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DESULFURIZATION OF PETROLEUM OILS

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This invention relates to a process of desulfurization of hydrocarbon oils. More particularly, it relates to a process for the removal of sulfur compounds from petroleum oils boiling below about 750° F. Still more particularly, it relates to a process for the removal of sulfur compounds from thermally cracked petroleum oils boiling in the gasoline range.

Practically all petroleum oils contain sulfur in the form of organic sulfur compounds. The presence of these sulfur compounds is objectionable because of odor, corrosion, gum formation, and interference with the burning qualities of kerosenes and heater oils. A very large number of processes have been developed for removing these sulfur compounds or converting them to non-objectionable types; for example, the sweetening processes wherein mercaptans are converted to disulfides. These processes are either dependent on chemical conversion and removal of the converted products, as in, acid treating, clay contacting at high temperatures, caustic treating at high temperatures, etc., or by removal of the compounds themselves through the use of selective solvents, such as, liquid sulfur dioxide, liquid hydrogen fluoride, etc. The removal of sulfur compounds from petroleum oils derived from thermal cracking or catalytic cracking is much more difficult than from virgin oils. The prior art processes are relatively ineffective in the removal of sulfur compounds from gasoline obtained by the thermal coking of heavy gas oils and reduced crudes.

An object of my invention is to provide a process for the removal of sulfur compounds normally present in petroleum oils. Another object is to remove sulfur compounds from petroleum oils which boil below about 750° F.; i. e. the so-called petroleum distillates. Still another object of my invention is to provide a process for the desulfurization of petroleum oils boiling in the gasoline range. A particular object of my invention is to provide a process for the removal of these sulfur compounds by contacting the liquid petroleum oil with asphaltenes. Yet another object is to desulfurize coke still naphthas by contacting these naphthas in the liquid state with asphaltenes derived from oxidized, cracked tars.

I have found that appreciable amounts of the sulfur compounds present in petroleum oils can be removed therefrom by contacting these oils in the liquid phase, at temperatures below about 250° F., with asphaltenes.

Asphaltenes are the materials precipitated from the bitumens in petroleum, petroleum products,

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or native bitumens upon dilution of said material with a large excess of light paraffin, such as n-hexane, and n-pentane. (For a discussion on the separation of asphaltenes see "The Chemical Constituents of Petroleum" by Sachanen, published 1945, pp. 390-392.) I have found that asphaltenes derived from various petroleum sources can be used to remove sulfur compounds naturally present in petroleum oils. Illustrative of these source materials are: the cracked tar obtained upon the treatment of hydrocarbons in the range of temperatures 850° F. and higher; residual tars obtained by removing some of the lower boiling constituents of cracked tar; oxidized, cracked tar obtained by air blowing of cracked tar, or residual tar; reduced crudes, particularly the reduced crude from the so-called asphaltic-base crudes; the asphaltic material obtained by propane treatment of reduced crudes such as Mid-Continent crude; oxidized asphalt prepared by air blowing straight-run asphalt. While the asphaltenes derived from all these sources are effective; particularly good results are obtained by using asphaltenes derived from oxidized, residual tar. (For a description of the preparation and properties of oxidized asphalt see "Asphalts and Allied Substances" by Abraham, 4th edition, pp. 440-452.)

The amount of desulfurization obtained appears to vary with the type of sulfur compounds present in the particular distillate. I have found that from about 1 to about 6 parts by weight of sulfur containing petroleum distillate can be contacted with 1 part by weight of the asphaltene before the sulfur-removing power of the asphaltene is exhausted. The amount of asphaltene needed to give the maximum amount of desulfurization will vary with the particular petroleum distillate being treated; as well as with variation in the source of the asphaltene. The amount of asphaltene needed can very readily be determined in each case by percolating some of the sulfur-containing distillate through a bed of the asphaltene that is to be used for the contacting. On the whole, I have found that for petroleum distillates containing difficultly removable sulfur compounds such as cracked gasoline, coke still naphtha, cycle gas oil, about 1 part of asphaltene will treat about 2 to 3 parts of distillate.

The reaction mechanism of my process appears to be adsorption of the sulfur compounds by the asphaltenes. This is evidenced by the fact that although the asphaltenes lose their ability to remove sulfur compounds fairly quickly, the activity can be restored completely by washing the

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spent asphaltenes with a solvent for the sulfur compounds, such as ethyl alcohol, isopropyl alcohol, acetone, etc.

I have found that appreciable desulfurization can be obtained by percolating the liquid petroleum oil through a body of asphaltene particles. However, faster liquid flow rates are obtained when the asphaltenes are mixed with a spacing material, such as finely crushed stone, sand, fuller's earth, Attapulugus clay, etc. Particularly good percolation times are obtained when a mixture of one to three parts of Attapulugus clay is mixed with one part of asphaltenes.

Instead of contacting the asphaltenes and sulfur-containing petroleum oil by the percolation method, the asphaltenes and oil may be contacted in an agitated vessel and the treated distillate separated from the asphaltenes by filtration or decantation, after a settling period. While the above methods of contacting work very well with petroleum distillates boiling in the gasoline range, I prefer to contact the higher boiling petroleum oils somewhat differently because of the solubility of some of the asphaltentic material in these petroleum oils. For oils such as kerosene, heater oil, cycle gas oil, lower boiling lube oil distillates, etc., I prefer to add the asphaltenes to the sulfur-containing petroleum oil in an agitated vessel. Upon the completion of the contacting, I dilute the mixture with a low boiling paraffin such as n-hexane or, preferably, n-pentane. The diluent precipitates substantially all the asphaltenes from the treated distillate. If not removed, the dissolved asphaltentic material seriously impair the color of the treated distillate. Besides the dilution technique, the dissolved asphaltentic material may be removed by percolation through fuller's earth or Attapulugus clay.

My process is not affected to any considerable extent by variation in the temperature of contacting until a fairly elevated temperature is reached, such as about 250° F. As the temperature increases above this point, the amount of desulfurization decreases rapidly. (A coke still naphtha contacted with asphaltene, followed by distilling away from the asphaltenes, showed no significant difference in sulfur content before and after treatment.) While temperatures below 250° F. may be used, I prefer to operate below about 110° F. in order to eliminate any necessity for heating or cooling the petroleum distillate.

In order to show the results that are obtainable when using my process, several examples are given below. It is to be understood that these examples are illustrative only and my process is not to be limited to these particular stocks or methods of operation.

Unless otherwise stated, the asphaltenes used in these examples were obtained by contacting 10 grams of 195° F. softening point asphalt with 100 ml. n-hexane. This asphalt was produced by atmospheric pipe-still reduction of a residual tar to about 140° F. softening point followed by heating to a temperature of about 350° to 500° F., and blowing with air at a rate of about 3 to 5 cubic feet per minute per gallon of charge to a softening point in the range 190° to 205° F., a penetration at 77° F. of not more than 3, a specific gravity at 60° F. of about 1.08, and a flash point (C. O. C.) of not less than 500° F. (These oxidation conditions are conventional in the art.) The mixture was allowed to stand for 24 hours at about 75° F. The hexane solution of oils and resins was decanted and the asphaltene precipi-

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tate was washed twice with 100 ml. portions of n-hexane, a soaking period of about 4 hours was allowed between washes. The asphaltene yield was about 35% by weight of the starting material.

Example I

A mixture of 3 parts of Attapulugus clay and 2 parts of asphaltenes were placed in a percolation column, ½" in diameter. The mixture of clay and asphaltenes filled the column to a height of 14". Virgin heavy naphtha, obtained by distillation from high sulfur West Texas crude, with a total sulfur content, by weight, of 0.30%, was percolated through the clay and asphaltenes, at a temperature of about 77° F. Some asphaltenes were dissolved by the virgin heavy naphtha so that the percolate had an unsatisfactory color. The color was restored by distilling the treated heavy naphtha away from the dissolved asphaltenes. In order to determine the effect of the clay and the distillation on the sulfur content of the treated virgin heavy naphtha, a blank run was made; the sulfur content of the clayed-rerun heavy naphtha was 0.25%. Two portions of percolate from the clay-asphaltene mixture run were obtained. The first portion, representing the first 15 ml., had a sulfur content after rerunning, of 0.15%, which represents a 39% desulfurization over that obtained by clay and rerunning only. The second portion of percolate, representing 15 ml. additional, had a sulfur content after rerunning of 0.26%, which indicates that the asphaltenes were spent before the first portion had completely passed through the mixture. In this case optimum desulfurization was obtained at about 3 parts of virgin heavy naphtha to 1 part of asphaltene.

Example II

The spent asphaltenes from Example I were washed with 100 ml. of ethyl alcohol. The alcohol was displaced from the asphaltenes by washing with n-hexane. The washed asphaltenes were air dried at 77° F. The experiment of Example I was repeated with a fresh amount of virgin heavy naphtha. The first 15 ml. portion of percolate had a sulfur content after rerunning of 0.15%. Thus the spent asphaltenes were restored by the alcohol washing to the same level of activity as the fresh asphaltenes.

Example III

A mixture of 1 part of asphaltenes and 1 part of Attapulugus clay were placed in a percolation column. Coke still naphtha, with a total sulfur content of 0.77%, obtained from the coking of heavy gas oil and reduced crudes from West Texas crude, was percolated through the asphaltene-clay mixture. At the same time a blank run through clay alone was made. A percolate, 2.5 parts of naphtha per part of asphaltene, was obtained with a sulfur content of 0.44%. The sulfur content of the coke still naphtha from the blank run through clay only had a sulfur content of 0.65%. Thus the asphaltenes removed about 33% of the sulfur compounds in the coke still naphtha.

Example IV

A so-called light recycle catalytic gas oil (1.5% sulfur, 28.9° API and ASTM distillation range of 417° F. to 522° F.) obtained by distillation of the product from the treatment of virgin gas oil at about 900° F. in the presence of a silica-alumina catalyst, was desulfurized by contacting 5 grams of asphaltenes in 30 grams of the gas oil at 210°

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F.; a major portion of the asphaltenes dissolved. The mixture was cooled to room temperature, and 225 ml. of n-pentane were added to precipitate the asphaltenes. The asphaltenes were filtered off and the remaining dissolved asphaltenes were removed from the pentane-gas oil solution by percolation through Attapulugus clay. The pentane was then separated from the gas oil; the sulfur content of the treated gas oil was 1.13%. A blank run was made by percolating a pentane solution of fresh gas oil through Attapulugus clay and separating the pentane; the sulfur content of this gas oil was 1.36%. Thus the asphaltenes removed about 16% of the sulfur content of this particular gas oil (gas oils from catalytic cracking are very refractory insofar as sulfur removal by conventional methods is concerned).

Example V

A coke still gas oil with a total sulfur content of 1.66% (28.3° API and ASTM distillation range of 400° F. to 710° F. at 85% overhead) was desulfurized by contacting 15 grams of the gas oil with 5 grams of asphaltene at 210° F. The mixture was cooled to room temperature and 50 ml. of n-pentane added to precipitate asphaltenes. The precipitated asphaltenes were filtered off and the cycle oil-pentane solution percolated through Attapulugus clay in order to remove dissolved asphaltenes. The pentane was then removed by distillation. The sulfur content of the treated cycle oil was 1.34%, whereas the sulfur content of a cycle oil from a blank run was 1.70%. Thus the asphaltenes removed about 19% of the sulfur compounds in the thermal gas oil.

Example VI

The asphaltenes used in this example were obtained by n-hexane precipitation from DAP asphalts. This asphalt was obtained by propane treatment of a 20% reduced crude derived from Mid-Continent crude. These asphaltenes are considerably more soluble in naphthas than those obtained from the oxidized cracked residual tar. 50 ml. of coke still naphtha were contacted with 10 grams of DAP asphaltene. A substantial portion of the asphaltene dissolved in the naphtha. The insoluble asphaltene was removed from the coke still naphtha by filtration; and the dissolved asphaltene by percolation through Attapulugus clay. The sulfur content of the asphaltene treated coke still naphtha was 0.51%, whereas the coke still naphtha from a blank run had a sulfur content of 0.65%. Thus the asphaltene treatment resulted in about 22% desulfurization of the coke still naphtha.

Example VII

In this example the asphaltenes were derived

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from an oxidized West Texas asphalt. This asphalt had been obtained by distilling a West Texas crude to a 10%-20% residuum yield, and then treating this residuum by the conventional asphalt air-oxidation procedure until a softening point of 180° F. was attained. The asphaltenes were contacted with a light cat gas oil by a procedure similar to Example VI. About a 5% desulfurization was obtained.

I claim:

1. A process for reducing the sulfur content of a sulfur-containing petroleum naphtha, which process comprises contacting said naphtha in the liquid state at a temperature below about 110° F. with a solid asphaltene in a weight ratio of naphtha-to-asphaltene from about 1 to about 6, and separating solid asphaltene from the treated naphtha, wherein said asphaltene is obtained by precipitation from a member of the class consisting of reduced crude, tars and bitumens by treatment thereof with an excess of a light paraffinic precipitation agent containing from 5 to 6 carbon atoms.
2. The process of claim 1 wherein said naphtha is a coke still naphtha.
3. The process of claim 1 wherein said tar is an oxidized cracked tar.
4. The process of claim 3 wherein said agent is n-hexane.
5. A process for reducing the sulfur content of a sulfur-containing naphtha, which process comprises percolating said naphtha in the liquid state at a temperature below about 110° F. through a bed consisting essentially of a spacing material and solid asphaltene in a ratio of asphaltene-to-spacing material from about 1 to 3, wherein the weight ratio of naphtha-to-asphaltene is from about 1 to about 6, wherein said asphaltene is obtained by precipitation from a member of the class consisting of reduced crude, tars and bitumens by treatment thereof with an excess of a light paraffinic precipitation agent containing from 5 to 6 carbon atoms.
6. The process of claim 5 wherein the spacing material is fuller's earth and the asphaltene is derived from an oxidized cracked tar using n-hexane as the precipitation agent.
7. The process of claim 5 wherein the treated naphtha is percolated through a bed of fuller's earth to remove dissolved asphaltene materials.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,215,732	Snelling	Feb. 13, 1917
1,592,329	Black et al.	July 13, 1926
2,041,364	Miller	May 19, 1936