

[54] **GUARD BED SYSTEM FOR REMOVING CONTAMINANT FROM SYNTHETIC OIL**

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[51] **Int. Cl.**..... **C10g 13/06**

[58] **Field of Search**..... 208/251 R, 253, 251 H, 208/88, 89, 295

[56] **References Cited**

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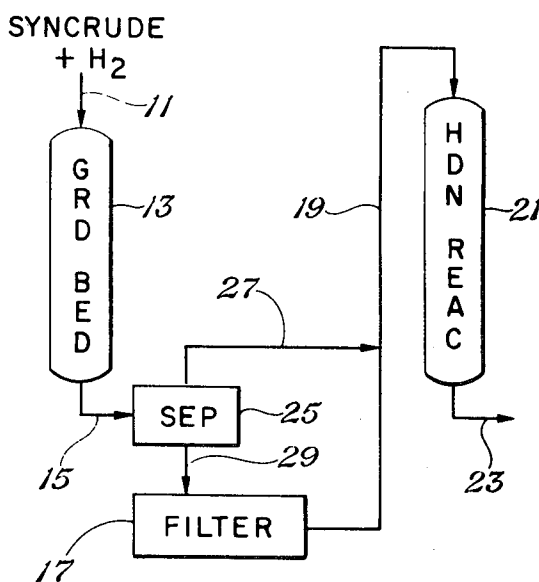
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[57] **ABSTRACT**

A method for removing a contaminant comprising at least one of arsenic and selenium from a synthetic crude oil or fraction thereof characterized by a multi-step process as follows. First, a guard bed is prepared from a plurality of particles of material that is either iron, cobalt, nickel, oxides or sulfides of these metals, or a mixture thereof. Next, the synthetic crude oil is admixed with hydrogen and flowed past the particles of material at a temperature and pressure great enough and with a residence time sufficient to allow the contaminant to be removed from the synthetic crude and be deposited on at least the surface layer of the particles of material. As the surface layer of the particles becomes substantially saturated with the contaminant, they are removed from the surface of the particles as small fines, entrained in the fluid stream and flowed from the guard bed. The small fines having the contaminant thereon are separated from the synthetic crude from which the contaminant has been removed. Thereafter, the synthetic crude oil is treated as desired. Also disclosed are specific methods of effecting the removal and separation of the contaminant and the fines; including specific and preferred process details.

9 Claims, 4 Drawing Figures



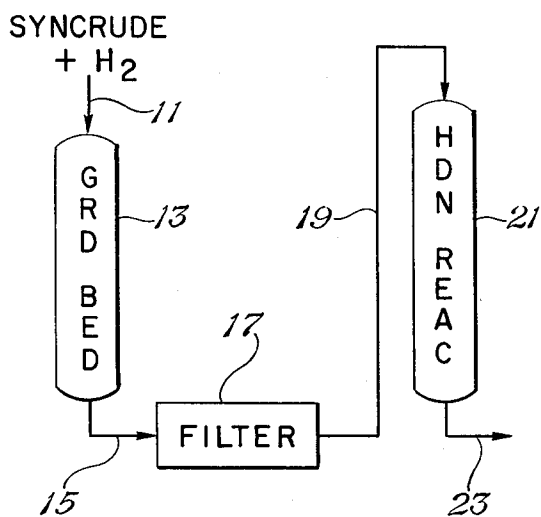


Fig. 1

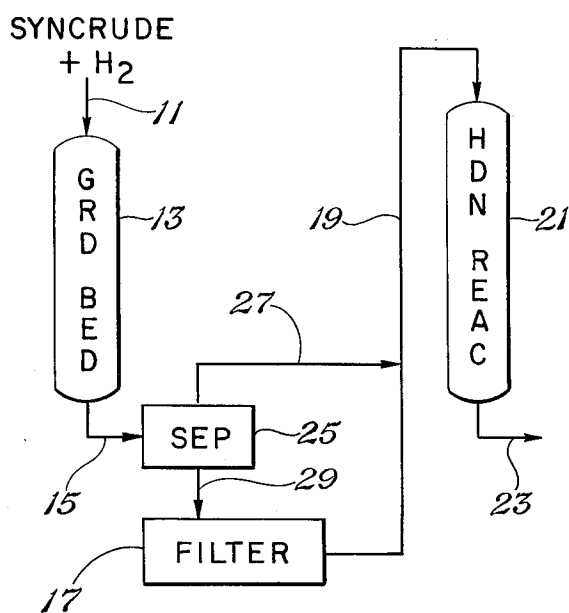


Fig. 2

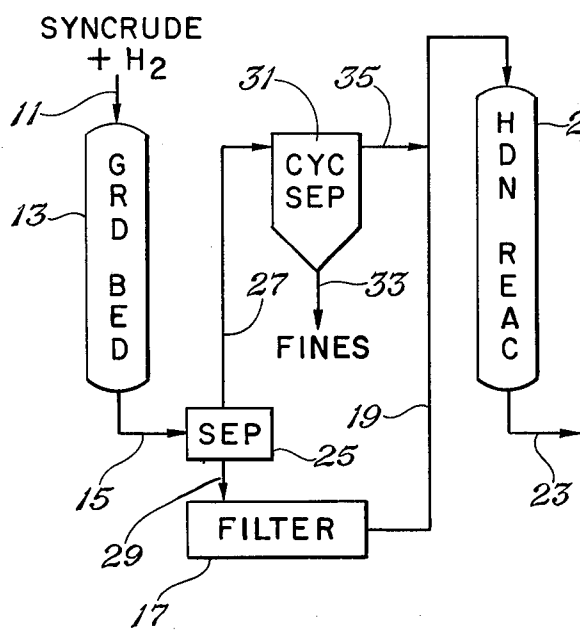


Fig. 3

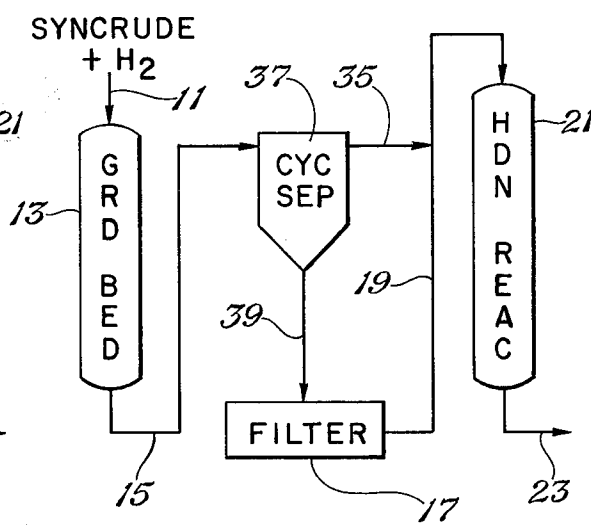


Fig. 4

GUARD BED SYSTEM FOR REMOVING CONTAMINANT FROM SYNTHETIC OIL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method of removing catalyst-poisoning impurities, or contaminants; such as, arsenic or selenium; from hydrocarbonaceous fluids; such as, synthetic crude oil and synthetic oil fractions.

2. Description of the Prior Art

There has been a resurgence of interest in sources of energy that were formerly noncompetitive. These sources of energy include the shale oil, or kerogen, such as derived from oil shale; the fluids, such as methanol or coal gas, that are synthesized from coal; the bitumen from the tar sands and the like. Many of these hydrocarbonaceous fluids contain contaminants, or impurities, that would poison expensive catalysts, such as platinum catalysts and the like, that are used in hydrogenation and other processes to which these hydrocarbonaceous fluids must be subjected before they can be satisfactorily used as sources of energy. The best prior art of which I am aware is disclosed in a co-pending application Ser. No. 314,015, filed Dec. 11, 1972, now abandoned in favor of Ser. No. 421,139, filed Dec. 3, 1973, with co-inventor Donald K. Wunderlich and entitled "Synthetic Oil Treatment." That descriptive matter will be briefly summarized hereinafter for the reader's convenience. The prior art has included a method for removing arsenic from hydrocarbon charge stocks, such as described in U.S. Pat. No. 2,778,779. Such methods have included using the iron, nickel and cobalt oxides to remove arsenic from streams of naturally occurring crude, such as naphtha or straight run gasoline. By employing the oxides at low temperature, such as from room temperature to about 200°F, by disregarding the atmosphere under which the reaction takes place, and by using substantial amounts of water, the oxide acts as an oxidizing agent and oxidizes the arsenic to a water soluble arsenic oxide. In this way the arsenic oxide is dissolved in the water and removed from the naturally occurring crude oil or oil fraction.

Also, arsenic has been removed from similar naturally occurring crude oils by contacting them with a metallic salt of a strong acid at low temperature, such as room temperature, without regard to the atmosphere under which the contacting takes place. In this particular process, it was taught that oxides do not work for removing arsenic and this process is disclosed in U.S. Pat. No. 2,781,297.

Processes that work for removing other contaminants, or catalyst-poisoning materials, such as organometallic compounds like iron porphyrins, are frequently inoperable for removing impurities like arsenic. For example, the catalytic hydrogenation of hydrocarbons to effect the precipitation of an insoluble iron salt of the iron porphyrin within a hydrogenating catalyst, as described in U.S. Pat. No. 3,496,099, cannot be employed satisfactorily in removing arsenic from synthetic crudes or the like.

The invention described in Ser. No. 314,015 improved significantly on the prior art, but had one drawback that prevented its being totally satisfactory. The contaminant tended to be concentrated in a surface layer from about 5 to about 60 microns thick, so the center portion of the larger pellets and the like were not useful and available for removing the contaminant.

In fact, none of the prior art processes have been completely satisfactory in removing catalyst-poisoning impurities, such as arsenic, from synthetic oil fractions.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a method of removing contaminants from a feed stream of synthetic crude or the like that does not require the use of aqueous, or hydrophilic, solutions, and alleviates the difficulties of the prior art.

More specifically, it is an object of this invention to provide a method of removing a contaminant from a feed stream that accomplishes the foregoing object and provides a stable guard bed that maintains a continuous high level of activity at all times, yet can be operated with economically feasible equipment, such as pressure vessels, separators and filters.

These and other objects will become apparent from the descriptive matter hereinafter.

The foregoing objects are achieved in accordance with this invention by the following multi-step process. First, a guard bed is prepared from a plurality of particles of material that is either iron, cobalt, nickel, oxides or sulfides of these metals, or a mixture thereof. Next, the hydrocarbonaceous fluid is admixed with hydrogen and flowed past the particles of material at a temperature and pressure great enough and with a residence time sufficient to allow the contaminant to be removed from the synthetic crude oil and be deposited on at least the surface layer of the particles of material. As the surface layer of the particles becomes substantially saturated with the contaminant, they are removed from the surface of the particles as small fines, entrained in the fluid stream and flowed from the guard bed. The small fines having the contaminant thereon are separated from the hydrocarbonaceous fluid from which the contaminant has been removed. Thereafter, the hydrocarbonaceous fluid is treated as desired.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow diagram of one embodiment of this invention employing filtering.

FIG. 2 is a flow diagram of the embodiment of FIG. 1 in which a gas stream is separated before the filtering.

FIG. 3 is a flow diagram of the embodiment of FIG. 2 in which fines are separated from the gas stream by a cyclone separator.

FIG. 4 is a flow diagram of the embodiment of FIG. 2 in which a cyclone separator is employed to separate the gas stream before filtering.

DESCRIPTION OF PREFERRED EMBODIMENTS

To facilitate understanding, the treatment of a stream of a synthetic crude, commonly referred to as syn-crude, with the particles of the material for removing the contaminant will be described hereinafter.

In carrying out the invention as outlined above, the guard bed, abbreviated GRD BED in the figures, is formed by depositing pellets, or other particles, of the material into a pressure vessel adapted to withstand the pressure and temperature to effect the removal of the contaminant of arsenic or selenium, whether in elemental or combined form. The pellets, or particles of material, may have any shape. The particles of material preferably have a size large enough to allow attrition of a surface layer of fines repeatedly in order to expose new and active material for removal of the contami-

nant. Ordinarily, the particles of material will comprise pellets from $\frac{1}{8}$ to $\frac{1}{4}$ inch or more in diameter and $\frac{1}{4}$ inch or more in length such as are conventionally extruded for various catalysts such as iron oxide shift catalysts. The particles of material preferably have a surface area of at least one square meter per gram, still more preferably, having a surface area of at least 50 square meters per gram. The particles of material may comprise active ingredient alone; such as, the iron oxide or iron sulfide; or may comprise the active ingredient in combination with a conventional support (carrier). Such conventional support may comprise silica, alumina, magnesia, zirconia, thoria, zinc oxide, chromium oxide, silicon carbide, naturally occurring carriers like clay, Kieselguhr, Fuller's earth, pumice, bauxite and the like, or any combination of two or more such carriers, whether naturally occurring or prepared.

After the syncrude has been mixed with hydrogen, the resulting admixture is flowed into contact with the guard bed of the particles of material with sufficient heat, pressure and residence time to effect removal of the contaminant from the syncrude and deposition of the contaminant into the matrix of at least the surface layer of the particles of material. This may be thought of as a reaction, or adsorption of the contaminant onto the particles of the material. In any event, the contacting of admixture and the particles of material is at a temperature of at least about 300°F. and preferably at least about 650°F. Still more preferably, the contacting is at a temperature in the range of from about 650° to about 850°F. The temperature may be effected by heating the constituents individually before admixing them, supplying heat to the admixture directly, or supplying heat to the guard bed. Ordinarily, it is advantageous to heat the fluid streams. The guard bed pressure vessel is, of course, suitably insulated to prevent infeasible heat losses. The guard bed is maintained at a pressure of at least about 500 pounds per square inch gauge (psig), preferably, at least about 1,500 psig. Depending upon the particular circumstances, which can vary widely, the residence times vary widely, but generally will be at least about ten seconds to afford the syncrude to contact the guard bed particles of material. This may be effected by a single large guard bed or a plurality of serially and/or parallel connected smaller and less expensive guard beds. Thus, the delineated heat, pressure and residence time allows sufficient time for the syncrude to intimately contact the particles of material and to have the contaminant removed from the syncrude. Specifically, the contaminant, such as arsenic, is dispersed in a surface layer of up to about 60 microns or more of the matrix of the material in a manner analogous to adsorption phenomena, as indicated hereinbefore, such that the contaminant is removed in non-water soluble form.

The invention may be understood by referring to the flow diagram of FIG. 1. Therein, the syncrude plus hydrogen comes in through incoming conduit 11 into the guard bed 13. In the guard bed, the contaminant is removed from the syncrude and disposed in at least the surface layer of the matrix of the particles of the material by the intimate contact at the delineated temperature and pressure.

As the surface layer of material becomes saturated with the contaminant; for example, at a concentration in the range of 15-20 percent by weight of active material; the surface layer begins to flake off in small fines

to expose new active material. The reason for this automatic flaking off of the surface layers to afford a pseudo automatic regulation of the activity in the system, is not exactly understood. The following theory is given by way of explanation, although this invention is not to be limited to the consequences of any theory, since it is operable whether or not the theory is accurate. It is theorized that the arsenic is large enough that when it is substituted into the matrix of the material for the sulfur or oxygen, the matrix is disrupted. Once the disruption becomes severe enough, the macroscopic particles, or fines, flake off. The fines are entrained in the fluid stream and carried out the effluent conduit 15. Initially, of course, there will be no flaking off of the fines as long as there is sufficient activity in the system. Once the activity begins to be reduced, or diminished, however, the flaking will begin to expose new and more active material, and afford an automatic regulation of the activity.

The fines are carried with the liquid stream into the filter 17 where the fines are removed from the fluid stream by filtration. The filter 17 may comprise any of the conventional type filters that have been employed in this type separation process. For example, high pressure, high temperature filter cartridges that are disposable may be employed. These high temperature, high pressure cartridges; including both container and replacement cartridge, per se; are available from a number of major filter suppliers or manufacturers.

The fines that are collected on the filter may then be processed as appropriate either to remove the contaminant, such as arsenic, for commercial use or to regenerate the fines for reuse, or simply to render the fines inert so that they may be discarded as any other inert material. In my copending patent application Ser. No. 435,637 entitled SLURRY SYSTEM FOR REMOVAL OF CONTAMINANT FROM SYNTHETIC OIL, filed Jan. 23, 1974, I described a system for employing small particles similar to the small particles that would be effected by the regenerated fines in this invention. That method was characterized by injection of the small particles into an incoming feed stream of syncrude or the like, removal of the contaminant and separation of the small particles and contaminant from the contaminant-free syncrude; and the descriptive matter of that patent application is embodied herein by reference for details that are necessary to a full understanding of that use of the regenerated fines. A co-worker, Mr. Ralph Styring, has invented and filed a patent application on a method of processing the solid particles, such as the fines, for removing the contaminant. The patent application is entitled METHOD OF REMOVING CONTAMINANT FROM SPENT CONTAMINANT-REMOVING MATERIAL, filed Jan. 23, 1974, Ser. No. 435,760, and assigned to the assignee of this application. That method is applicable for treating the filter cake (from filter 17, FIG. 1) comprising the fines of the material that contain the contaminant, such as arsenic, in accordance with this invention; and the descriptive matter of that application is incorporated herein by reference for the details of that method.

Any amount of the particles of material can be employed in the guard bed. A given volume of fluid, or predetermined volume of fluid based on contaminant concentration therein and bed capacity, can be flowed through the guard bed before switching if desired. The predetermined volume can be determined theoretically

or empirically. On the other hand, the effluent stream from the guard bed can be monitored for the contaminant and if detected in a small concentration near zero, the particular guard bed can be "switched out" and the admixture of hydrogen and syncrude routed through another guard bed. The particles of material in the spent guard bed are thereafter changed out and replaced by new and active material.

Referring again to FIG. 1, the effluent stream of the syncrude without the contaminant therein and the hydrogen are then transported via conduit 19 to the hydrogenation reactor (HDN REAC) 21. In the hydrogenation reactor 21, hydrogenation conditions are employed in accordance with conventional practice such that the hydrogenated stream will effluent via conduit 23. This conventional hydrogenation need not be described in detail herein, since a plurality of references disclose the details and their disclosure is embodied herein by reference.

A flow diagram of another embodiment of the invention is illustrated in FIG. 2. Therein, a gaseous stream is separated from the admixture of the syncrude, hydrogen and fines saturated with the contaminant before the fines are filtered from the slurry left after the gas stream has been separated. Specifically, the incoming stream of syncrude and hydrogen passes through conduit 11 and into contact with the guard bed 13 containing the particles of material at the requisite temperature and pressure for removing the contaminant from the syncrude, similarly as described with respect to FIG. 1. The admixture of hydrogen and syncrude without the contaminant pass on through. Ultimately, the admixture will entrain the fines that are substantially saturated with contaminant to form a dilute slurry. Thereafter, the dilute slurry will pass through conduit 15 to a separator 25. The separator 25 comprises a conventional gas-liquid separator with conventional liquid level controls. The gas passes overhead through conduit 27 to join the effluent stream from the filter 17 that is being flowed through conduit 19 to the hydrogenation reactor 21, similarly as described with respect to FIG. 1. After the gas stream is separated in the separator 25, there remains a slurry comprising the fines of the particles of material containing the contaminant and the liquid portion of the syncrude. The gaseous portion of the syncrude comprises hydrogen and any gaseous hydrocarbons formed, ordinarily a minor amount in the absence of a hydrogenation catalyst. The slurry of liquid syncrude and the fines pass through conduit 29 to the filter 17. The filter 17 in FIG. 2 effects a more nearly uniform filtration of the fines from the liquid phase, since there is less turbulence effected by an intermixed gas phase. The filter 17 may comprise any conventional filter, such as the high temperature, high pressure cartridge filter, or filter bank described hereinbefore with respect to FIG. 1. The liquid syncrude without the contaminant and with the fines filtered therefrom, passes out conduit 19, as indicated immediately hereinbefore.

The gas and liquid streams are recombined upstream of the hydrogenation reactor 21. In the hydrogenation reactor 21, the hydrogenation reaction is carried out, as described with respect to FIG. 1 and as is conventional.

Still another embodiment of the invention is illustrated in the flow diagram of FIG. 3. Therein, the incoming syncrude and hydrogen pass through the guard

bed where the contaminant is removed from the syncrude and dispersed in the particles of guard bed. As described hereinbefore, the surface layers that become substantially saturated with contaminant ultimately flake off as the fines. The fines are entrained in the syncrude and hydrogen and pass with them through conduit 15 to the separator 25. When small separators are employed as the separator 25, the gaseous component that is separated may contain fines that are entrained therewithin, particularly at relatively higher velocities. Consequently, the gas stream effluents through the conduit 27 to a cyclone separator (CYC SEP) 31. The cyclone separator 31 may comprise any of the conventional pressurized cyclone separators for separating small particles such as dust particles or the like from gaseous fluid streams at an elevated pressure. The fines are thrown toward the wall by centrifugal force of the cyclonic effect and fall downwardly into the funnel-shaped portion and outwardly through conduit 33. The fines flowing out conduit 33 may be so small as to create dusting problems or the like and may be uneconomically feasible to be regenerated for reuse. If such is the case, the arsenic will be removed and these fines disposed of as a conventional inert material. On the other hand, the fines can be agglomerated in conventional sols for regenerating the particles of material originally employed. The fines from conduit 33 may or may not be combined with the filter cake from the filter 17 before the arsenic is removed from the collected fines, both in the filter cake and from the conduit 33.

The slurry left after the gas stream is separated passes out the bottom of the separator 25 through conduit 29 to filter 17. The fines are separated as filter cake by the filter 17, similarly as described with respect to FIG. 2. The liquid syncrude, without the contaminant, passing through conduit 19 upstream of the hydrogenation reactor 21 is recombined with the gas stream passing from the cyclone separator 31 through conduit 35. As described hereinbefore, the hydrogenation reaction is carried out in the hydrogenation reactor 21 in accordance with conventional practice.

A flow diagram of still another embodiment of this invention is illustrated in FIG. 4. The incoming feed stream of syncrude and hydrogen passes through conduit 11 and into contact with the particles of material in the guard bed 13. The contaminant is transferred from the syncrude onto the surface of the particles of material in the guard bed 13. Ultimately, the surface layers of the particles of material becomes substantially saturated with the contaminant and begin to flake off and be entrained with the syncrude and hydrogen. The admixture of the syncrude, hydrogen and fines flow through conduit 15 to the cyclone separator 37.

The cyclone separator 37 is somewhat larger than the cyclone separator 31, FIG. 3. In the cyclone separator 37, both the liquid and the fines are thrown toward the walls by the centrifugal force developed by the cyclonic motion of the fluids. The slurry of liquid and fines fall into the funnel-shaped portion and out through conduit 39 to the filter 17. The gas stream passes outwardly through the conduit 35 to be combined with the liquid syncrude in conduit 19.

The slurry from conduit 39 passes into the filter 17 and the fines are removed from the liquid by the filters as described hereinbefore with respect to the other embodiments. The liquid syncrude without the contaminant passes outwardly through the conduit 19. The gas-

eous and liquid streams comprising the hydrogen, any gaseous hydrocarbons, and the liquid syncrude are recombined upstream of the hydrogenation reactor 21.

The usual hydrogenation reaction is carried out in accordance with conventional practice and as described hereinbefore in the hydrogenation reactor 21.

The fines collected by the filters 17 in the respective embodiments are all treated as described hereinbefore with respect to FIG. 1.

Cyclone separators are conventionally available for separation of fines, such as dust particles from gas streams, as well as separating both liquid and solid particles, such as the slurry of the liquid syncrude and the fines, from the gas stream. Accordingly, there is no need to embellish the already lengthy descriptive matter herein by the inclusion of such well known and conventional apparatus.

While cartridge type filters, or filter banks, have been described hereinbefore with respect to the filter 17, any other suitable filters or method of filtration that will withstand the high temperature and pressure can be employed. For example, rotary self cleaning filters may be employed, as well as other metallic or high temperature filters. If desired, the high temperature bag filters can be employed to facilitate removal of the filter cake.

While the oxides and sulfides of iron have been described specifically hereinbefore, the particles of material that are useful in this invention as active materials may comprise nickelic, ferric, cobaltic, ferrous, nickelous, and cobaltous forms. For example, ferric oxide, both Fe_2O_3 and Fe_3O_4 , nickelic oxide Ni_2O_3 and Ni_3O_4 and cobaltic oxide Co_2O_3 and Co_3O_4 can be employed. Similar reasoning is applicable to the comparable sulfides of the metals and to the ferrous, cobaltous and nickelous forms of the oxides and sulfides.

EXAMPLE

A fixed bed containing Fe_2O_3 particles in the form of right cylinders $\frac{1}{4}$ inch in diameter and $\frac{1}{4}$ inch in length is exposed to a molecular hydrogen-shale oil (containing about 80 ppm arsenic) stream prepared by mixing about 4,000 standard cubic feet of hydrogen per barrel (42 U.S. gallons) of shale oil. Said stream is passed through said bed at a rate of about 5 weight hourly space velocity and at a temperature of about 700°F. and a hydrogen partial pressure of about 1,500 psig.

The thus treated stream is recovered from said fixed bed and passed through a 7 micron SWAGELOK stainless steel filter to remove solid fines which are saturated with arsenic thereby leaving a shale oil stream containing less than 10 ppm arsenic. This shale oil stream is now in a condition to be passed through a conventional hydrogenation system.

From the foregoing, it can be seen that this invention effects the objects set out hereinbefore and alleviates the difficulties of the prior art processes.

Having thus described the invention, it will be understood that such description has been given by way of illustration and example and not by way of limitation, reference for the latter purpose being had to the appended claims.

What is claimed is:

1. A method of removing a contaminant comprising one of arsenic and selenium from a synthetic hydrocarbonaceous fluid obtained from normally solid coal, oil shale or tar sand, comprising the steps of:

- a. preparing a guard bed consisting essentially of a plurality of particles of a material selected from the group consisting of iron, cobalt, nickel, at least one oxide of said metals, at least one sulfide of said metals and a combination thereof; said particles being of a size sufficiently large to allow attrition of a plurality of surface layers up to at least 60 microns in thickness for exposing new, more active material;
 - b. admixing said hydrocarbonaceous fluid with hydrogen to form an admixture of fluid streams;
 - c. removing said contaminant from said synthetic hydrocarbonaceous fluid by flowing said admixture past said particles in said guard bed at a temperature and pressure and with a residence time sufficient to effect removal of said contaminant from said synthetic hydrocarbonaceous fluid and depositing said contaminant on the surfaces of said particles of material; said pressure being at least 500 pounds per square inch gauge (psig), and said temperature being at least 300°F.;
 - d. substantially saturating the surface of said particles with said contaminant to cause flaking of small fines which are substantially saturated with contaminant from the surface of said particles to expose new and more active surface for removing said contaminant;
 - e. entraining said substantially saturated small fines in said admixture of fluid streams and flowing both from said guard bed; and
 - f. separating said substantially saturated small fines containing said contaminant from said admixture of said fluid streams and said fines to leave said hydrocarbonaceous fluid substantially free of said contaminant.
2. The method of claim 1 wherein said temperature is in the range of from about 650° to about 850°F. and said pressure is at least about 1,500 psig.
3. The method of claim 1 wherein said hydrocarbonaceous fluid substantially freed of contaminant is hydrotreated.
4. The method of claim 1 wherein said fines are removed from the combined stream of gas, liquid and fines by filtration.
5. The method of claim 1 wherein:
- a. a gas stream comprising hydrogen and gaseous hydrocarbonaceous fluid is separated to leave a slurry of hydrocarbonaceous liquid and said fines; and
 - b. said fines are thereafter separated from said slurry to leave an effluent liquid stream comprising said hydrocarbonaceous liquid without said contaminant.
6. The method of claim 5 wherein said gas and liquid streams are recombined after said fines have been removed; and before being hydrotreated.
7. The method of claim 6 wherein said gas is separated by a gas-liquid separator and said fines are separated from the slurry by filtration.
8. The method of claim 7 wherein said gas includes entrained small fines and said entrained small fines are separated from said gas stream by a cyclone separator before said gas stream is recombined with said hydrocarbonaceous liquid.
9. The method of claim 6 wherein a slurry of hydrocarbonaceous liquid and fines is separated from a combined stream by a cyclone separator to leave gas, and said fines are thereafter separated from said slurry by filtration; and said gas and liquid streams are recombined and hydrotreated.

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