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TREATING HYDROCARBON DISTILLATES

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This invention relates to the treatment of sour hydrocarbon distillates in order to produce a distillate of reduced mercaptan content and of acceptable color.

Sour hydrocarbon distillates are subjected to sweetening in order to reduce the mercaptan content of the distillate. In the sweetening reaction, the mercaptans are oxidized to disulfides. The disulfides are soluble in the hydrocarbon distillate and remain in the distillate. However, when certain kerosenes are subjected to sweetening, the color of the kerosene depreciates. This is objectionable because consumers prefer a good color kerosene and difficulty is encountered in marketing the off color kerosene. The present invention provides a novel process for improving the color of the kerosene after sweetening.

The exact mechanism which causes discoloration of the hydrocarbon distillate during sweetening has not been elucidated. Apparently some of the constituents of the hydrocarbon distillate undergo reaction to form color bodies. Accordingly, in order to improve the color of the hydrocarbon distillate after sweetening, it is important to act upon these color bodies but not to adversely affect the other constituents of the other hydrocarbon distillate. It is a particular advantage of the novel process of the present invention that the further treatment of the sweetened kerosene apparently reacts with the color bodies but does not react with the other constituents. For example, the disulfides entrained in the sweetened kerosene should not be converted back to mercaptans. As will be shown in an example appended to the present specifications, treatment of the sweetened kerosene in the manner herein set forth did not cause an increase in the mercaptan content of the finally treated kerosene.

In one embodiment the present invention relates to a combination process for treating sour hydrocarbon distillate to produce a distillate of reduced mercaptan content and of acceptable color, which comprises oxidizing mercaptans contained in said distillate to disulfides and thereafter treating the distillate with a borohydride.

In a specific embodiment the present invention relates to a process of treating sour kerosene which comprises reacting mercaptans contained in said kerosene with air in the presence of a phthalocyanine catalyst and thereafter treating said kerosene with an aqueous solution of sodium borohydride.

The novel process of the present invention is used for the treatment of any hydrocarbon fraction. While the process may be used for the treatment of normally gaseous hydrocarbons, gasoline, naphtha, etc., it is particularly useful for the treatment of hydrocarbon distillates heavier than gasoline, including kerosene, solvent, stove oil, range oil, burner oil, gas oil, fuel oil, etc. In general, the kerosene will have an initial boiling point of from about 300° to about 450° F. and an end boiling point of from about 475° to about 550° F. Solvents and stove oil, for example, usually have initial boiling points within the range of from about 350° to about 500° F. and end boiling points of from about 525° to about 600° F.

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Any suitable sweetening process may be employed. One process comprises the conventional doctor sweetening process in which the hydrocarbon distillate is treated with doctor solution (sodium plumbite) and sulfur to oxidize the mercaptans to disulfides. Another conventional process is the copper treating process in which the mercaptans are reacted with copper chloride, either as a slurry or as a fixed bed, to oxidize the mercaptans to disulfides. Other sweetening processes include the Hypochlorite process, and various modifications of the processes set forth above.

Another process for oxidizing mercaptans to disulfides utilizes a phthalocyanine catalyst. Any suitable phthalocyanine catalyst may be used and preferably comprises a metal phthalocyanine. Particularly preferred metal phthalocyanines include cobalt phthalocyanine and vanadium phthalocyanine. Other metal phthalocyanines include iron phthalocyanine, copper phthalocyanine, nickel phthalocyanine, chromium phthalocyanine, etc. The metal phthalocyanine, in general, is not readily soluble in aqueous solvents and, therefore, when used in an aqueous alkaline solution or for ease of compositing with a solid carrier, a derivative of the phthalocyanine is preferred. A particularly preferred derivative is the sulfonated derivative. Thus, an especially preferred phthalocyanine catalyst is cobalt phthalocyanine sulfonate. Such a catalyst comprises cobalt phthalocyanine disulfonate and also contains cobalt phthalocyanine monosulfonate. Another preferred catalyst comprises vanadium phthalocyanine sulfonate. These compounds may be obtained from any source or prepared in any suitable manner as, for example, by reacting cobalt or vanadium phthalocyanine with 25-50% fuming sulfuric acid. While the sulfonic acid derivatives are preferred, it is understood that other suitable derivatives may be employed. Other derivatives include particularly the carboxylated derivative which may be prepared, for example, by the action of trichloroacetic acid on the metal phthalocyanine or by the action of phosgene and aluminum chloride. In the latter reaction the acid chloride is formed and may be converted to the desired carboxylated derivative by conventional hydrolysis.

Treatment of the hydrocarbon distillate in the presence of the phthalocyanine catalyst preferably is effected in the presence of an alkaline reagent. Any suitable alkaline reagent may be employed. A preferred reagent comprises an aqueous solution of an alkali metal hydroxide such as sodium hydroxide (caustic), potassium hydroxide, etc. Other alkaline solutions include aqueous solutions of lithium hydroxide, rubidium hydroxide, cesium hydroxide, etc. although, in general, these hydroxides are more expensive and, therefore, generally are not preferred for commercial use. Preferred alkaline solutions are aqueous solutions of from about 1% to about 50% and more preferably 5% to 25% by weight concentration of sodium hydroxide or potassium hydroxide. While water is the preferred solvent, it is understood that other suitable solvents may be used including, for example, an aqueous solution of alcohol.

When using the phthalocyanine catalyst, air, oxygen or other suitable oxidizing agent is introduced into the reaction zone. In some cases, the hydrocarbon distillate may contain entrained air in a sufficient amount to effect the desired oxidation, but usually it is desirable to intro-

duce extraneous air in order to be sure that sufficient air is present for the desired purpose.

Treating of the hydrocarbon distillate with the phthalocyanine catalyst is effected at any suitable temperature, which may range from ambient to 210° F. when operating at atmospheric pressure, or up to about 400° F. or more when operating at superatmospheric pressure. In general, it is preferred to utilize a slightly elevated temperature which may range from about 100° F. to about 175° F. Atmospheric pressure or superatmospheric pressure, which may range up to 1000 pounds or more, may be used.

Treatment of the hydrocarbon distillate with the phthalocyanine catalyst is effected in any suitable manner and may be either batch or continuous type of operation. Regardless of which method is used, the phthalocyanine catalyst is employed either as a solution or as a fixed bed. When the catalyst is employed in solution, the amount of catalyst may range from 5 to 1000 parts per million or more and preferably from about 20 to about 500 parts per million by weight of the alkaline reagent solution. In one embodiment the catalyst previously is prepared as a solution in a suitable solvent including ammoniated water, aqueous sodium hydroxide, etc., and then is introduced in this manner to the oxidation zone. In another embodiment the catalyst is added as such to the oxidation zone, to become dissolved in the alkaline reagent solution therein.

When the catalyst is employed as a fixed bed in the oxidation zone, the catalyst is prepared as a composite with a solid support. Any suitable support may be employed and preferably comprises activated charcoal, coke or other suitable forms of carbon. In some cases the support may comprise silica, alumina, magnesia, etc. or mixtures thereof. The solid catalyst is prepared in any suitable manner. In one method, preformed particles of the solid support are soaked in a solution containing the catalyst, after which excess solution is drained off and the catalyst is used as such or is subjected to a drying treatment, mild heating, blowing with air, hydrogen, nitrogen, etc., or successive treatments using two or more of these treatments prior to use. In other methods of preparing the solid composite, a solution of the phthalocyanine catalyst may be sprayed or poured over the particles of the solid support, or such particles may be dipped, suspended, immersed or otherwise contacted with the catalyst solution. The concentration of phthalocyanine catalyst in the composite may range from 0.1% to 10% by weight or more of the composite.

In a batch type operation, the sour hydrocarbon distillate, alkaline reagent solution and catalyst are disposed in a reaction zone, and air is bubbled therethrough until the desired oxidation is completed. In a continuous type operation, the sour hydrocarbon distillate, alkaline reagent solution and catalyst, when the latter is employed in dissolved form, are supplied to the oxidation zone, preferably at a lower portion thereof. It is understood that the catalyst and alkaline reagent solution may be introduced to the reaction zone either separately or in admixture and either commingled with or separate from the sour hydrocarbon distillate. In a fixed bed continuous process, the catalyst is disposed as a fixed bed in a reaction zone, and the sour hydrocarbon distillate, air and alkaline solution, when desired, are passed into the reaction zone, in upward or downward flow, and either together or separately.

Regardless of the particular operation employed, the products are separated to recover treated hydrocarbon distillate of reduced mercaptan content and to separate alkaline reagent solution for reuse in the process. When the soluble catalyst is employed, the catalyst is recovered in admixture with the alkaline reagent solution and is recycled therewith for further use in the process. When desired, additional quantities of phthalocyanine catalyst may be added continuously or intermittently during the treatment of the sour hydrocarbon distillate.

As hereinbefore set forth, the hydrocarbon distillate, following the treatment with phthalocyanine catalyst, in many cases, will be of poor color. As will be shown in an example appended to the present specification, such treatment of kerosene having an initial Saybolt color of 18 resulted in a treated kerosene having a color of 13 or below. In accordance with the present invention, the kerosene now is treated with a borohydride.

Any suitable borohydride may be used in accordance with the present invention. Sodium borohydride is particularly preferred. Other borohydrides include potassium borohydride, lithium borohydride, rubidium borohydride and cesium borohydride. Still other borohydrides include calcium borohydride, strontium borohydride, barium borohydride, magnesium borohydride, etc. It is understood that the different borohydrides are not necessarily equivalent.

Treatment of the hydrocarbon distillate with the borohydride is effected in any suitable manner. In one method a solution of sodium borohydride in aqueous sodium hydroxide is formed, and the aqueous solution is used to wash the hydrocarbon distillate. The washing is effected either in a continuous type countercurrent or concurrent method or in a batch type operation. Regardless of which method is employed, the hydrocarbon distillate and aqueous solution of borohydride are intimately contacted in a suitable vessel, which preferably is provided with stirring means and/or side to side pans, bubble trays, etc. and/or a fixed bed of inert packing material. Following the contacting, the reaction mixture is allowed to separate into a hydrocarbon phase and an aqueous phase in either the same or different zone, and each phase is separately withdrawn.

The treatment of the hydrocarbon distillate with the borohydride preferably is effected at mild temperature which may range from atmospheric and generally will not exceed about 200° F. The pressure will vary with the particular type operation and may range from atmospheric to 1000 pounds or more, generally being within the range of from atmospheric to 200 pounds per square inch.

For economic reasons it is preferred to use the borohydride in as small a concentration as satisfactory for the purpose. Because the borohydride decomposes during use, provision should be made in a continuous type process for the addition of borohydride as required, said addition being either intermittently or continuously. As hereinbefore set forth, the borohydride may be prepared as a solution in an alkaline reagent. The concentration of borohydride generally will be within the range of from about 0.0001% to about 1% by weight of the alkaline reagent.

While the combination process of the present invention is particularly applicable to the treatment of sour hydrocarbon distillates, it is understood that it may be used for the treatment of mercaptan-containing fractions from other sources as, for example, alcohols. In still another application, the novel features of the present invention are employed for the oxidation of mercaptans synthetically prepared or recovered as a special fraction containing the mercaptan as a substantial or major portion thereof. In such cases, the mercaptan is oxidized to the corresponding disulfide and color depreciation is minimized.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

Example I

A commercial kerosene having a mercaptan content of 0.0262% by weight and a Saybolt color of 18 was treated at 104° F. with air and an aqueous 20° Baumé sodium hydroxide solution containing 250 parts per million of cobalt phthalocyanine disulfonate catalyst. Subsequently, a 1000 g. sample of the kerosene, which now has a mercap-

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tan sulfur content of 0.0003% by weight and a Saybolt color of 13, was washed with 100 g. of an aqueous 14° Baumé sodium hydroxide solution containing 0.1 g. of sodium borohydride for one-half hour at ambient temperature. The washing was effected by mechanically stirring the mixture of kerosene and caustic solution containing the borohydride. Following the mixing, the reaction mixture was allowed to settle into an upper kerosene layer and a lower aqueous caustic layer. The kerosene now had a Saybolt color of 21 and a mercaptan sulfur content of 0.0003% by weight.

From the above data it will be seen that the treatment of the kerosene with sodium borohydride improved the Saybolt color from 13 to 21 and did not increase the mercaptan content. As hereinbefore set forth, it is important that this treatment does not convert disulfides contained in the kerosene to mercaptans.

Example II

A West Texas kerosene having a boiling range of 357° to 489° F. and a mercaptan sulfur content of 0.1% by weight is treated with vanadium phthalocyanine sulfonate at 120° F. and 50 pounds per square inch in a batch type operation. The kerosene, in admixture with potassium hydroxide and air, is passed upwardly through a zone containing the phthalocyanine catalyst as a fixed bed in a reaction zone, and the effluent products are passed into a settling zone where excess air is vented. The hydrocarbon separates from potassium hydroxide solution and the latter is recycled within the process. The hydrocarbon phase then is washed by a water solution containing 0.01% sodium borohydride at ambient temperature. The finally treated kerosene is reduced in mercaptans and is of acceptable color.

Example III

Aromatic solvent containing mercaptans is treated with air in the presence of cobalt phthalocyanine sulfonate catalyst at 150° F. and 100 pounds per square inch in a batch type operation. The partially treated solvent then is treated with a water solution of 0.1% sodium borohydride at room temperature. The finally treated solvent is reduced in mercaptan content and is of acceptable color.

Example IV

Sour jet fuel is sweetened in a conventional doctor treating process in which the jet fuel is mixed with fresh sodium plumbite solution at ambient temperature, after which free sulfur is added and the mixing is continued. The reaction mixture then is allowed to settle and the spent doctor solution is separated from the treated jet fuel. The jet fuel, now reduced in mercaptans, then is washed with a caustic solution containing 0.1% by weight of sodium borohydride. The washing is effected at ambient temperature in a continuous type process in which the jet fuel is passed upwardly through a descending stream of caustic solution containing sodium borohydride.

Example V

Sour kerosene is agitated in a batch type operation with an aqueous copper chloride solution, and air is supplied thereto. The reaction is continued until the kerosene is substantially sweet. Following separation of the partially treated kerosene, the kerosene then is washed with an aqueous caustic solution containing 0.05% by weight of sodium borohydride. This serves to improve the color of the sweetened kerosene.

I claim as my invention:

1. A combination process for treating a sour hydrocarbon fraction to produce a product of reduced mercaptan content and of acceptable color, which comprises oxidizing mercaptans contained in said fraction to disulfides, separating the resultant products to recover a treated hydrocarbon fraction of reduced mercaptan con-

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tent, and thereafter treating the separated fraction with an aqueous solution of a borohydride.

2. A combination process for treating sour kerosene to produce a kerosene of reduced mercaptan content and of acceptable color, which comprises oxidizing mercaptans contained in said kerosene to disulfides, separating the resultant products to recover a treated kerosene of reduced mercaptan content, and thereafter treating the separated kerosene with an aqueous solution of a borohydride.

3. A combination process for treating sour hydrocarbon distillate to produce a distillate of reduced mercaptan content and of acceptable color, which comprises reacting mercaptans contained in said distillate with an oxidizing agent in the presence of a phthalocyanine catalyst to form disulfides, separating the resultant products to recover a treated hydrocarbon distillate of reduced mercaptan content, and thereafter treating the separated distillate with an aqueous solution of a borohydride.

4. A combination process for treating sour kerosene to produce a kerosene of reduced mercaptan content and of acceptable color, which comprises reacting mercaptans contained in said kerosene with air in the presence of cobalt phthalocyanine sulfonate catalyst and alkaline solution to oxidize said mercaptans to disulfides, separating the resultant products to recover a treated kerosene of reduced mercaptan content, and thereafter treating the separated kerosene with an aqueous solution of sodium borohydride.

5. A combination process for treating sour kerosene to produce a kerosene of reduced mercaptan content and of acceptable color, which comprises reacting mercaptans contained in said kerosene with air in the presence of vanadium phthalocyanine sulfonate catalyst and alkaline solution to oxidize said mercaptans to disulfides, separating the resultant products to recover a treated kerosene of reduced mercaptan content, and thereafter treating the separated kerosene with an aqueous solution of sodium borohydride.

6. A combination process for treating sour kerosene to produce a kerosene of reduced mercaptan content and of acceptable color, which comprises reacting mercaptans contained in said kerosene with air in the presence of cobalt phthalocyanine sulfonate catalyst and caustic solution to convert the mercaptans to disulfides, separating the resultant products to recover a treated kerosene of reduced mercaptan content, and thereafter treating the separated kerosene with caustic solution containing sodium borohydride.

7. A combination process for treating sour kerosene to produce a kerosene of reduced mercaptan content and of acceptable color, which comprises reacting mercaptans contained in said kerosene with air in the presence of vanadium phthalocyanine sulfonate catalyst and caustic solution to convert the mercaptans to disulfides, separating the resultant products to recover a treated kerosene of reduced mercaptan content, and thereafter treating the separated kerosene with caustic solution containing sodium borohydride.

8. A combination process for treating sour hydrocarbon distillate to produce a distillate of reduced mercaptan content and of acceptable color, which comprises reacting mercaptans contained in said distillate with sodium plumbite solution to oxidize mercaptans to disulfides, separating the resultant products to recover a treated hydrocarbon distillate of reduced mercaptan content, and thereafter treating the separated distillate with an aqueous solution of a borohydride.

9. A combination process for treating sour kerosene distillate to produce a distillate of reduced mercaptan content and of acceptable color, which comprises reacting mercaptan contained in said distillate with sodium plumbite solution to oxidize mercaptans to disulfides, separating the resultant products to recover a treated hydrocarbon distillate of reduced mercaptan content, and

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thereafter treating the separate distillate with an aqueous solution of sodium borohydride.

10. A combination process for treating sour hydrocarbon distillate to produce a distillate of reduced mercaptan content and of acceptable color, which comprises reacting mercaptans contained in said distillate with copper chloride to oxidize mercaptans to disulfides, separating the resultant products to recover a treated hydrocarbon distillate of reduced mercaptan content, and thereafter treating the separated distillate with an aqueous solution of a borohydride. 10

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11. A combination process for treating sour kerosene distillate to produce a distillate of reduced mercaptan content and of acceptable color, which comprises reacting mercaptans contained in said distillate with copper chloride to oxidize mercaptans to disulfides, separating the resultant products to recover a treated hydrocarbon distillate of reduced mercaptan content, and thereafter treating the separated distillate with an aqueous solution of sodium borohydride. 5

No references cited.