

PATENT SPECIFICATION

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(54) MERCAPTAN CONVERSION PROCESS FOR A PETROLEUM DISTILLATE CHARGE STOCK

(71) We, UOP INC, a corporation organized under the laws of the State of Delaware, United States of America, of Ten UOP Plaza, Algonquin & Mt. Prospect Roads, 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:—

This invention relates to a process for the conversion of mercaptans contained in a petroleum distillate charge stock. More specifically, this invention relates to the mercaptan conversion of a petroleum distillate charge stock containing one or more mercaptans as well as one or more olefinic and dienic compounds.

The treatment of petroleum distillates for mercaptan conversion is well known in the prior art. For example, it is well known that a gasoline charge stock containing one or more mercaptans may be treated using metal phthalocyanine compounds for the conversion of the mercaptan(s) contained in the gasoline charge stock to disulfide(s) (see for example our BG Patent No. 1,337,494). The necessity of the conversion of the mercaptan(s) in a petroleum distillate charge stock is as a result of the bad odor of the mercaptan(s) which necessitate conversion to a "doctor-sweet" product. The easiest means of conversion known to the art is by means of the oxidation of the mercaptan(s) to disulfide(s). The difficulty of converting the mercaptan(s) will depend on which mercaptan(s) are present in the petroleum distillate charge stock. In lighter charge stocks such as a straight run gasoline the mercaptans comprise lower alkyl mercaptans which are fairly easily oxidized by any of the metal phthalocyanine catalysts known to the art. However, as the complexity of the blend of the charge stock increases the complexity of the different mercaptans will increase and therefore the degree of difficulty of conversion also becomes greater. Petroleum distillate charge stocks which have

high contents of mercaptan(s), olefinic and dienic compounds, such as an FCC gasoline charge stock, will contain one or more mercaptans which are very difficult to convert such as aromatic mercaptans or branched chained alkyl mercaptans, e.g. dodecyl mercaptan. It is known as a problem of mercaptan treating or conversion that certain FCC gasoline charge stocks possess mercaptans which are unconvertible in the presence of the commonly used mercaptan - conversion catalysts. For example, it is known that a mercaptan-containing FCC gasoline charge stock is very difficult to convert to a sweet or substantially mercaptan-free FCC charge stock in the presence of 4,4'-cobalt phthalocyanine disulfonate.

We have now found that mercaptans found in an FCC gasoline and other petroleum distillate charge stocks containing one or more mercaptans as well as one or more olefinic and dienic compounds may be converted to disulfides by treatment in an atmosphere of a gas comprising oxygen in a medium possessing a pH of from 8 to 14 in the presence of a catalyst comprising a sulfonated cobalt phthalocyanine of which at least a major proportion is 4,4',4'',4''' - cobalt phthalocyanine tetrasulfonate and that the treated charge stock may then be recovered.

The utilization of the present invention will allow the operator of fluid catalytic cracking units to obtain a doctor-sweet reactor effluent convert mercaptan materials present in the FCC gasoline charge stock effluent. The utilization of this invention will also allow the manufacturer or refiner a more ecologically acceptable method for the preparation of petroleum distillates which are high in dienic and olefinic compound content as a result of the elimination of harmful and malodorous compounds.

A specific embodiment of this invention, the features of which are preferred singly and in combination, resides in a process for the treatment of an FCC gasoline charge stock, which may contain 240 parts per

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million by weight mercaptan, in the presence of air, a sodium hydroxide medium, which may possess a pH of about 11, and a catalyst dissolved in said medium and consisting essentially of 4,4',4'',4''' - cobalt phthalocyanine tetrasulfonate as the catalytically active ingredient at a temperature of 25°C. and a pressure of 1 atmosphere and recovering the resultant treated FCC gasoline charge stock after a period of time comprising 4 minutes.

The treatment of the petroleum distillate charge stock containing one or more mercaptans as well as one or more olefinic and dienic compounds is suitably carried out at a temperature of from 15°C. to 300°C. and a pressure of from 1 atmosphere to 100 atmospheres. When superatmospheric pressures are used in the process of this invention they may be afforded by the introduction of the oxygen source gas to the treatment zone at the appropriate pressure or, if desired, any substantially inert gas may be intermixed with the oxygen source gas to afford the total pressure of the system. Gases comprising oxygen which may be used include essentially pure oxygen, oxygen-nitrogen mixtures (e.g. air), oxygen-xenon mixtures, oxygen - nitrogen - helium mixtures, oxygen - helium mixtures, and oxygen - argon - krypton mixtures.

The charge stocks treated in accordance with the invention typically contain from 20 ppm by weight mercaptan calculated as sulfur to 1000 ppm by weight mercaptan calculated as sulfur. The diene content of the petroleum distillate charge stock will typically range from 0.5 grams of dienic compound(s) to 3.5 grams of dienic compound(s) as determined by the grams of iodine per 100 grams of petroleum distillate. The content of olefinic compounds will typically range from 20 grams to 70 grams of olefinic material as determined by the grams of bromine per 100 grams of petroleum distillate. A particularly suitable petroleum distillate for treatment is an FCC gasoline petroleum distillate. It is known in the art of catalytic cracking of gasoline that FCC gasoline petroleum distillates possess different chemical properties depending on such factors as the original charge stock ingressed to the FCC unit, the catalytic composition within the FCC unit and the method of performing the catalytic cracking of the original charge stock. It is contemplated within the scope of this invention that any gasoline derived from an FCC unit may be utilized as the petroleum distillate charge stock. The mercaptan content of FCC gasoline petroleum distillates usually includes one or more components that are aromatic in nature, e.g. one or more thiophenols. Part of the mercaptan content may be aliphatic in nature, e.g. methyl mercaptan, ethyl mercaptan, propyl mercaptan, butyl

mercaptan, amyl mercaptan, hexyl mercaptan, heptyl mercaptan, nonyl mercaptan, decyl mercaptan, or other various straight-chained aliphatic mercaptans containing up to 20 carbon atoms. The mercaptan content of the FCC gasoline petroleum distillate may also comprise one or more branched-chain aliphatic mercaptans, e.g. dodecyl mercaptan, or other mercaptans which are hard to treat. The thiophenolic mercaptans may be substituted in the benzene nucleus with one or more further substituents such as alkyl, carboxyl, alkoxy, aryl, alkaryl, aralkyl or alcoholic moieties.

The catalytic composition used in the present invention comprises a sulfonated cobalt phthalocyanine of which all or a major proportion is 4,4',4'',4''' - cobalt phthalocyanine tetrasulfonate. This compound is known in the art as obtainable by various methods of catalyst manufacture. One such method of catalyst manufacture is the reaction of triammonium sulfophthalate with urea and cobalt sulfate heptahydrate in the presence of boric acid. It is contemplated within the scope of this invention that the catalytic composition may be present in the form of a liquid - liquid two phase petroleum distillate charge stock 4,4',4'',4''' - cobalt phthalocyanine tetrasulfonate system. The liquid liquid system is defined as having two phases, one of which is the petroleum distillate charge stock containing one or more mercaptans and one or more olefinic and dienic compounds, and the second of which is the cobalt phthalocyanine tetrasulfonate catalyst which is present in a reaction medium which is liquid in nature and possesses a pH of from 8 to 14. The conversion of the mercaptan compounds in the liquid-liquid system will be effected at the interface of the two systems on the basis of contact with the catalytic composition. The reaction medium of the liquid-liquid system can comprise any alkaline material, e.g. sodium hydroxide, potassium hydroxide, lithium hydroxide, rubidium hydroxide, cesium hydroxide, barium hydroxide, strontium hydroxide, calcium hydroxide, magnesium hydroxide, beryllium hydroxide, ammonium hydroxide, pyridine, piperidine, picoline, lutidine, quinoline, pyrrole, indole, carbazole or acridine, or any suitable quaternary ammonium compound, e.g. tetrabutyl ammonium hydroxide, tetraamyl ammonium hydroxide, tetrapropyl ammonium methoxide, tetraamyl ammonium methoxide, tetraethyl ammonium ethoxide, diethyl amine, triethyl amine, tetramethylenediamine, tetraethylenepentamine or phenylenediamine, provided that the pH in the reaction medium is in the range from 8 to 14, more preferably from 9 to 11.

In a preferred embodiment of the present invention the catalyst composition is present as a fixed bed system. The fixed bed system

of catalytic treatment is well known in the art and it is contemplated within the present invention that the 4,4',4'',4''' - cobalt phthalocyanine tetrasulfonate is dispersed on the fixed bed, which fixed bed may comprise any suitable inert solid material, e.g. alumina, silica, magnesia, thallia, zirconia, carbon, charcoal, γ -alumina, mordenite, faujasite or pumice.

The 4,4',4'',4''' - cobalt phthalocyanine tetrasulfonate may be present in the total catalyst system in a weight percent relative to the entire reaction system of from 0.0001 weight percent to 10 weight percent. The aforementioned weight percentages are applicable to both the fixed treating system and the liquid-liquid two phase petroleum distillate charge stock 4,4',4'',4''' - cobalt phthalocyanine tetrasulfonate system.

The treated charge stock produced by the process of the invention will be a petroleum distillate charge stock containing substantially the same quantity of olefinic and dienic material but a greatly reduced mercaptan content. The mercaptans are converted to disulfides to the extent that the resultant petroleum distillate is substantially free of mercaptan compounds. The remaining quantity of mercaptan compounds will in general be small enough to qualify the petroleum distillate as a doctor-sweet petroleum distillate. The term doctor-sweet is relative to the type of analysis to determine mercaptan content but generally denote ranges from about 5 ppm mercaptan calculated as sulfur, in gasoline, to about 20 ppm mercaptan calculated as sulfur, in kerosene petroleum distillates.

The following Examples II and III illustrate the present invention, whereas Example I is comparative.

EXAMPLE I

This Example was effected for the purpose of comparing the treatment of an FCC gasoline charge stock utilizing a mainly disulfonated cobalt phthalocyanine compound in contrast to the treatment with a catalyst consisting essentially of cobalt phthalocyanine tetrasulfonate as the active ingredient, c.f. Example II. The unexpected results of the present invention may be viewed from the increased conversion of the mercaptans in Example II in the presence of the tetrasulfonate over a shorter period of time in con-

tradistinction to the limited conversion of the mercaptans in the presence of the disulfonate of Example I. The disulfonated cobalt phthalocyanine compound was prepared and analyzed and found to contain a spectrum of the sulfonated derivatives as set forth in Table I below:

TABLE I

Isomer	Weight Percent
Monosulfonate	6.3
Disulfonate	59.6
Trisulfonate	25.6
Tetrasulfonate	8.5
	100.0

An FCC gasoline charge stock was treated with air in a reaction medium comprising 10% Bé caustic of sodium hydroxide over a period of time comprising 8 minutes in the presence of the aforementioned catalyst at a temperature of 25°C. and a pressure of 1 atmosphere. The relative mercaptan content over the 8 minute period of time is set forth in Table II below:

TABLE II

Time	Wt.-ppm mercaptan
0	240
2	25
4	23
6	15
8	Doctor Sweet

EXAMPLE II

In this example a tetrasulfonated catalyst was prepared and analyzed and found to contain 100% 4,4',4'',4'''-cobalt phthalocyanine tetrasulfonate. This catalyst was used in the treatment of a similar aliquot portion of the FCC gasoline charge stock utilized in Example I in the presence of the same reaction medium comprising sodium hydroxide and in the presence of the same quantity of air and reaction temperature and pressure. The results of the mercaptan sweetening process are set forth in Table III below:

TABLE III

Time (minutes)	Mercaptan (wt.-ppm)
0	240
2	13
4	2 Doctor-sweet
6	<1
8	<1

21

A comparison of Example II with Example I in the treatment of the same charge stock will show the unexpected results of the present invention. In Example I the mercaptan content after a 4 minute period of time was 23 parts per million in comparison with the 2 parts per million mercaptan content after the same period in the tetrasulfonated catalyst treatment process of Example II. It can also be seen that it required between 6 to 8 minutes in Example I to render a doctor-sweet product where in the Example II utilizing the tetrasulfonated cobalt phthalocyanine derivative the doctor-sweet product was formed somewhere between 2 and 4 minutes.

EXAMPLE III

In this example a FCC gasoline charge stock containing mercaptans, olefins and dienes is treated in a medium comprising sodium hydroxide and air in a fixed bed method of treatment which comprises the passage at a LHSV of 3.0 of the FCC gasoline mercaptan-containing charge stock over a fixed bed of 4,4',4'',4''' - cobalt phthalocyanine tetrasulfonate dispersed on γ -alumina. The treatment is effected at a treatment temperature of 100°C. and a pressure of 5 atmospheres as afforded by the introduction of the air to the reaction system. The FCC gasoline charge stock is recovered subsequent to the fixed bed and analyzed for mercaptan content, said mercaptan content analysis showing a doctor-sweet FCC gasoline.

WHAT WE CLAIM IS:—

1. A process for the mercaptan conversion of a petroleum distillate charge stock containing one or more mercaptans as well as one or more olefinic and dienic compounds, comprising the treatment of said petroleum distillate in an atmosphere of a gas comprising oxygen in a medium possessing a pH of from 8 to 14 in the presence of a catalyst comprising a sulfonated cobalt phthalocyanine of which at least a major proportion is 4,4',4'',4'''-cobalt phthalocyanine tetrasulfonate, and recovering the resultant treated charge stock.

2. The process of Claim 1 wherein the treatment is carried out at a temperature of from 15°C. to 300°C. and a pressure of from 1 atmosphere to 100 atmospheres.

3. The process of Claim 1 or 2 wherein the gas comprising oxygen is essentially pure oxygen.

4. The process of Claim 1 or 2 wherein the gas comprising oxygen is air.

5. The process of any of Claims 1 to 4 wherein the petroleum distillate charge stock is an FCC gasoline.

6. The process of any of Claims 1 to 5 wherein the petroleum distillate charge stock contains one or more aromatic mercaptans.

7. The process of Claim 6 wherein the one or more aromatic mercaptans are one or more thiophenols.

8. The process of any of Claims 1 to 7 wherein the treatment is effected in a liquid-liquid two phase petroleum distillate charge stock 4,4',4'',4''' - cobalt phthalocyanine tetrasulfonate system.

9. The process of any of Claims 1 to 7 wherein the treatment is effected in the presence of a fixed bed system.

10. The process of Claim 9 wherein the fixed bed consists essentially of 4,4',4'',4'''-cobalt phthalocyanine tetrasulfonate dispersed on γ -alumina.

11. The process of Claim 9 wherein the fixed bed consists essentially of 4,4',4'',4'''-cobalt phthalocyanine tetrasulfonate dispersed on silica.

12. The process of Claim 9 wherein the fixed bed consists essentially of 4,4',4'',4'''-cobalt phthalocyanine tetrasulfonate dispersed on charcoal.

13. The process of Claim 9 wherein the fixed bed consists essentially of 4,4',4'',4'''-cobalt phthalocyanine tetrasulfonate dispersed on magnesia.

14. The process of Claim 9 wherein the fixed bed consists essentially of 4,4',4'',4'''-cobalt phthalocyanine tertasulfonate dispersed on pumice.

15. The process of Claim 9 wherein the fixed bed consists essentially of 4,4',4'',4'''-cobalt phthalocyanine tetrasulfonate dispersed on mordenite.

16. A process for the conversion of mercaptan compounds to disulfide compounds in a petroleum distillate charge stock carried out substantially as described in either of the foregoing Examples II and III.

17. A doctor-sweet effluent obtained by treatment of an FCC gasoline charge stock by a process as claimed in any of claims 1 to 16.

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(21)

A comparison of Example II with Example I in the treatment of the same charge stock will show the unexpected results of the present invention. In Example I the mercaptan content after a 4 minute period of time was 23 parts per million in comparison with the 2 parts per million mercaptan content after the same period in the tetrasulfonated catalyst treatment process of Example II. It can also be seen that it required between 6 to 8 minutes in Example I to render a doctor-sweet product where in the Example II utilizing the tetrasulfonated cobalt phthalocyanine derivative the doctor-sweet product was formed somewhere between 2 and 4 minutes.

EXAMPLE III

In this example a FCC gasoline charge stock containing mercaptans, olefins and dienes is treated in a medium comprising sodium hydroxide and air in a fixed bed method of treatment which comprises the passage at a LHSV of 3.0 of the FCC gasoline mercaptan-containing charge stock over a fixed bed of 4,4',4'',4''' - cobalt phthalocyanine tetrasulfonate dispersed on γ -alumina. The treatment is effected at a treatment temperature of 100°C. and a pressure of 5 atmospheres as afforded by the introduction of the air to the reaction system. The FCC gasoline charge stock is recovered subsequent to the fixed bed and analyzed for mercaptan content, said mercaptan content analysis showing a doctor-sweet FCC gasoline.

WHAT WE CLAIM IS:—

1. A process for the mercaptan conversion of a petroleum distillate charge stock containing one or more mercaptans as well as one or more olefinic and dienic compounds, comprising the treatment of said petroleum distillate in an atmosphere of a gas comprising oxygen in a medium possessing a pH of from 8 to 14 in the presence of a catalyst comprising a sulfonated cobalt phthalocyanine of which at least a major proportion is 4,4',4'',4''' -cobalt phthalocyanine tetrasulfonate, and recovering the resultant treated charge stock.

2. The process of Claim 1 wherein the treatment is carried out at a temperature of from 15°C. to 300°C. and a pressure of from 1 atmosphere to 100 atmospheres.

3. The process of Claim 1 or 2 wherein the gas comprising oxygen is essentially pure oxygen.

4. The process of Claim 1 or 2 wherein the gas comprising oxygen is air.

5. The process of any of Claims 1 to 4 wherein the petroleum distillate charge stock is an FCC gasoline. 60

6. The process of any of Claims 1 to 5 wherein the petroleum distillate charge stock contains one or more aromatic mercaptans. 65

7. The process of Claim 6 wherein the one or more aromatic mercaptans are one or more thiophenols.

8. The process of any of Claims 1 to 7 wherein the treatment is effected in a liquid-liquid two phase petroleum distillate charge stock 4,4',4'',4''' - cobalt phthalocyanine tetrasulfonate system. 70

9. The process of any of Claims 1 to 7 wherein the treatment is effected in the presence of a fixed bed system. 75

10. The process of Claim 9 wherein the fixed bed consists essentially of 4,4',4'',4''' -cobalt phthalocyanine tetrasulfonate dispersed on γ -alumina.

11. The process of Claim 9 wherein the fixed bed consists essentially of 4,4',4'',4''' -cobalt phthalocyanine tetrasulfonate dispersed on silica. 80

12. The process of Claim 9 wherein the fixed bed consists essentially of 4,4',4'',4''' -cobalt phthalocyanine tetrasulfonate dispersed on charcoal. 85

13. The process of Claim 9 wherein the fixed bed consists essentially of 4,4',4'',4''' -cobalt phthalocyanine tetrasulfonate dispersed on magnesia. 90

14. The process of Claim 9 wherein the fixed bed consists essentially of 4,4',4'',4''' -cobalt phthalocyanine tetrasulfonate dispersed on pumice. 95

15. The process of Claim 9 wherein the fixed bed consists essentially of 4,4',4'',4''' -cobalt phthalocyanine tetrasulfonate dispersed on mordenite. 100

16. A process for the conversion of mercaptan compounds to disulfide compounds in a petroleum distillate charge stock carried out substantially as described in either of the foregoing Examples II and III.

17. A doctor-sweet effluent obtained by treatment of an FCC gasoline charge stock by a process as claimed in any of claims 1 to 16. 105

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