

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Process for Catalytic Treatment of Sour Hydrocarbon Distillates

5 We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, 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:—

10 This invention relates to improvements in the treatment of sour hydrocarbon distillates, and more particularly, to a method of converting mercaptans contained in said distillates by oxidizing the same to disulfides in the presence of an improved catalyst composition.

15 The process of the invention is particularly applicable to the treatment of petroleum distillates such as sour gasolines of cracked, straight run or natural origin, or mixtures thereof, also naphtha, jet fuel, kerosene, aromatic solvent, stove oil, range oil or fuel oil. Other hydrocarbon distillates which may be treated include lubricating oil and normally gaseous fractions.

20 It is known to use a phthalocyanine catalyst for treating a sour hydrocarbon distillate. In the known process, such as the process of our British Patent Specification No. 849,998 the phthalocyanine catalyst is dissolved or suspended in an alkaline reagent solution and contacted with the sour hydrocarbon distillate and oxidizing agent in a liquid phase operation. Because the phthalocyanine catalyst is soluble in the alkaline reagent solution, it has been the practice to carry the catalyst into the treating zone in solution in the alkaline reagent solution and also to remove the catalyst from the treating zone in the alkaline reagent solution. The known method however has not been entirely satisfactory because of the

necessity of providing special means for assuring intimate contact between the liquid charge stock and the catalyst-containing solution and also because of the required continuous recirculation of the latter solution. Because of the aforesaid solubility of the phthalocyanine catalyst in the alkaline reagent solution it was not thought possible to prepare the catalyst in a solid composite form which would resist the leaching effect of the alkaline solution and thus serve effectively over long periods of time. It has been found however that the phthalocyanine catalyst can be combined with solid support materials to produce composite catalysts which exhibit unexpectedly good stability.

The present invention therefore provides an improvement in the process for oxidizing mercaptans contained in sour hydrocarbon distillate wherein said distillate is contacted with an oxidizing agent in the presence of an alkaline reagent and a phthalocyanine catalyst, said improvement being characterized by effecting said contact in the presence of a fixed bed of a phthalocyanine catalyst composited with a solid support. Thus in accordance with the present invention the phthalocyanine catalyst is composited with a suitable carrier and utilized as a fixed bed in the treating zone. The fixed bed of catalyst and carrier serves a dual purpose of providing a catalyst required for the oxidation of mercaptans and also to provide a packing material in the treating zone which gives highly efficient contact between catalyst and reactants.

Suitable phthalocyanine catalysts which may be utilized in the present invention comprise metal-free phthalocyanine or metal phthalocyanine, preferably a metal phthalocyanine. Particularly preferred metal phthalocyanines comprise cobalt phthalocyanine and vanadium

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phthalocyanine. Still more preferably a derivative of the metal phthalocyanine catalyst is utilized, for example the sulfonated derivative. Thus, a particularly preferred phthalocyanine catalyst comprises cobalt phthalocyanine sulfonate. Such a catalyst is available commercially and comprises cobalt phthalocyanine disulfonate and also contains the monosulfonate. Another excellent catalyst comprises vanadium phthalocyanine sulfonate. These compounds may be obtained or prepared in any suitable manner as, for example, by reacting cobalt, vanadium or other metal phthalocyanine with fuming sulfuric acid. While the sulfonates are particularly preferred, it is understood that other suitable derivatives may be employed, such as the carboxylated derivatives. The latter 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.

Any suitable alkaline reagent may be employed in the process. A preferred reagent comprises an aqueous solution of an alkali metal hydroxide, such as sodium hydroxide solution or potassium hydroxide solution. Other alkaline solutions include aqueous solutions of lithium hydroxide, rubidium hydroxide and cesium hydroxide, although, in general, these hydroxides are more expensive and therefore are not preferred for commercial use. In some cases the alkaline solution will contain a solubilizer or solutizer including, for example, alcohols such as methanol, ethanol, phenols, cresols, tannin or isobutyrate. A particularly suitable alkaline solution is an aqueous solution of from 1 to 50% by weight concentration of sodium hydroxide, preferably with methanol as solutizer in a concentration of from 1 to 200 volume percent of the caustic or other alkaline solution. The amount of the alkaline reagent solution to be used is not critical. Thus in some cases it is found that by merely wetting the solid catalyst with the reagent, a sufficient amount may be absorbed for a long period of use. In other cases it may be necessary, or convenient, to maintain a continuous flow of the reagent. The rate of flow may vary from 1% or less of the distillate rate up to several times the distillate rate.

The support material of the catalyst should be insoluble in or substantially unaffected by the caustic solution and hydrocarbons under the conditions prevailing in the treating zone. Activated carbon is particularly preferred because of its high adsorptivity and stability under these conditions. Other carbon carriers include coke, charcoal from any suitable source including bone char, wood charcoal, charcoal made from coconut or other nut shells or fruit pits. Other carriers include

silica, for example, sand, glass beads, clays and silicates including those synthetically prepared and naturally occurring, preferably acid-treater or heat-treated, as, for example, attapulugus clay, china clay, diatomaceous earth, feldspar, fuller's earth, halloysite, kaoline, kieselguhr, mica, montmorillonite and pumice, aluminas and particularly alpha aluminas including corundum and emery, ceramics, porcelain, various magnesium compounds. As hereinbefore set forth, the choice of the carrier will be made with reference to its adsorptive or spacing properties and its stability in the alkaline reagent solution and hydrocarbons at the conditions prevailing in the treating zone.

The composite of phthalocyanine and carrier may be prepared in any suitable manner. In one method the carrier may be formed into particles of uniform or irregular size and shape, including spheres, pills, pellets, rings, saddles or flakes, and the carrier is then intimately contacted with a solution of the phthalocyanine catalyst. An aqueous or alkaline solution of the phthalocyanine catalyst is prepared and, in a preferred method, the carrier particles are soaked, dipped, suspended, or otherwise immersed in the solution. Alternatively, the solution may be sprayed or poured over the carrier. Excess solution may then be removed and the carrier containing the catalyst allowed to dry at room temperature, dried in an oven or by means of hot gases passed thereover, or in any other suitable manner.

In general it is preferred to composite as much catalyst with the carrier as will form a stable composite, although a lesser amount may be so deposited if desired. In one preparation, 1% by weight of cobalt phthalocyanine sulfonate catalyst was composited with activated carbon by soaking granules of the carbon in a solution of the phthalocyanine catalyst. In another method, the carrier may be placed in the treating zone and the phthalocyanine catalyst solution passed therethrough to form the catalyst composite in situ. If desired, the solution may be recycled one or more times in order to prepare the desired composite. Alternatively the chamber containing the support particles may be simply filled with a solution of the catalyst, thereby forming the composite in situ. In general the amount of phthalocyanine catalyst which will be absorbed upon the support material to form an effective catalyst will be within the range from 0.1 to 1% by weight of the support. However, composites of support material and phthalocyanine catalysts containing greater amounts of the latter up to as high as 10% by weight, which are prepared by surface deposition of the phthalocyanine compound upon the support or physically mixing the two, are also effective catalysts. In carrying out the process the sour hydrocarbon dis-



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tillate is introduced, preferably continuously into the treating zone containing the fixed bed of composite catalyst and is passed through the catalyst bed in the presence of the oxidizing agent and the alkaline reagent. Desirably the distillate, together with an oxidizing agent such as air and for example an aqueous solution of sodium hydroxide, is introduced into the lower portion of the treating zone and passed upwardly through the catalyst bed, the resulting reaction mixture being withdrawn from the upper portion of the treating zone. The distillate, air and sodium hydroxide solution may be supplied to the treating zone as individual streams or as a single combined stream. If desired the distillate, alkaline reagent and oxidizing agent may be supplied to the upper portion of the treating zone and passed downwardly through the bed. Alternatively, an oxidizing agent such as air may be passed upwardly countercurrently to descending distillate and alkaline reagent. In another alternative method the distillate and air may be passed upwardly countercurrently to descending alkaline reagent. The latter, as stated above, in some cases will not be used as a continuous stream at all, but rather only intermittently, as required to maintain an effective amount of reagent present at the point of reaction.

The contact between the sour hydrocarbon distillate, oxidizing agent, alkaline reagent and fixed bed of catalyst in the treating zone generally is effected at ambient temperature, although elevated temperature may be used and generally will not exceed 150° C. Atmospheric pressure generally is employed, although pressures up to 68 atmospheres or more may be employed, if desired. The time of contact in the treating zone will be selected to give the desired reduction in mercaptan content and may range from 1 to 48 hours or more, depending upon the size of the treating zone, the amount of catalyst and the particular hydrocarbon distillate being treated. The rate of flow of distillate over the catalyst bed may be varied over wide limits, depending largely upon mercaptan concentration, catalyst age or activity, and temperature. Flow rates in the range from 0.25 to 20 or more volumes of distillate per volume of catalyst per hour may be used.

When upward flow of the distillate and alkaline reagent is employed the total reaction mixture is withdrawn from the upper section of the treating zone and passed into a settler. Excess air is removed from the top of the settler and may be vented or reused in the process if desired. The treated hydrocarbon distillate is withdrawn from intermediate elevation of the settler and is recovered as the desired product of the process. Alkaline solution is withdrawn from the bottom of the settler, and while a portion thereof may be discarded, preferably at least a portion thereof

is recycled to the treating zone. Fresh alkaline solution and/or additional phthalocyanine catalyst may be introduced into the process as needed. When downward flow of distillate and alkaline reagent is utilized, countercurrently, to upflowing air, the latter is withdrawn from the top of the treating zone and the liquid reaction mixture will be withdrawn from the bottom of the treating zone and passed to a settler for separation and separate withdrawal of treated hydrocarbon distillate and alkaline reagent. Any minor amounts of catalyst which may be removed from the treating zone in solution in the alkaline reagent will be returned thereto in the re-cycled alkaline reagent and will be adsorbed on the carrier at least in part.

While air is preferred for use as oxidizing agent, it is understood that any other suitable oxidizing agent may be employed, including oxygen or other oxygen-containing gases. In some cases the sour hydrocarbon distillate may contain entrained oxygen or air in sufficient concentration to accomplish the desired treating, but generally it is preferred to introduce air into the treating zone. The amount of air must have be at least sufficient to effect oxidation of the mercaptans, although an excess thereof generally is not objectionable.

The phthalocyanine catalyst is active and stable. Accordingly, the fixed bed catalyst composite may be used for treating a large volume of sour hydrocarbon distillate.

In some cases, and particularly with sour gasoline, it may be desirable to extract a major proportion of the mercaptan sulfur from the distillate prior to further treating in the manner herein set forth. This may be accomplished by countercurrently contacting the sour hydrocarbon distillate with caustic or other alkaline solution, and separating a partly treated distillate from the caustic solution. The partly treated distillate then is further treated in the manner hereinbefore set forth.

The following examples are introduced to illustrate further the novelty and utility of the present invention.

EXAMPLE I

A composite of cobalt phthalocyanine sulfonate on activated carbon was prepared as follows: The carbon used was a commercially available product marketed under the trade name of "Nuchar Type WA" and of .42 to .59 mm. in size. This material is prepared from residual organic material which is recovered during the manufacture of pulp and then is carbonized and activated by heating. A small scale preparation was made by dissolving 0.15 grams of cobalt phthalocyanine sulfonate in 25 cc of water to which 1 cc of ammonium hydroxide (28%) solution was added. 100 cc of water then was added thereto and the mixture was stirred. 15 grams



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(100 cc) of the activated carbon granules were poured into the solution, stirred slightly and allowed to stand over night. The following day, the mixture was filtered to separate excess water. 41.9 grams of solid material were recovered and were dried under water pump vacuum to leave a dry composite of 15.2 grams. The filtrate was a faint blue color but was analysed and found to contain no cobalt. Accordingly, the final catalyst composite contained 1% by weight of the phthalocyanine catalyst.

The catalyst composite prepared as described was installed as a fixed bed in a treating zone and used for the treatment of various hydrocarbon distillates. One distillate treated was a jet fuel having a specific gravity of 0.754, a boiling range of 65° to 250° C. and a mercaptan sulfur content of 0.0132% by weight. The treating zone contained 100 cc of the catalyst composite. The alkaline solution used was a 10° Baume aqueous solution of sodium hydroxide. The flow rates used were: jet fuel at 50 cc per hour, caustic at 30 cc per hour and air at 96 cc per hour. These streams were commingled and passed through the treating zone in upward flow. The treating zone was maintained at a temperature of 40° C. and a pressure of 6.8 atmospheres. This run continued for 28 hours, during which time the mercaptan sulfur content was reduced to 0.00026% by weight or lower. The jet fuel recovered from the settler was sweet to the doctor test.

A commercial kerosene having a mercaptan sulfur content of 0.0058% by weight was treated next. The flow rates used were: kerosene at 100 cc per hour, caustic at 50 cc per hour and air at 96 cc per hour. The caustic solution and treating zone temperature and pressure were the same as for the jet fuel.

This run continued for 41 hours, during which time the mercaptan sulfur content of the kerosene was reduced to 0.00022—0.00034% by weight. In all cases the kerosene was sweet to the doctor test.

The distillate next treated was a blend of thermally cracked and straight run gasolines, the blend having a specific gravity of 0.7175, a boiling range of 32° to 200° C. and a mercaptan sulfur content of 0.0130% by weight. The gasoline blend was treated in the same manner as described above using the same alkaline solution and the same treating zone temperature and pressure. The flow rates in this case were hydrocarbon at 100 cc per hour, alkaline solution at 30 cc per hour and air at 96 cc per hour.

The above runs continued for 40 hours, during which time the mercaptan sulfur content of the gasoline blend was reduced to 0.00028 to 0.00040% by weight. In all cases the gasoline was sweet to the doctor test.

EXAMPLE II

The hydrocarbon distillate of this example is a C₅ hydrocarbon fraction recovered as an overhead from a depentanizer fractionating column. The solid bed of catalyst was prepared by soaking 100 cc of carbon Raschig rings in a 10° Baume aqueous solution of sodium hydroxide containing 50 parts per million of cobalt phthalocyanine sulfonate, followed by filtering and drying in the manner hereinbefore described. The catalyst composite was disposed as a fixed bed in the treating zone and the reaction mixture passed therethrough in upward flow. The rates were as follows: C₅ hydrocarbon charge at 100 cc per hour, alkaline solution recycle rate at about 40 cc per hour and air at 54 cc per hour. The treating zone was maintained at a temperature of 40° C. and a pressure at 2 atmospheres gauge.

The above run was continued for 63 hours, during which the mercaptan sulfur content of the C₅ fraction was reduced to 0.0002% to 0.0004% by weight. In all cases the product was sweet to the doctor test.

EXAMPLE III

This example describes treating a No. 2 commercial fuel oil having a mercaptan sulfur content of about 0.040% by weight. The catalyst used in this example was vanadium phthalocyanine sulfonate composited with sand, filtered and dried and used as a fixed bed in a treating zone. The alkaline reagent solution was potassium hydroxide of 12° Baume. The fuel oil, potassium hydroxide solution were passed downwardly through a treating zone containing a bed of the catalyst composite countercurrently to upflowing air. The treating was effected at room temperature and 2 atmospheres gauge pressure. In this operation, the mercaptan sulfur content of the fuel oil was reduced to below 0.025%. This reduction is more than satisfactory to produce a final blend of the treated fuel oil with other refinery products to meet the specific mercaptan sulfur specifications of below 0.01% by weight.

WHAT WE CLAIM IS:—

1. In the process for oxidizing mercaptans contained in a sour hydrocarbon distillate wherein said distillate is contacted with an oxidizing agent in the presence of an alkaline reagent and a phthalocyanine catalyst, the improvement which is characterized by effecting said contact in the presence of a fixed bed of a phthalocyanine catalyst composited with a solid support.
2. Process according to claim 1, further characterized in that the phthalocyanine catalyst comprises a metal phthalocyanine.
3. Process according to claim 2, further characterized in that the phthalocyanine cata-

(100 cc) of the activated carbon granules were poured into the solution, stirred slightly and allowed to stand over night. The following day, the mixture was filtered to separate excess water. 41.9 grams of solid material were recovered and were dried under water pump vacuum to leave a dry composite of 15.2 grams. The filtrate was a faint blue color but was analysed and found to contain no cobalt. Accordingly, the final catalyst composite contained 1% by weight of the phthalocyanine catalyst.

The catalyst composite prepared as described was installed as a fixed bed in a treating zone and used for the treatment of various hydrocarbon distillates. One distillate treated was a jet fuel having a specific gravity of 0.754, a boiling range of 65° to 250° C. and a mercaptan sulfur content of 0.0132% by weight. The treating zone contained 100 cc of the catalyst composite. The alkaline solution used was a 10° Baume aqueous solution of sodium hydroxide. The flow rates used were: jet fuel at 50 cc per hour, caustic at 30 cc per hour and air at 96 cc per hour. These streams were commingled and passed through the treating zone in upward flow. The treating zone was maintained at a temperature of 40° C. and a pressure of 6.8 atmospheres. This run continued for 28 hours, during which time the mercaptan sulfur content was reduced to 0.00026% by weight or lower. The jet fuel recovered from the settler was sweet to the doctor test.

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The above runs continued for 40 hours, during which time the mercaptan sulfur content of the gasoline blend was reduced to 0.00028 to 0.00040% by weight. In all cases the gasoline was sweet to the doctor test.

EXAMPLE II

The hydrocarbon distillate of this example is a C₈ hydrocarbon fraction recovered as an overhead from a depentanizer fractionating column. The solid bed of catalyst was prepared by soaking 100 cc of carbon Raschig rings in a 10° Baume aqueous solution of sodium hydroxide containing 50 parts per million of cobalt phthalocyanine sulfonate, followed by filtering and drying in the manner hereinbefore described. The catalyst composite was disposed as a fixed bed in the treating zone and the reaction mixture passed therethrough in upward flow. The rates were as follows: C₈ hydrocarbon charge at 100 cc per hour, alkaline solution recycle rate at about 40 cc per hour and air at 54 cc per hour. The treating zone was maintained at a temperature of 40° C. and a pressure at 2 atmospheres gauge.

The above run was continued for 63 hours, during which the mercaptan sulfur content of the C₈ fraction was reduced to 0.0002% to 0.0004% by weight. In all cases the product was sweet to the doctor test.

EXAMPLE III

This example describes treating a No. 2 commercial fuel oil having a mercaptan sulfur content of about 0.040% by weight. The catalyst used in this example was vanadium phthalocyanine sulfonate composited with sand, filtered and dried and used as a fixed bed in a treating zone. The alkaline reagent solution was potassium hydroxide of 12° Baume. The fuel oil, potassium hydroxide solution were passed downwardly through a treating zone containing a bed of the catalyst composite countercurrently to upflowing air. The treating was effected at room temperature and 2 atmospheres gauge pressure. In this operation, the mercaptan sulfur content of the fuel oil was reduced to below 0.025%. This reduction is more than satisfactory to produce a final blend of the treated fuel oil with other refinery products to meet the specific mercaptan sulfur specifications of below 0.01% by weight.

WHAT WE CLAIM IS:—

1. In the process for oxidizing mercaptans contained in a sour hydrocarbon distillate wherein said distillate is contacted with an oxidizing agent in the presence of an alkaline reagent and a phthalocyanine catalyst, the improvement which is characterized by effecting said contact in the presence of a fixed bed of a phthalocyanine catalyst composited with a solid support.

2. Process according to claim 1, further characterized in that the phthalocyanine catalyst comprises a metal phthalocyanine.

3. Process according to claim 2, further characterized in that the phthalocyanine cata-



lyst comprises cobalt phthalocyanine sulfonate.

4. Process according to claim 2, further characterized in that the phthalocyanine catalyst comprises vanadium phthalocyanine sulfonate.

5. Process according to claim 2, further characterized in that the phthalocyanine catalyst comprises cobalt phthalocyanine carboxylate.

6. Process according to claim 2, further characterized in that the phthalocyanine catalyst comprises vanadium phthalocyanine carboxylate.

7. Process according to any of the claims 1 to 7, further characterized in that the phthalocyanine catalyst is composited with the support in a concentration within the range from 0.1 to 10% by weight of said support.

8. Process according to any of the claims 1 to 7, further characterized in that the solid support comprises carbon.

9. Process according to any of the claims 1 to 8, further characterized in that the alkaline reagent comprises an aqueous solution of an alkali metal hydroxide.

10. Process according to any of the claims 1 to 9, further characterized in that the oxidizing agent comprises air.

11. Process according to any of the claims 1 to 10, further characterized in that the

hydrocarbon distillate is contacted with the oxidizing agent at a temperature within the range of from 0° to 150° C.

12. Process according to any of the claims 1 to 11, further characterized in that a stream comprising the hydrocarbon distillate and air is passed upwardly through a treating zone containing a fixed bed of the catalyst, reaction mixture is withdrawn from the upper portion of the treating zone and treated hydrocarbon distillate is separated from said reaction mixture.

13. Process for the catalytic treatment of a sour hydrocarbon distillate, substantially as described.

14. Catalyst composition for use in the treating process of the foregoing claims, characterized by having been prepared by steps comprising forming a solution of a metal phthalocyanine catalyst in an aqueous solvent, commingling said solution with particles of an absorptive solid support to incorporate a catalytic amount of the metal phthalocyanine catalyst into said support, and subsequently drying the resultant composite of catalyst and solid support.

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