate boils in excess of 135°C.

- 105 11. A process for treating a mercaptan-containing sour petroleum distillate carried out substantially as hereinbefore specifically described or exemplified in the foregoing Example II.

12. Sweetened petroleum fractions when obtained by a process as claimed in any of claims 1 to 11.

- 115 13. A catalytic composite comprising a metal chelate mercaptan oxidation catalyst impregnated on a solid adsorbent support, an alkaline reagent and a quaternary ammonium compound of the general formula



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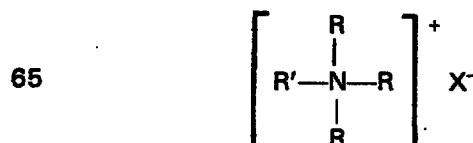
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reagent and a substituted ammonium halide of the general formula



where each R independently is an alkyl, cycloalkyl, aryl, aralkyl or alkaryl radical of up to 20 carbon atoms, R' is a substantially straight-chain alkyl radical of from 5 to 20 carbon atoms, and X⁻ is the chloride, fluoride, bromide or iodide ion.

- 70 2. A process as claimed in claim 1 wherein the alkaline reagent is sodium hydroxide in a from 2 to 30 wt.% aqueous solution.

3. A process as claimed in claim 1 or 2 wherein the substituted ammonium halide is employed in a molar ratio of from 0.001:1 to 1:1 with the alkaline reagent.

4. A process as claimed in any of claims 1 to 3 wherein the catalyst is a supported metal
80 phthalocyanine catalyst.

5. A process as claimed in claim 4 wherein the supported mercaptan oxidation catalyst is a charcoal-supported cobalt phthalocyanine monosulfonate.

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9. A process as claimed in claim 8 wherein the substituted ammonium halide is selected from dimethylbenzyl dodecylammonium chloride, dimethylbenzyl tetradecylammonium chloride, dimethylbenzyl hexadecylammonium chloride and dimethylbenzyl octadecylammonium chloride.

10. A process as claimed in any of claims 1 to 9 wherein the sour petroleum distillate boils in excess of 135°C.

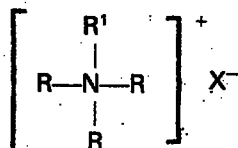
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where each R independently is an alkyl, cycloalkyl, aryl, alkaryl or aralkyl radical containing up to 20 carbon atoms, R¹ is a substantially straight-chain

5 alkyl radical containing from 5 to 20 carbon atoms and X⁻ is the chloride, fluoride, bromide or iodide ion.

14. A catalytic composite as claimed in claim 13 obtained by wetting a metal chelate

10 mercaptan oxidation catalyst impregnated on a support with an aqueous solution of an alkaline reagent containing the quaternary ammonium compound.