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HYDROCARBON DESULFURIZATION PROCESS WHEREIN THE SULFUR COMPOUNDS ARE ADSORBED BY METALLIC SILVER

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The present invention relates to the desulfurization of sulfur-containing hydrocarbon mixtures. More particularly, it relates to a method wherein a mixture of hydrocarbons is contacted with finely divided silver metal in a manner such that the silver removes sulfur compounds from the mixture through the phenomenon of chemisorption. The invention has particular application to the desulfurization of petroleum fractions that boil up to about 500° F. and especially to gasoline and petroleum fractions that boil within the gasoline boiling range.

The problem of desulfurization is one that has interested the petroleum industry almost since the inception of the industry itself. In recent years, however, the problem has become particularly acute; and petroleum refiners have greatly increased their efforts toward finding more suitable desulfurization processes. The presence of sulfur in the light petroleum distillates including naphthas, gasolines, diesel fuels, kerosene and the like constitutes a particularly serious problem to the refiners. The sulfur compounds in these fractions tend to impart undesirable odor, color and burning characteristics to the fractions; and in the case of gasoline, the sulfur compounds present additional problems in that (1) they greatly reduce the otherwise beneficial anti-knock effect that lead tetraethyl has upon the addition to gasoline, (2) they tend to cause the formation of undesirable deposits within gasoline-powered engines and especially within the combustion chambers of such engines. The presence of combustion chamber deposits in gasoline engines has recently become a very important consideration, since the deposits increase the octane requirements of the engines. In other words, a gasoline engine that is operated for a substantial period of time on a sulfur-containing gasoline generally experiences a very noticeable increase in its knocking tendency and therefore requires a gasoline of progressively increasing octane quality.

In an effort to combat the problems that sulfur compounds cause in gasoline and other petroleum products, refiners have resorted to a wide variety of desulfurization processes. Thus, refiners have employed such processes as hydrodesulfurization and treatment with sulfuric acid, caustic solution, sodium plumbite, etc. They have also attempted to contact sulfur-containing fractions with different metals under conditions adapted to promote a reaction between the metals and the sulfur to form metallic sulfides that can be readily separated from the fractions. The last-named process, however, has not met with any particular favor, since it is necessary to recover the metals from the sulfides in order to render the processes economically attractive. Since the recovery of metals generally entails high temperature roasting operations followed by hydrogen-treating operations, a satisfactory desulfurization process designed along these lines has not as yet been commercially feasible.

Having presented the general status of the desulfurization problem in the peroleum industry, attention is now directed toward the present invention and the objectives that are realized by the invention. Specifically, it is an

objective of the present invention to provide a new and different method for desulfurizing hydrocarbon mixtures and in particular petroleum fractions that boil below about 500° F. It is a further objective of the invention to provide a desulfurization process wherein a mixture of sulfur-containing hydrocarbons is contacted with finely divided metallic silver under conditions such that chemisorption occurs between the silver and the sulfur compounds that are present in the mixture. Furthermore, it is a particular object of the invention to provide a process wherein petroleum fractions that boil within the gasoline boiling range may be desulfurized to extremely low sulfur levels.

In accordance with the present invention, the aforementioned objectives may be realized by contacting a sulfur-containing hydrocarbon mixture with finely divided silver metal under conditions such that the sulfur compounds in the mixture are chemisorbed by the silver. At this point it is well to note that the term "chemisorption" and related terms as employed in this description are intended to denote a phenomenon or process wherein one substance appears to be chemically bound to a second substance without the actual occurrence of a chemical reaction and without the decomposition of either of the substances. In the present case, therefore, the term is intended to denote the phenomenon that occurs when silver combines with the sulfur compounds in a hydrocarbon mixture without the formation of silver sulfides and without decomposition of the original sulfur compounds.

In accordance with the present invention, a sulfur-containing hydrocarbon mixture is contacted with finely divided metallic silver at substantially ambient atmospheric temperatures. Under these conditions it has been observed that the sulfur compounds in the mixtures are chemisorbed by the silver and the sulfur content of the mixture greatly reduced. It has further been observed that the chemisorbed sulfur compounds may be readily stripped from the silver, thus making for a process that is substantially continuous in that the silver may be continually regenerated or refreshed and returned to the chemisorption step. It has been particularly observed that substantially all the sulfur compounds that are chemisorbed by the silver may be removed from the silver by contacting the silver with a stream of a conventional stripping gas or vapor such as nitrogen, steam, methane, hydrogen, water gas, etc. at a temperature within the range from about 200 to 500° F.

Hydrocarbon mixtures that may be desulfurized in accordance with the present invention include distillate hydrocarbons as well as residual-type hydrocarbons. Thus, the invention has application to the entire range of hydrocarbons that occur in petroleum crude oils. The invention, however, has particular application to petroleum fractions that boil below about 500° F. and especially to petroleum hydrocarbons that boil within the gasoline boiling range. The invention is especially attractive for treating of naphtha fractions that boil from about 100° F. to 400° F. and that contain relatively low amounts of sulfur ranging from about 100 to 1000 p. p. m. of sulfur. It will be noted, furthermore, that the invention has application to straight-run petroleum fractions as well as petroleum fractions that are derived at least in part from thermal or catalytic cracking operations.

While the invention has been indicated to be best suited for the processing of petroleum fractions that contain from 100 to 1000 p. p. m. of sulfur, it will be observed that it may also be applied to the processing of fractions that possess sulfur in amounts that are greater than the stated range. In this instance, however, it is desirable to employ the present process in combination with other desulfurization processes that have been conventionally employed to date toward desulfurizing petroleum fractions. Thus, it is particularly contemplated that a petro-

leum fraction containing in excess of 1000 p. p. m. of sulfur be first desulfurized in accordance with one of the conventional desulfurization techniques and that the partially desulfurized fractions then be further desulfurized in accordance with the present invention. It follows that the conventional treating process should be of a type adapted to reduce the sulfur content of the original fraction to a point within the range of 100 to 1000 p. p. m. Among the processes that may be utilized for this purpose are (1) hydrodesulfurization, (2) contacting with metals such as sodium, potassium, calcium, and the like, (3) treatment with sulfuric acid, (4) treatment with aluminum chloride, (5) extraction with aqueous boron fluoride solutions and other known desulfurization agents.

As mentioned hereinbefore, the desulfurization agent of the present invention is silver in a finely divided metallic form. Since the chemisorption of sulfur compounds by metallic silver is a phenomenon that occurs only on the metallic surface, it is important to have a high ratio of surface to weight of silver in order to achieve a satisfactory utilization of the metal. The high ratio of surface to weight is achieved by employing the silver in a finely divided form. For this purpose various forms of colloidal silver may be utilized; for example, colloidal silver produced by an electric arc between silver electrodes or by the reduction of silver salt solutions by reducing agents such as hydroxylamine in the presence of protective colloids. However, as hereinafter described, the fine state of subdivision of the silver is preferably achieved by depositing the silver on the surface of a high surface area carrier. In general, it is contemplated that the particle size or crystallite diameter of the silver particles shall be less than about one micron. Preferably, the crystallite size is less than about one-half micron.

To realize the objectives of the invention and to achieve intimate contacting between the silver and the fraction to be treated, therefore, it is contemplated that the silver (1) be intimately dispersed throughout the fraction or (2) be impregnated on a conventional, high surface area support of a type that is conventionally employed in the fabrication of most catalysts. It is further contemplated that the latter procedure is by far the more satisfactory procedure to employ. In other words, it is particularly desired that the silver treating agent be provided by impregnating a suitable support with the finely divided metal. Suitable supports include natural clays such as montmorillonite clay and bentonite clay; metal oxides such as alumina, magnesia, zirconia, titania, silica gel; commercial catalysts, such as silica-alumina, or silica-magnesia cracking catalysts; and activated chars such as cocoanut charcoal, carbon blacks, etc.

At this point, it will be noted that the various activated chars appear to possess a unique value for the purposes of the present invention in that these supports permit the ready recovery of the valuable silver metal after the contacting mass is completely exhausted to the extent that its activity for chemisorption can no longer be restored by the regeneration techniques hereinafter described. This may be accomplished by simply burning the carbon support and recovering the silver metal.

In general, any of the supports should preferably have a particle size within the range of about 0.1 to 10 mm. and especially about 0.2 to 2 mm. Furthermore, it is desired that the supports have a surface area greater than 50 square meters per gram, and particularly greater than 100 square meters per gram. Generally speaking, the higher the surface area of the support the greater the amount of silver metal that can be deposited on the support while still maintaining the silver in a satisfactory state of subdivision. In general, the amount of silver deposited upon the support should be less than about 1 milligram of silver metal per square meter of support area and is preferably less than 0.5 milligram of silver per square meter.

A support that is contemplated to be particularly and uniquely suited for the utilization of the present invention is a high surface area carbonaceous material produced by air oxidation at relatively low temperature of coke particles produced by the fluid coking process. Fluid coking is a recently developed process for thermally cracking residual petroleum oils or tars by contacting with a fluidized bed of hot coke particles. In this process the hot coke particles grow by accretion as additional coke is deposited as a result of the cracking reaction. One of the products of the fluid coking process is a particulate coke having an average particle size in the range of about 0.1 to 1.0 millimeter, usually about 0.2 to 0.5 millimeter. As produced in the fluid coking process, this "fluid" coke has a relatively low surface area, in the order of about 5 square meters per gram. However, the coke is converted into a high surface area material having a surface area in the range of 100 to 500 square meters per gram suitable as a carrier for silver desulfurizing agents by a suitable oxidation procedure. This may be accomplished by oxidation of the coke with air at a temperature in the range of about 600° to 1000° F. to a yield of oxidized coke in the range of 50% to 97%, preferably 80% to 95%. The preparation of this high surface area support by oxidation of "fluid" coke is more fully described in our copending application Serial Number 431,412.

A particularly attractive form of treating agent may be prepared by impregnating the aforementioned carbon with silver lactate and thereafter converting the silver lactate into metallic silver. This may be achieved by saturating the adsorbent with an aqueous silver lactate solution in an amount and concentration sufficient to provide the desired amount of silver on the adsorbent. The resulting wet adsorbent may then be dried as by heating in a muffle furnace at about 1000° F. in an inert atmosphere. The silver deposited within the adsorbent may then be reduced by contacting the adsorbent at about 500° F. with an amount of hydrogen gas sufficient to convert the silver deposit substantially entirely to metallic silver. Treating agents of this type may be readily made that contain up to about 15 wt. percent silver. In general, it is contemplated that the objectives of the invention may be best realized by employing an adsorbent that contains from about 5 to 12 wt. percent silver.

While the foregoing paragraph has been concerned primarily with the impregnation of a particular carbon base with silver, it will be appreciated that the same general procedure may be employed in connection with the other adsorbents that have been mentioned earlier in this description. Furthermore, it will be noted that these other adsorbents or high surface area supports may contain substantially the same amounts of silver as were advocated in connection with the carbon supports.

In contacting the present treating agents with a sulfur-containing hydrocarbon mixture, it has been stated that it is desired that the contacting operation be carried out at substantially ambient atmospheric temperatures. Thus, it is desired that contacting temperatures within the range from about 50 to 200° F. and particularly about 70 to 150° F. be employed. It has been observed that a temperature of about 75° F. has been particularly effective.

A sulfur-containing hydrocarbon mixture should be contacted with a metallic silver treating agent at the aforementioned temperatures for a period of time sufficient to cause the silver to chemisorb sulfur compounds from the mixture. In general, it is contemplated that the length of time necessary for this step is directly related to the temperature employed. And in this connection, it is desired that each portion of the mixture contact the metallic silver for a period of time not less than about 5 minutes, since contacting times less than this fail to provide complete desulfurization. Contact times in excess of about 3 hours are considered to be superfluous. Thus, contacting times within the range from about 5 minutes to 3 hours and particularly about 0.5 to 1 hour are preferred.

In arriving at the proper contact time to employ for any given hydrocarbon mixture, it is necessary to take into consideration the volume of the mixture, the volume of the treating agent, and the temperature. Thus, if only a portion of the mixture sees the silver at any one time, it is necessary that the mixture be passed through or contacted with the treating agent at a rate such that each portion of the mixture experiences adequate silver contact time. For example, when it is desired to desulfurize 10 volumes of a hydrocarbon mixture by contacting the same for 10 minutes with one volume of treating agent (e. g. metallic silver deposited on a support), it is necessary to pass the mixture through the treating agent at a rate of about 6 volumes of mixture per hour per volume of treating agent until the entire amount of mixture has been passed through the agent.

In carrying out the desulfurization operation, it is further necessary to provide an amount of silver sufficient to chemisorb all of the sulfur compounds that must be removed from the hydrocarbon mixture. It is contemplated that the amount of silver should be sufficient to provide at least 8 parts by weight of silver per part of sulfur in the feed and preferably at least 20 parts of silver per part of sulfur. It will be appreciated that the amount of silver necessary is a direct function of the amount of sulfur in the feed mixture and an indirect function of the contact time between the silver and the mixture. For the sulfur contents, contact times and operating temperatures hereinbefore described, however, it is contemplated that 8 to 35 parts of silver per part of sulfur by weight will suffice. For the sulfur range of 100–1000 p. p. m. in the feed this active chemisorbent component may be expressed as one part of silver per 30 to 1250 parts of feed.

It will be realized that the ability of the silver to chemisorb sulfur compounds from a mixture of hydrocarbon will diminish with time and that regeneration of the silver must eventually be accomplished. It is at this point of the process that the present invention possesses especial merit, since the treating agents may be readily and substantially freed of sulfur compounds by merely contacting them with a suitable stripping medium. Material that may be employed as the stripping medium includes gases such as hydrogen, nitrogen, water gas, methane, ethane, the chemically inert gases, etc. and vapors such as steam, or hydrocarbon vapors. It is apparent from this list of suitable materials that any gas or vapor that is non-reactive with metallic silver under conventional stripping conditions may be employed. The selection of a suitable stripping medium will accordingly be readily apparent to persons skilled in the art.

The stripping phase of the present process is more readily performed with treating agents that consist of metallic silver impregnated on a high surface area support; and treating agents of this types are therefore preferred over silver that is simply in finely divided metallic form such as colloidal silver. It is apparent that the silver in impregnated form is much easier to handle and process than would be the finely divided metal itself.

In stripping the sulfur compounds that are chemisorbed by silver impregnated upon a suitable support, it is necessary to utilize a stripping temperature of about 250 to 700° F., preferably from about 300 to 500° F. A stripping temperature of about 400° F. has been observed to be particularly effective.

The stripping medium should be passed through the sulfur-laden treating agent until the desired amount of sulfur compound has been stripped from the agent. At the temperatures mentioned earlier, it is contemplated that stripping times of about 0.5 to 2.0 hours will be necessary when employing from 100 to 1000 volumes of stripping gas per volume of treating agent per hour. It is apparent, of course, that the stripping time is related to the amount of sulfur on the treating agent, the feed rate of the stripping gas, the temperature of the stripping action, etc. The selection of the optimum conditions for any given situation will be readily apparent to those skilled in the art.

While the stripping technique just described has been observed to be remarkably satisfactory in removing substantially all of the sulfur compounds that may be chemisorbed by the present treating agents, it is contemplated that some sulfur compounds may not be completely removed therefrom by employing this technique. Thus, certain sulfur compounds such as hydrogen sulfide and elemental sulfur are considered to be much more strongly chemisorbed by metallic silver than are other sulfur compounds such as mercaptans, sulfides, disulfides, polysulfides, thiophenes, thiophenols, thionaphthenes, and the like. Inasmuch as the former compounds exist to at least a small extent in some petroleum fractions and other hydrocarbon mixtures, it is considered that additional regeneration techniques other than the aforedescribed stripping stemps may be occasionally required for complete regeneration of the sulfur treating agents. It will be understood, however, that these additional techniques merely supplement the stripping technique and would be used only occasionally.

Regeneration procedures that would be satisfactory for removing difficulty desorbable sulfur compounds from metallic silver includes those procedures wherein the compounds are vaporized and/or decomposed by the use of high temperatures and/or oxidation agents. In accordance with one procedure, a silver treating agent may be contacted with air at a temperature within the range of 800 to 1200° F. whereby the compounds are vaporized or decomposed. It will be appreciated that at least a portion of the silver under such conditions is converted to silver oxide. This feature requires that the silver therefore be treated with a reducing agent in order to convert the silver oxide back to metallic silver. Reduction of this type may be achieved by treating the silver with a reducing gas such as hydrogen, carbon monoxide, etc. at a temperature between 500 and 1000° F. It will be noted that this combination ignition and reduction regeneration procedure is roughly equivalent to the procedures that are conventionally employed for converting the oxides of metals such as copper, nickel and the like, corresponding metals. Thus, it is felt that a minutely detailed description of this phase of the overall procedure is not required in this presentation.

It will be appreciated that still other well known chemical reactions may be employed for ridding the silver treating agents of any strongly chemisorbed sulfur compounds. For example, the agents may be contacted at temperatures of about 50 to 200° F. with an oxidizing agent such as hydrogen peroxide, ozone, and the peracids such as perphosphoric acids, permolybdic acid, pertungstic acid, performic acid, etc. Hypochlorites such as sodium hypochlorite or hypochlorous acid may also be employed. These oxidizing agents are preferably employed in a dilute aqueous solution containing about 0.1 to 3% of available oxygen. The silver contacting agent is contacted with the aqueous oxidizing solution for a period of about 5 minutes to one hour, preferably at ambient temperature. After treatment with the oxidizing solution the silver contacting agent may be washed with water to remove the excess treating solution. Although the regenerated silver agent may be used without subsequent reduction, superficial oxidation of the silver that occurs during the oxidation treatment generally results in some decrease in capacity of the silver to chemisorb sulfur compounds. It is therefore preferred to reduce the regenerated silver agent prior to re-use. This may be accomplished by treating the silver contacting agent with an aqueous reducing solution such as hydroxylamine at ambient temperature or with hydrogen gas at about 500° F.

Still another procedure that may be employed to desorb very strongly chemisorbed sulfur compounds is one wherein a silver treating agent is treated with a weakly ionized

acid such as formic acid, oxalic acid, acetic acid, etc. Such a treatment is carried out at about 50 to 150° F. and is characterized by liberation of the chemisorbed sulfur containing molecule usually by replacement with the acid anion. This treatment is preferably followed by a hydrogen reduction procedure in which a stream of hydrogen is contacted with the treating agent at a temperature of about 500 to 1000° F.

The present invention may be even better understood by reference to a specific example involving a petroleum naphtha fraction boiling within the range from about 175 to 350° F., containing 0.06 wt. percent sulfur and being derived from the distillation of mixed coastal crudes. The naphtha was passed at room temperature of about 75° F. in the liquid phase through a chemisorbent consisting of 10 wt. percent metallic silver on activated alumina. The chemisorbent itself was prepared by impregnating activated alumina having a surface area of about 350 square meters per gram with aqueous silver nitrate solution, thereafter drying the material in an oven at about 220° F. and then decomposing the nitrate in a muffle furnace at 1000° F. The calcined material was reduced at about 500° F. by contacting it with hydrogen gas. The alumina had a particle size of 20 to 80 mesh.

The naphtha was passed through a bed of the alumina-silver chemisorbent at a rate of about 1 volume of naphtha per hour per volume of chemisorbent until a total of about 15 volumes of naphtha per volume of chemisorbent had been so processed. The naphtha product was sampled periodically and each sample was analyzed for its sulfur content. The results of these analyses are presented in the following table:

Desulfurization by chemisorption

[10 wt. percent silver on act. Al_2O_3.]

Time of Sample	Wt. percent Sulfur in Product
After passage of 1 vol. naphtha	0.0005
After passage of 6 vols. naphtha	0.002
After passage of 10 vols. naphtha	0.002
After passage of 13 vols. naphtha	0.008
After passage of 15 vols naphtha	0.03

It is apparent from the foregoing table that the silver-alumina treating agent was very effective in markedly reducing the sulfur content of the naphtha feed. Moreover, it is apparent that about 0.1 part by weight of sulfur was chemisorbed for each part by weight of silver contained in the contacting agent.

The partially spent chemisorbent was then removed and heated in an oven in an atmosphere of air at about 220° F. for about two hours. This heating step served to remove adhering naphtha and strip off a portion of the chemisorbed sulfur compounds.

The material from the oven, freed of most of the physically adsorbed naphtha was then heated in a muffle furnace at about 1000° F. for a period of about two hours whereby all of the chemisorbed sulfur compounds were stripped or otherwise removed from the silver. Since the muffle furnace treatment caused a portion of the silver to be converted to silver oxide, the treating agent was subsequently reduced with hydrogen at about 500° F. for a period of about two hours. The material so treated proved to be completely reactivated and demonstrated desulfurizing ability equivalent to the fresh material in a repeat run employing the aforementioned naphtha fraction. The results obtained with the regenerated treating agent were substantially identical with the results that were obtained with the fresh treating agent.

In another experiment the silver-alumina chemisorbent was activated by treating with hydrogen for two hours at 500° F. The activated material was then contacted at about 75° F. with a naphtha of 0.06% sulfur content in increments of 5, 10 and 5 (total 20) volumes of naphtha per volume of chemisorbent. This treatment was sufficient to inactivate the desulfurization agent. This spent material was thereupon stripped with a hydrogen-steam mixture (H_2/steam ratio 1.17) for a 2-hour period at 400° F. at a total gas rate of 890 v./v./hr. (volumes of gas per volume of adsorbent per combined hour). The adsorbed sulfur compounds were removed and were collected together with condensed water from the operation. Following the stripping operation, the chemisorbent was contacted with additional sulfur containing naphtha as before and was found to have substantially the same desulfurization activity as the fresh contacting agent.

It will be realized that the present invention is not to be limited in its scope to the particular specific example above. Thus, the present invention may utilize metallic silver deposited upon suitable supports that are ground for use in a fixed bed, moving bed or fluidized bed type of operation. When employing a fixed bed of the treating agent, it is generally desirable to retain the treating agent within a single treating zone and to pass the sulfur-containing feed as well as stripping medium and other regeneration gases or fluids through the single zone. On the other hand, when employing a moving bed or fluidized bed of the treating agent, it is more desirable to continuously or intermittently transfer the bed of treating agent from the desulfurization zone to a separate stripping zone. Furthermore, when other regeneration fluids are employed, it may be desirable to transmit the stripped treating agent from the stripping zone to still another zone, specifically a regeneration zone. At this point it will be observed that it is contemplated that the objectives of the invention may be best obtained by utilization of a fixed bed type of operation.

What is claimed is:

1. A method of desulfurizing sulfur containing naphthas, said naphthas containing no more than about 1,000 p. p. m. of sulfur which comprises contacting the naphthas at a temperature of about 50° F. to 100° F. with finely divided supported metallic silver, said supported silver being the sole re-agent, whereby sulfur-containing compounds in the naphthas form chemical bonds with the silver without substantial decomposition of the compounds, and thereafter separating the contacted naphthas from the supported silver and the chemisorbed sulfur-containing compounds.

2. A method of desulfurizing naphthas containing about 100–1000 p. p. m. of sulfur which comprises contacting said naphthas at substantially ambient atmospheric temperatures with finely divided supported metallic silver, said supported silver being the sole re-agent, whereby sulfur-containing compounds in the naphtha are chemisorbed without substantial decomposition by the silver, the total amount of silver being sufficient to provide at least about 8 parts by weight of silver per part by weight of sulfur, the contact time between each portion of hydrocarbon in the mixture and the silver being at least about 5 minutes, and separating the contacted mixture from the silver.

3. A method of desulfurizing naphthas that boil up to about 400° F. and that contains from about 100 to 1000 p. p. m. of sulfur which comprises contacting the naphthas at about 75° F. with an amount of metallic silver sufficient to provide about 20 parts by weight of silver per part by weight of sulfur, the silver being very finely divided and impregnated upon a high surface area support, said supported silver being the sole re-agent, maintaining a contact time of about 0.5 to 1 hour between the silver and the hydrocarbons in the mixture whereby the silver chemisorbs sulfur-containing compounds from the mixture, and separating the contacted mixture from the silver.

4. A method of desulfurizing a sulfur-containing naphtha fraction containing about 0.06 wt. percent sulfur which comprises passing the naphtha through a bed of chemisorbent at a temperature of 75° F. and a rate of about

1 volume of naphtha per volume of chemisorbent per hour, the chemisorbent consisting of activated alumina impregnated with about 10 wt. percent metallic silver, said supported silver being the sole re-agent.

5. The process of claim 1 wherein said silver is reactivated by a stripping gas.

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