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DESULFURIZING PETROLEUM FRACTIONS WITH NITROGEN DIOXIDE AND SULFURIC ACID

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The present invention relates to a process for treating hydrocarbon streams to reduce their sulfur content. More particularly, the present invention is directed to the treatment of petroleum fractions with mixtures of various nitrogen compounds, oxygen, and sulfuric acid to reduce the sulfur content of these hydrocarbons.

A number of methods have been suggested for use in removing corrosion producing sulfur from petroleum fractions. These methods have not provided an entirely satisfactory solution to the sulfur problem. The desulfurization of hydrocarbons by treatment with sulfuric acid, for example, is well known to the art. One of the major shortcomings of sulfuric acid desulfurization is its limited applicability over a wide range of refinery stocks. The restricted effectiveness of this agent is largely due to the difficulty encountered in oxidizing the sulfur compounds normally found in higher boiling petroleum fractions. The amount of sulfuric acid required for desulfurization also is quite substantial. A mixture of nitrogen dioxide and sulfuric acid has also been used to combat the presence of sulfur in stocks. It is also known to purify petroleum fractions by desulfurization with mixtures of nitric acid and sulfuric acid. These mixtures also have not proven to be fully satisfactory answers to the problems caused by sulfur.

One of the principal objects of the present invention is to provide a process for desulfurizing petroleum fractions which can be used in connection with a wide range of refinery stocks.

Another object of the invention is to provide a process which is capable of reducing the sulfur content of refinery stocks to levels heretofore unobtainable by sulfuric acid or by mixtures of either sulfuric acid and nitrogen dioxide or sulfuric acid and nitric acid.

Still another object of the invention is to provide a process for desulfurizing petroleum stocks which cannot be purified by known methods.

Another object is to provide a process for desulfurizing petroleum stocks which requires far less sulfuric acid than known methods.

Other objects will become apparent to those skilled in the art from the following detailed description of the invention.

In general, the subject invention involves the discovery that the removal of sulfur compounds from a hydrocarbon stream with sulfuric acid can be greatly enhanced by the presence of air or other oxygen-containing gases and the compound nitrosyl sulfuric acid. Nitrogen dioxide and its tetromer N_2O_4 can be reacted with sulfuric acid to form nitrosyl sulfuric acid. Specific treating agents include mixtures of NO_2 or N_2O_4 and sulfuric acid, mixtures of nitrosyl sulfuric acid and sulfuric acid, and mixtures containing nitrosyl sulfuric acid, nitric acid, and sulfuric acid. The presence of oxygen is essential to the success of the process and must always accompany the liquid treating agents as air or in some other form. It has

been found that a combination of the liquid agents described above and air greatly increases the oxidizing power of sulfuric acid causing the sulfur compounds to be oxidized to readily extractable forms. The presence of the nitrogen compound also increases the solubility of the various oxidized sulfur compounds in the sulfuric acid.

In carrying out the process operating temperatures between 30° F. and 250° F. can be used, although operating temperatures of 70° F. to 120° F. are preferred. The temperature that is used is dictated in part by the boiling range of the hydrocarbon material being treated. The process has been found to be applicable on sulfur containing hydrocarbon streams having a specific gravity of from 0.5 to 1.0

The air:$HNOSO_4$:H_2SO_4 ratios utilized in the process are important. It has been found that $HNOSO_4$:H_2SO_4 ratios of from one to two thousand to one to ten are effective. Ratios in excess of the above, although theoretically capable of extraction, would tend to decrease in applicability. The optimum range of applicability is between the ratios of 1 to 50 and 1 to 20. All of the above ratios are calculated on a weight basis.

As was indicated above, $HNOSO_4$ can be produced by reacting NO_2 or N_2O_4 with sulfuric acid. When nitrogen dioxide and sulfuric acid are mixed they react on contact to form nitrosyl sulfuric acid and nitric acid in accordance with the following equation:

$$\underset{\text{Sulfuric Acid}}{H_2SO_4} + \underset{\text{Nitrogen Dioxide}}{2NO_2} \rightleftarrows \underset{\text{Nitrosyl Sulfuric Acid}}{HNOSO_4} + \underset{\text{Nitric Acid}}{HNO_3}$$

Where ratios of NO_2 or N_2O_4:H_2SO_4 are used which are comparable to the ratios set forth above with respect to $HNOSO_4$:H_2SO_4, the reaction proceeds to completion fairly rapidly due to the large excess of H_2SO_4.

Air is required in sufficient quantity to provide oxygen for the oxidation of the sulfur compounds present in the hydrocarbon. In place of air, mixtures of oxygen and other inert gases in various compositions as well as the use of normally liquid or gaseous oxygen donors are contemplated. The process is found to proceed more satisfactorily when the oxygen exceeds the amount theoretically required. The amount of excess to be used would, of course, be dictated by the design of the equivalent and the safety factors to be considered. To predict the exact amount of oxygen required, one would have to know the exact composition of the sulfur compounds present in the hydrocarbon and the oxidized reaction product of each of these sulfur compounds. Due to the large variety of sulfur compounds which may exist in the hydrocarbon stream, the above prediction is impracticable. Therefore, to be sure that sufficient oxygen is supplied to the system, one must assume that all of the sulfur present exists as that type of sulfur compound which requires the maximum amount of oxygen to react to completion. In most cases, it is assumed that the sulfur exists as mercaptan sulfur and is to be oxidized to a sulfonic acid.

An amount of about 50 to 100 percent excess of oxygen over theoretical requirements would be adequate for use in the process. Greater or lesser amounts, however, could certainly be used. Amounts varying from 50% of theoretical to 1,000% in excess theoretical might be employed under certain circumstances. In commercial operations one can use, for example, about 1 to 6 mols of oxygen per mol of sulfur.

The contact time between the hydrocarbon stream and

the sulfuric acid, $HNOSO_4$, and air mixture largely depends upon the type and quantity of the various sulfur compounds present in the hydrocarbon stream. Contact times of from 0.1 second to 1 hour may be employed in this process. The contact time is the average length of time that the liquid hydrocarbon and the treating acid remain in intimate contact. Contact times of between 1 and 30 minutes are preferred for most petroleum fractions.

The quantity of liquid treating agent used ($HNOSO_4$ and H_2SO_4) depends upon the quantity of sulfur compounds to be extracted and the desired sulfur content of the treated product. Quantities of from 0.1 volume percent to 10 volume percent have been employed with success. The upper limit, of course, is determined by economic considerations. High volume percentage treats result in higher chemical costs. Higher volume percentage treats are possible when a portion of the acid mixture is recirculated. The low volume percentage treats result in a lower extracting efficiency. In general, the optimum in volume percentage treat is between 0.5 and 2.0 volume percent on most petroleum fractions. The results achieved with the present invention at this level of treatment are greatly improved over that obtained from 96% H_2SO_4.

In carrying out the process the liquid hydrocarbon to be desulfurized is metered to a mixing device containing sufficient volume to give the desired contact time. The $HNOSO_4$-sulfuric acid mixture preferably is metered and mixed into the liquid hydrocarbon immediately before entry into the mixer. The mixing device should be capable of imparting sufficient mechanical energy to the system to keep the acid and hydrocarbon intimately mixed. Air either may be metered and bubbled into the system or sufficient air pressure may be maintained on the system to cause a theoretical excess of oxygen to be present in the mixing device at all times. The acid-hydrocarbon mixture leaving the reactor passes to a deaerification vessel where entrained gases are removed. The deaerified mixture is separated immediately into an acid phase and a hydrocarbon phase. This separation may be caused to take place either by gravity settling, electrical coalescence, mechanical coalescence, centrifugal force, or by a combination of these or other methods. In our preferred embodiment the separation is carried out by electrical coalescence. The hydrocarbon then may be neutralized and water washed if this treatment is so desired.

The above processing flow description is illustrative of a means of practicing the process. The process, however, would lend itself equally well to batch-type operations where a given quantity of petroleum distillate may be stored for batch treatment. In a batch-type operation, the air-nitrosyl sulfuric acid-sulfuric acid mixture could be mixed with the hydrocarbon in a reaction vessel and the treatment carried out in situ, or a pump-around system could be employed.

In U.S. Patent 3,066,087, equipment is disclosed which can be used in carrying out the subject process. The disclosure of U.S. Patent 3,066,087 is specifically incorporated in the subject specification.

The following examples are illustrative of the present invention.

Example 1

In this example, 96.0% sulfuric acid, a nitrogen dioxide-sulfuric acid mixture, and an air-nitrosyl sulfuric acid-sulfuric acid mixture are compared as desulfurizing agents for naphtha. The naphtha used in all runs had a specific gravity of 0.675 and contained 555 p.p.m. total sulfur and 420 p.p.m. mercaptans. All runs were made at a contact time of 4.5 minutes with 1 volume percent of treating agent. An enclosed stainless steel autoclave with a high speed impeller mounted from the bottom was used to make all runs. All runs were made at 80° F.

Run A.—A 1,000 ml. sample of naphtha was treated with 1 volume percent of 96.0% H_2SO_4 under the above described conditions. The treated hydrocarbon contained 260 p.p.m. total sulfur.

Run B.—A 1,000 ml. sample of naphtha was treated with 1 volume percent of nitrogen dioxide-sulfuric acid mixture containing 3.8 weight percent $HNOSO_4$. The run was made under the above conditions in the absence of air. The treated hydrocarbon product contained 116 p.p.m. total sulfur.

Run C.—A 1,000 ml. sample of naphtha was treated with 1 volume percent nitrosyl sulfuric-sulfuric acid mixture containing 3.8 weight percent $HNOSO_4$. The run was made under the conditions described above except that the air was bubbled into the liquid mixture during the entire mixing operation. The treated hydrocarbon product contained 32.0 p.p.m. total sulfur.

Run D.—A 1,000 ml. sample of naphtha was treated with 1 volume percent $HNOSO_4$-sulfuric acid mixture containing 3.8 weight percent $HNOSO_4$. The run was made under the above conditions except that 20 p.s.i.g. of air pressure was maintained on the treating vessel during the entire mixing time. The treated hydrocarbon contained 60.0 p.p.m. total sulfur.

Run E.—A 1,000 ml. sample of naphtha was treated with 1 volume percent $HNOSO_4$-sulfuric acid mixture containing 3.8 weight percent $HNOSO_4$. The run was made under the above conditions except that 40 p.s.i.g. of air pressure was maintained on the treating vessel during the entire mixing time. The treated hydrocarbon contained 48.5 p.p.m. total sulfur.

Run F.—A 1,000 ml. sample of naphtha was treated with 1 volume percent $HNOSO_4$-sulfuric acid mixture containing 3.8 weight percent $HNOSO_4$. The run was made under the above conditions except that 60 p.s.i.g. of air pressure was maintained on the treating vessel during the entire mixing time. The treated hydrocarbon contained 42.5 p.p.m. total sulfur.

Run G.—A 1,000 ml. sample of naphtha was treated with 1 volume percent $HNOSO_4$-sulfuric acid mixture containing 3.8 weight percent $HNOSO_4$. The run was made under the above conditions except that 80 p.s.i.g. of air pressure was maintained on the treating vessel during the entire mixing time. The treated hydrocarbon contained 36.0 p.p.m. total sulfur.

Example 2

In this example, a comparison was made of 96.0% sulfuric acid and mixtures of nitrogen dioxide-sulfuric acid and air-nitrogen dioxide-sulfuric acid as desulfurizing agents for kerosene. The kerosene used for these runs was obtained from Tujmaza Crude and had a specific gravity of 0.89. The untreated kerosene had a mercaptan content of 680 p.p.m. and a total sulfur content of 1,080 p.p.m. All runs were made at a contact time of 3 minutes and an operating temperature of 95° F. An enclosed stainless steel autoclave with a high speed impeller mounted from the bottom was used to make all runs.

Run A.—A 1,000 ml. sample of kerosene was treated with 1 volume percent of 96.0% H_2SO_4 under the above conditions. The treated product contained 413 p.p.m. total sulfur.

Run B.—A 1,000 ml. sample of kerosene was treated with 1 volume percent of a nitrogen dioxide-sulfuric acid mixture containing 6.4 weight percent NO_2. The run was made under the above conditions in the absence of air. The treated product contained 217 p.p.m. total sulfur.

Run C.—A 1,000 ml. sample of kerosene was treated with 1 volume percent of nitrogen dioxide-sulfuric acid mixture containing 6.4 weight percent NO_2. Nitrosyl sulfuric acid was formed from the reactants. The run was made under the above conditions except with a continuous air purge. The treated product contained 105 p.p.m. total sulfur.

Example 3

In this example, the effect of the nitrogen dioxide content on the desulfurization of naphtha was determined. The following runs were made using various concentrations of nitrogen dioxide in sulfuric acid. Varying the NO_2 content, of course, correspondingly varied the content of nitrosyl sulfuric acid. All runs were made in the presence of air at 85° F. and at a contact time of 4.5 minutes. The naphtha used contained 420 p.p.m. mercaptans and 555 p.p.m. total sulfur.

Run A.—A 1,000 ml. sample of naphtha was treated with 1 volume percent nitrogen dioxide-sulfuric acid mixture containing 6.44 weight percent NO_2. The treated product contained 44.5 p.p.m. total sulfur.

Run B.—A 1,000 ml. sample of naphtha was treated with 1 volume percent nitrogen dioxide-sulfuric acid mixture containing 5.15 weight percent NO_2. The treated product contained 26.3 p.p.m. total sulfur.

Run C.—A 1,000 ml. sample of naphtha was treated with 1 volume percent nitrogen dioxide-sulfuric acid mixture containing 3.86 weight percent NO_2. The treated product contained 21.0 p.p.m. total sulfur.

Run D.—A 1,000 ml. sample of naphtha was treated with 1 volume percent nitrogen dioxide-sulfuric acid mixture containing 2.58 weight percent NO_2. The treated product contained 30.9 p.p.m. total sulfur.

Run E.—A 1,000 ml. sample of naphtha was treated with 1 volume percent nitrogen dioxide-sulfuric acid mixture containing 1.29 weight percent NO_2. The treated product contained 87.3 p.p.m. total sulfur.

Run F.—A 1,000 ml. sample of naphtha was treated with 1 volume percent of 96.0% sulfuric acid. The treated product contained 206 p.p.m. total sulfur.

Example 4

The effect of contact time on the desulfurization of naphtha with air-$HNOSO_4$-sulfuric acid mixtures was determined in the tests set forth below. The naphtha used in the runs had a specific gravity of 0.675 and contained 420 p.p.m. mercaptans and 555 p.p.m. total sulfur. The runs were made at 90° F. in the presence of air and at $HNOSO_4$-sulfuric acid treats of 0.5 volume percent. The treating acid contained 6.44 weight percent $HNOSO_4$.

Run A.—A 1,000 ml. sample of naphtha was contacted with the treating acid at the above conditions for 1.5 minutes. The treated hydrocarbon contained 84.3 p.p.m. total sulfur.

Run B.—A 1,000 ml. sample of naphtha was contacted with the treating acid at the above conditions for 3.0 minutes. The treated hydrocarbon contained 68.6 p.p.m. total sulfur.

Run C.—A 1,000 ml. sample of naphtha was contacted with the treating acid at the above conditions for 6.0 minutes. The treated hydrocarbon contained 40.8 p.p.m. total sulfur.

Run D.—A 1,000 ml. sample of naphtha was contacted with the treating acid at the above conditions for 10.0 minutes. The treated hydrocarbon contained 35.3 p.p.m. total sulfur.

As is pointed out above, the provision of an oxygen supply in the oxidation reaction is an important factor in achieving a successful process. A preferred source of oxygen is air. The invention may be practiced, however, by making oxygen available to the process system from any source, e.g., by chemical reaction, feed from a liquid oxygen storage, etc.

In the process, nitrogen dioxide or its tetromer can be mixed with sulfuric acid to form nitrosyl sulfuric acid. The treating liquid, therefore, can be either nitrogen dioxide or N_2O_4 plus sulfuric acid (nitrosyl sulfuric acid would be formed by the reaction of NO_2 or N_2O_4 with H_2SO_4) or the treating agent can be a mixture of nitrosyl sulfuric acid and sulfuric acid. Nitric acid can also be added to the liquid if such is desired. A preferred mixing means for dispersing the treating agents in the treated hydrocarbon is a rotating multistage mixer with impellers of the flat-blade turbine type.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for treating a hydrocarbon stream containing sulfur components which comprises: intimately and vigorously admixing nitrosyl sulfuric acid and sulfuric acid with said stream while adding oxygen to said stream, the amount of oxygen being in excess of the amount required to oxidize the sulfur compounds present in the hydrocarbon, the mixing of said hydrocarbon stream and the treating agents being carried out at a temperature of from about 30 to about 250° F.

2. A process for treating a hydrocarbon stream containing sulfur components which comprises: intimately and vigorously admixing nitrosyl sulfuric acid and sulfuric acid with a hydrocarbon stream having a specific gravity of from 0.5 to 1.0, said mixing taking place while adding oxygen to said stream, the amount of oxygen being in excess of the amount required to oxidize the sulfur compounds present in the hydrocarbon, the volume percent of liquid treating agent being from about 0.01 to 10 volume percent based on the volume of said hydrocarbon stream, the mixing of the treating agents and said hydrocarbon stream being carried out at a temperature of from about 30 to about 250° F. for a period of from about 0.1 second to about 1 hour.

3. A process for treating a hydrocarbon stream containing sulfur components which comprises: intimately and vigorously admixing nitrosyl sulfuric acid and sulfuric acid with a hydrocarbon stream having a specific gravity of from 0.5 to 1.0, said mixing taking place while adding oxygen to said stream, the amount of oxygen being in excess of the amount required to oxidize the sulfur compounds present in the hydrocarbon, the volume percent of liquid treating agent being from about .05 to 2 volume percent based on the volume of said hydrocarbon stream, the mixing of the treating agents and said hydrocarbon stream being carried out at a temperature of from about 70 to about 120° F. for a period of from about 1 minute to about 30 minutes.

4. A process for treating a hydrocarbon stream containing sulfur components which comprises: mixing nitrogen dioxide and sulfuric acid, intimately and vigorously admixing the resultant reaction mixture with said hydrocarbon stream while bubbling air into said stream, the mixing of said hydrocarbon stream and the treating agents being carried out at a temperature of from about 30 to about 250° F.

5. A process for treating a hydrocarbon stream containing sulfur components which comprises: mixing nitrogen dioxide and sulfuric acid, intimately and vigorously admixing the resultant reaction mixture with said hydrocarbon stream while bubbling air into said stream, said stream having a specific gravity of from 0.5 to 1.0, the volume percent of liquid treating agent being from about 0.01 to 10 volume percent based on the volume of said hydrocarbon stream, the mixing of the treating agents and said hydrocarbon stream being carried out at a temperature of from about 30 to about 250° F. for a period of from about 0.1 second to about 1 hour, the amount of oxygen added to said stream being from about 1 to about 6 mols per mol of sulfur in said stream.

6. A process for treating a hydrocarbon stream containing sulfur components which comprises: mixing nitrogen dioxide and sulfuric acid, intimately and vigorously admixing the resultant reaction mixture with said hydrocarbon stream while bubbling air into said stream, said stream having a specific gravity of from 0.5 to 1.0, the volume percent of liquid treating agent being from

about .05 to 2 volume percent based on the volume of said hydrocarbon stream, the mixing of the treating agents and said hydrocarbon stream being carried out at a temperature of from about 70 to about 120° F. for a period of from about 1 minute to about 30 minutes, the amount of oxygen added to said stream being from about 1 to about 6 mols per mol of sulfur in said stream.

7. A process as in claim 4 wherein the weight ratio of NO_2:H_2SO_4 is from about 1:10 to 1:2,000.

8. A process as in claim 6 wherein the weight ratio of NO_2:H_2SO_4 is from about 1:20 to 1:50.

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