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CRUDE OIL HYDROREFINING PROCESS

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The present invention relates to a method for preparing a novel catalyst particularly adaptable for utilization in the hydrorefining of petroleum crude oils, heavy vacuum gas oils, heavy cycle stocks, crude oil residuum, topped crude oils, etc. More specifically, the present invention is directed toward a process for hydrorefining petroleum crude oil and other heavy hydrocarbon charge stocks to effect the removal of nitrogen and sulfur therefrom, and affords unexpected advantages in effecting the destructive removal of organo-metallic contaminants and/or the conversion of pentane-insoluble hydrocarbonaceous material.

Petroleum crude oil, and the heavier hydrocarbon fractions and/or distillates obtained therefrom, particularly heavy vacuum gas oils and topped crudes, generally contain nitrogenous and sulfurous compounds in large quantities. In addition, petroleum crude oils contain detrimentally excessive quantities of organo-metallic contaminants which exert deleterious effects upon the catalyst utilized in various processes to which the crude oil, topped crude oil, or heavy hydrocarbon fraction thereof may be ultimately subjected. The more common of such metallic contaminants are nickel and vanadium, often existing in concentrations in excess of about 50 p.p.m., although other metals including iron, copper, etc., may be present. These metals may exist within the petroleum crude oil in a variety of forms: they may exist as metal oxides or as sulfides, introduced into the crude oil as a form of metallic scale; they may be present in the form of soluble salts of such metals; usually, however, they are present in the form of organo-metallic compounds such as metal porphyrins and various derivatives thereof. Although metallic contaminants, existing as oxide or sulfide scale, may be removed, at least in part, by a relatively simple filtering technique, and the water-soluble salts are at least in part removable by washing and a subsequent dehydration procedure, a much more severe treatment is required to effect the destructive removal of the organo-metallic compounds, particularly to the degree which is necessary to produce a crude oil or heavy hydrocarbon fraction suitable for further processing.

In addition to organo-metallic contaminants, including metal porphyrins, crude oils contain greater quantities of sulfurous and nitrogenous compounds than are generally found in lighter hydrocarbon fractions such as gasoline, kerosene, light gas oil, etc. For example, a Wyoming sour crude having a gravity of 23.2, ° API at 60° F., contains about 2.8% by weight of sulfur and approximately 2700 p.p.m. of total nitrogen, calculated as the elements thereof. Upon being subjected to a catalytic hydrorefining process, the nitrogenous and sulfurous compounds are converted into hydrocarbons, ammonia and hydrogen sulfide. However, the reduction in the concentration of the organo-metallic contaminants is not easily achieved, and to the extent that the same no longer exert a detrimental effect with respect to further processing of the crude oil. Notwithstanding that the total concentration of these metallic contaminants may be relatively small, for example, less than about 10 p.p.m. of metal porphyrins, calculated as the elemental metals, subsequent processing techniques will be adversely affected thereby. Thus, when a hydrocarbon charge stock containing metals in excess of about 3.0 p.p.m., is subjected to a cracking process for the purpose of producing lower-boiling components, metals become deposited upon the

catalyst employed, steadily increasing in quantity until such time as the composition of the catalytic composite is changed to the extent that undesirable results are obtained. That is to say, the composition of the cracking catalyst is closely controlled with respect to the nature of the charge stock being processed and to the desired product quality and quantity. This composition is changed considerably as a result of the deposition of the metallic contaminants thereupon, the changed composite inherently resulting in changed catalytic characteristics. Such an effect is undesirable since the deposition of metallic contaminants upon the catalyst results in a lesser quantity of valuable liquid hydrocarbon product, and in large amounts of hydrogen and coke, the latter also producing relatively rapid catalyst deactivation.

In addition to the foregoing described contaminating influences, crude oils and other heavier hydrocarbon fractions contain excessive quantities of pentane-insoluble material. For example, the Wyoming sour crude described above consists of about 8.3% by weight of pentane-insoluble asphaltenes; these are hydrocarbonaceous compounds considered to be coke precursors having the tendency to become immediately deposited within the reaction zone and onto the catalytic composite in the form of a high molecular weight, gummy residue. Since this constitutes a relatively large loss of charge stock, it is economically desirable to convert such asphaltenes into useful hydrocarbon oil fractions, thereby increasing the liquid yield of desired product, based upon the quantity of oil charged to the process.

The object of the present invention is to provide a much more efficient process for hydrorefining heavier hydrocarbonaceous material, and particularly petroleum crude oil, utilizing an unsupported catalyst prepared in a particular manner. The term "hydrorefining," as employed herein, connotes the catalytic treatment, in an atmosphere of hydrogen, of a hydrocarbon fraction or distillate for the purpose of eliminating and/or reducing the concentration of the various contaminating influences previously described. As hereinabove set forth, metals are generally removed from the charge stock by deposition of the same onto the catalyst employed. This increases the amount of catalyst, actively shields the catalytically active surfaces and centers from the material being processed, and thereby generally precludes the efficient utilization of a fixed-bed catalyst system for processing such contaminated crude oil. Various moving-bed processes, employing catalytically active metals deposited upon a carrier material consisting of silica and/or alumina, for example, or other refractory inorganic oxide material, are extremely erosive, causing plant maintenance to become difficult and expensive. The present invention teaches the preparation of a colloidally dispersed, unsupported catalytic material useful in a slurry process, which catalytic material will not cause extensive erosion or corrosion of the reaction system. The present process yields a liquid hydrocarbon product which is more suitable for further processing without experiencing the difficulties otherwise resulting from the presence of the foregoing contaminants. The process of the present invention is particularly advantageous for effecting the conversion of the organo-metallic contaminants without significant product yield loss, while simultaneously converting pentane-insoluble material into pentane-soluble liquid hydrocarbons.

The unsupported catalyst, utilized in the process of the present invention, is decomposed vanadyl acetylacetonate. We have previously found that beta-diketone complexes selected from the metals of Group VI–B of the Periodic Table (having an atomic number greater than 24), molybdenum and tungsten, and the iron-group, when added to the petroleum crude oil and decomposed there-

in, resulted in a totally unexpected degree of decontamination of the hydrocarbonaceous material. On the other hand, vanadyl acetylacetonate did not effect an acceptable degree of decontamination of the crude oil, and the resulting hydrocarbon product effluent necessarily required additional hydrorefining in order to make the same suitable for further processing. We have now found that significantly improved results are afforded, utilizing vanadyl acetylacetonate, when the hydrorefining reactions are effected in the presence of hydrogen sulfide which is added at the outset of the process, prior to initiating the hydrorefining reactions. As hereinafter indicated by specific example, notwithstanding that some hydrogen sulfide may be formed during the process, an essential feature of the present invention is that a hydrogen sulfide be added prior to attaining the level of operating conditions employed.

In addition to vanadyl acetylacetonate, other organovanadium compounds have now been found to produce an acceptable degree of decontamination of crude oils when utilized in the presence of added hydrogen sulfide. Such organovanadium compounds include vanadium xanthates, the vanadium esters of various alcohols, the vanadium thioesters of various mercaptans, etc.

In a broad embodiment, therefore, the present invention relates to a process for hydrorefining a hydrocarbon charge stock which comprises admixing said charge stock with an organovanadium compound, and reacting the resulting mixture with hydrogen in the presence of added hydrogen sulfide.

In another broad embodiment, the present invention involves a process for hydrorefining a hydrocarbon charge stock which process comprises admixing said charge stock with vanadyl acetylacetonate, and reacting the resulting mixture with hydrogen in the presence of added hydrogen sulfide.

A more limited embodiment of the present invention involves a process for hydrorefining a hydrocarbon charge stock which comprises admixing said charge stock with vanadyl acetylacetonate, heating the resulting mixture at a temperature less than about 310° C. and for a time sufficient to decompose said vanadyl acetylacetonate, and reacting the resulting colloidal suspension with hydrogen and added hydrogen sulfide.

A specific embodiment of the present invention encompasses a process for hydrorefining a petroleum crude oil containing pentane-insoluble asphaltenes, which process comprises admixing said crude oil with vanadyl acetylacetonate, heating the resulting mixture at a temperature below about 310° C. and for a time sufficient to decompose said vanadyl acetylactonate, reacting the resulting colloidal suspension with hydrogen and added hydrogen sulfide, at a temperature within the range of from about 225° C. to about 500° C. and at a pressure of from about 500 to about 5000 pounds per square inch gauge, and recovering said crude oil substantially free from pentane-insoluble asphaltenes.

From the foregoing embodiments, it will be noted that the method of the present invention involves a preparation of a colloidal suspension of the catalytic material within the hydrocarbonaceous crude oil ultimately subjected to the hydrorefining reactions. Furthermore, the decomposition of the catalytic material, in this instance vanadyl acetylacetonate, is effected below a temperature of about 310° C. to prevent premature cracking of the petroleum crude oil, particularly in the absence of hydrogen and added hydrogen sulfide. Briefly, the preferred method of the present invention involves dissolving vanadyl acetylacetonate in an appropriate solvent such as an alcohol, ketone or ester containing up to and including about 10 carbon atoms per molecule. The solution is added to petroleum crude oil and the mixture heated at a temperature less than about 310° C. to remove the solvent and decompose the vanadyl acetylacetonate, thereby creating a colloidally dispersed catalyst suspended within the petroleum crude oil. The quantity of vanadyl acetylacetonate is such that the colloidal suspension or dispersion, resulting when the material is decomposed, comprises from about 1.0% to about 10.0% by weight, calculated, however, as elemental vanadium.

Typical of the alcohols suitable for use in preparing the solution of vanadyl acetylacetonate, include isopropyl alcohol, isopentyl alcohol, methyl alcohol, amyl alcohol, mixtures thereof, etc. The resulting colloidal dispersion is then passed into a suitable reaction zone maintained at a temperature within the range of from about 225° C. to about 500° C. and under a hydrogen pressure within the range of about 500 to about 5000 pounds per square inch gauge. The process may be conducted as a batch type procedure or in an enclosed vessel through which the colloidal suspension is passed; when effected in a continuous manner, the process may be conducted in either upward flow or downward flow. The normally liquid hydrocarbons are separated from the total reaction zone effluent by any suitable means, for example, through the use of a centrifuge or settling tanks, at least a portion of the resulting catalyst-containing sludge being combined with the fresh petroleum crude oil, and recycled to the reaction zone. In order to maintain the highest possible degree of activity, it is preferred that at least a portion of the catalyst-containing sludge be removed from the process prior to combining the remainder with fresh crude oil. The precise quantity of catalyst-containing sludge removed from the process will be dependent upon the desired degree of contaminant removal. It is further desirable to add a quantity of fresh vanadyl acetylacetonate to the petroleum crude oil in order to compensate for that quantity of vanadium, calculated as the elemental metal, removed from the catalyst-containing sludge.

The colloidal dispersion of decomposed vanadyl acetylacetonate, or other organovanadium compound such as the vanadyl ester of isoamyl alcohol, the ester of t-butyl alcohol, etc., and crude oil is reacted with hydrogen under the operating conditions aforesaid, and in the presence of added hydrogen sulfide. When dispersed within the crude oil, the vanadyl acetylacetonate, appears to be reduced to the extent of forming a crystalline structure as yet unidentified. As such, the catalytic material is capable of hydrogenating, and/or hydrocracking, the more easily reduced sulfur compounds within the crude oil, thereby producing hydrogen sulfide. However, when the reactions are initiated in the presence of added hydrogen sulfide, a more active form of catalyst is produced immediately, which catalyst is capable of the destructive removal of the less easily reduced sulfur compounds. As hereinafter indicated by specific example, the more active form of catalyst is also capable of a greater degree of nitrogenous compound removal, yields a hydrorefined product effluent containing lesser quantities of metallic contaminants and effects the conversion of a greater portion of the pentane-insoluble fraction. Since this more active form of catalyst appears to have the same crystalline structure, also not as yet identified, as the catalyst employed in the absence of added hydrogen sulfide, the precise physical and/or chemical change effected therein is not known with accuracy. The beneficial effects of the added hydrogen sulfide appear to occur only when the latter is present at the time the hydrogenation reactions are being initiated. The hydrogen sulfide is added to the hydrogen atmosphere in an amount of from about 1.0 to about 15.0 mol percent.

The following examples are given to illustrate the present invention, and to indicate the effectiveness thereof in hydrorefining a petroleum crude oil to remove various contaminating influences. It is not intended to limit the present invention to the catalyst, concentrations of material, charge stock and/or conditions of operation utilized in presenting these examples.

The crude oil employed was a Wyoming sour crude having a gravity of 23.2 ° API at 60 ° F., containing about

2.8% by weight of sulfur, approximately 2700 p.p.m. of nitrogen, 18 p.p.m. of nickel and 81 p.p.m. of vanadium as metal porphyrins, computed as the elemental metals. In addition, the sour crude consisted of about 8.3% by weight of pentane-insoluble asphaltenes. As hereinafter indicated, the process of the present invention not only effects the conversion of a significant proportion of the pentane-insoluble asphaltenes, but also results in a substantial production of lower-boiling hydrocarbons as indicated by an increase in gravity, ° API at 60° F., of the normally liquid hydrocarbon portion of the total product effluent.

Example I

Vanadyl acetylacetonate in an amount of 21.0 grams, was added to 100 grams of the Wyoming sour crude oil hereinabove described. The resulting mixture was placed in an 850 cc. rocker-type autoclave, pressured to 100 atmospheres with hydrogen, and slowly heated to a temperature of 400° C., resulting in a pressure of 227 atmospheres; these conditions were maintained for a period of 8 hours. The autoclave was allowed to cool, and was depressured; the normally liquid hydrocarbons indicated a gravity, ° API at 60° F., of 32.6. Analyses indicated that the liquid hydrocarbon fraction continued to be contaminated by 2180 p.p.m. of nitrogen, 1.86% by weight of sulfur, 3.36% by weight of pentane-insoluble asphaltenes, 7.1 p.p.m. of nickel and 39.6 p.p.m. of vanadium, calculated as the elemental metals.

Vanadyl acetylacetonate in an amount of 42.0 grams was added to 250 grams of the sour crude oil, accompanied by intimate mixing and heating to a temperature of 250° C. for a period of 1 hour. A total of 100 grams of the resulting mixture were placed in the 850 cc. rocker-type autoclave, initially pressured to 100 atmospheres with hydrogen, and subsequently heated to a temperature of 400° C., resulting in a pressure of 206 atmospheres. After a period of 4 hours, the normally liquid hydrocarbon portion of the product effluent indicated a gravity, ° API at 60° F., of 25.0, and was contaminated by the continued presence of 2490 p.p.m. of nitrogen, 1.68% by weight of sulfur, 3.7% by weight of pentane-insoluble asphaltenes, 0.02 p.p.m. of nickel porphyrins and more than 100 p.p.m. of vanadium porphyrins, calculated as the elements thereof.

This example is given for the purpose of showing the inadequacy of vanadyl acetylacetonate to function as a suitable hydrorefining catalyst when admixed with the petroleum crude oil, and subjected to hydrorefining conditions in the absence of added hydrogen sulfide. Notwithstanding that there has been effected a partial clean-up of the crude oil, the same is obviously not suitable for further processing without additional hydrorefining pretreatment. It should be noted that, notwithstanding the virtually complete elimination of nickel, there has been an increase in the quantity of vanadium, indicating that at least a portion of the catalyst reacted to form additional contaminants.

Example II

Vanadyl acetylacetonate, in an amount of 42.0 grams, was added to 500 grams of normal amyl alcohol, and heated over a steam bath to dissolve the vanadyl acetylacetonate. The solution was added to 250 grams of this Wyoming sour crude, distilling off the amyl alcohol as the same was added. Upon complete addition, the temperature was raised to 180° C. for a period of 30 minutes, and 100 grams of the resulting mixture was placed in an autoclave and pressured to 100 atmospheres of hydrogen. After a period of 8 hours at a temperature of 400° C. and a resulting final pressure of 205 atmospheres, the normally liquid portion of the product effluent indicated a gravity, ° API at 60° F. of 38.5, and was contaminated by the presence of 942 p.p.m. of nitrogen, 0.40% by weight of sulfur, 0.64% by weight of pentane-insoluble asphaltenes, 0.1 p.p.m. of nickel and 63.0 p.p.m. of vanadium.

Sufficient vanadyl acetylacetonate was added to 125 grams of the Wyoming sour crude in alcohol solution, to result in a colloidal suspension containing 2.90% by weight of vanadium. The mixture was intimately admixed at a temperature of 250° C. for a period of 1 hour, and placed in the rocker-type autoclave, initially pressured to 10 atmospheres with hydrogen sulfide then to 100 atmospheres with hydrogen. The autoclave was heated to a temperature of 400° C., resulting in a pressure of 201 atmospheres. After a period of 8 hours, the normally liquid portion of the total product effluent, indicated a gravity, ° API at 60° F. of 37.5, contained 61 p.p.m. of nitrogen, 0.01% by weight of sulfur, less than 0.03 p.p.m. of nickel and only 0.07 p.p.m. of vanadium, there being no indication of the continued presence of pentane-insoluble asphaltenes.

This example indicates the much improved results obtained when the vanadyl acetylacetonate is dispersed as an alcohol solution within the petroleum crude oil, and hydrogen sulfide is added prior to initiating the hydrogenating-hydrocracking reactions. The utilization of the vanadyl acetylacetonate has been shown to result in a liquid hydrocarbon product suitable for further processing without the accompanying detrimental effects otherwise resulting through the presence of the various contaminating influences.

Example III

The vanadyl ester of isoamyl alcohol, in an amount of 20.0 grams, was added to 100 grams of the Wyoming sour crude oil, the mixture being heated at a temperature of about 250° C. to decompose the ester, thereby producing a colloidal suspension of 2.7% by weight of vanadium within the crude oil. The colloidal dispersion was placed in the rocker autoclave and initially pressured to 10 atmospheres with hydrogen sufide. Hydrogen was added to a pressure of 100 atmospheres, and the temperature increased to 400° C., resulting in a pressure of 200 atmospheres. The normally liquid portion of the product effluent, after 4 hours, indicated a gravity of 40.8 ° API at 60° F., and contained 145 p.p.m. of nitrogen, 0.19% by weight of sulfur and 0.04% by weight of pentane-insoluble asphaltenes.

Example IV

The vanadyl ester of t-butyl alcohol, in an amount of 35.0 grams was added to 200 grams of the crude oil. Without decomposition of the ester at a lower temperature, the mixture was placed in the autoclave under a pressure of 10 atmospheres of hydrogen sulfide and 90 atmospheres of hydrogen. Upon heating to 400° C., the final pressure was 203 atmospheres, which conditions were maintained for a period of 4 hours. The normally liquid portion of the product effluent indicated a gravity of 29.6° API at 60° F., and contained 1960 p.p.m. of nitrogen, 1.41% by weight of sulfur and 1.76% by weight of pentane-insoluble asphaltenes.

When the ester was decomposed prior to placing the mixture in the autoclave, under a pressure of 10 atmospheres of hydrogen sulfide and 90 atmospheres of hydrogen, the liquid product effluent indicated a gravity of 30.6° API, and contained 239 p.p.m. of nitrogen and 0.28% by weight of sulfur, there being no indication of the continued presence of pentane-insoluble asphaltenes.

This example is presented to show the improved results obtained when the catalytic agent is decomposed within the charge stock, thereby forming a colloidal dispersion.

The foregoing specification and examples clearly indicate the benefits afforded a process for hydrorefining heavy hydrocarbonaceous material through the use of the present invention. The contaminating influences have been removed to the extent required for further processing without incurring the deleterious effects otherwise resulting.

We claim as our invention:

1. A process for hydrorefining a hydrocarbon charge stock which comprises admixing said charge stock with an organovanadium compound, and reacting the resulting mixture with hydrogen and added hydrogen sulfide at hydrorefining conditions, the hydrorefining reaction being initiated in the presence of the added hydrogen sulfide.

2. A process for hydrorefining a hydrocarbon charge stock which comprises admixing said charge stock with an organovanadium compound decomposable at a temperature below about 310° C., heating the resulting mixture at a temperature below 310° C. for a time sufficient to decompose said organovanadium compound, and reacting the resulting colloidal dispersion with hydrogen in the presence of added hydrogen sulfide, the hydrorefining reaction being initiated in the presence of the added hydrogen sulfide.

3. The process of claim 2 further characterized in that said organovanadium compound comprises vanadyl acetylacetonate.

4. The process of claim 2 further characterized in that said organovanadium compound comprises the vanadyl ester of isoamyl alcohol.

5. The process of claim 2 further characterized in that said organovanadium compound comprises the vanadyl ester of t-butyl alcohol.

6. A process for hydrorefining a hydrocarbon charge stock which comprises admixing said charge stock with vanadyl acetylacetonate, heating the resulting mixture at a temperature less than about 310° C. and for a time sufficient to decompose said vanadyl acetylacetonate, and reacting the resulting colloidal suspension with hydrogen and added hydrogen sulfide at a temperature above about 225° C. and at a pressure greater than about 500 pounds per square inch gauge, the hydrorefining reaction being initiated in the presence of the added hydrogen sulfide.

7. The process of claim 6 further characterized in that said colloidal suspension is reacted with hydrogen and added hydrogen sulfide at a temperature within the range of from about 225° C. to about 500° C. and under an imposed pressure of from about 500 to about 5000 pounds per square inch gauge.

8. The process of claim 6 further characterized in that said colloidal suspension comprises from about 1.0% to about 10.0% by weight of decomposed vanadyl acetylacetonate, calculated as elemental vanadium.

9. A process for hydrorefining a petroleum crude oil containing pentane-insoluble asphaltenes which comprises admixing said crude oil with vanadyl acetylacetonate, heating the resulting mixture at a temperature less than about 310° C. and for a time sufficient to decompose said vanadyl acetylacetonate, reacting the resulting colloidal suspension with hydrogen and added hydrogen sulfide at a temperature above about 225° C. and at a pressure greater than about 500 pounds per square inch gauge, the hydrorefining reaction being initiated in the presence of the added hydrogen sulfide, and recovering said crude oil substantially free from pentane-insoluble asphaltenes.

10. The process of claim 9 further characterized in that said hydrogen sulfide is added in an amount within the range of from about 1.0 to about 15.0 mol percent.

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