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HYDROREFINING OF CRUDE OIL AND CATALYST THEREFOR

William K. T. Gleim, Island Lake, and John G. Gatsis, Des Plaines, Ill., assignors to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware

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The present invention relates to a process for the hydrorefining of petroleum crude oil, crude oil residuum, topped crudes, heavy vacuum gas oil, heavy oil cycle stocks, etc. More specifically, the present invention is directed toward the catalytic hydrorefining of heavy hydrocarbonaceous material through the utilization of a process involving the autogeneration and recirculation of the catalyst, without frequent external regeneration thereof.

In one embodiment, the present invention relates to a process for hydrorefining of heavy hydrocarbon charge stocks for the purpose of effecting the removal of nitrogen and sulfur therefrom, and affords unexpected advantages when employed for the removal of metallic contaminants and/or the conversion of the pentane-insoluble portion of the charge stock into useful pentane-soluble hydrocarbon oils. Crude petroleum oil, and the heavier hydrocarbon fractions and/or distillates obtained therefrom, generally contains nitrogenous and sulfurous compounds in large quantities. In addition, crude oil and such heavier hydrocarbon fractions contain quantities of organometallic contaminants which possess the propensity to exert detrimental effects upon the catalyst utilized in various processes to which the crude oil or heavy hydrocarbon fraction is ultimately subjected. The more common of such metallic contaminants are nickel and vanadium, although other metals including iron, copper, etc., are often present. These metals may occur in a variety of forms: they may exist as metal oxides or as sulfides, introduced into the crude oil as metallic scale or particles; they are often present in the form of soluble salts of such metals; usually, however, they exist in the form of organometallic compounds such as metal porphyrins and various derivatives thereof.

Although the 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 in part removable by water washing, accompanied by a subsequent dehydration technique, a much more severe treatment is required to remove the organometallic compounds and to the degree required in order that the resulting crude oil or heavy hydrocarbon fraction becomes suitable for further processing. In addition to organo-metallic contaminants, including metal porphyrins, crude oils contain much larger 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 about 2700 p.p.m. of total nitrogen. These nitrogenous and sulfurous compounds are converted, upon being subjected to catalytic hydrorefining, into hydrocarbons, ammonia and hydrogen sulfide. Reduction in the concentration of the organometallic contaminants is not as easily achieved, particularly to the degree required for further processing of the

petroleum crude oil or heavy fraction thereof. Notwithstanding that the total concentration of these contaminants is relatively small, for example, less than about 10 p.p.m., calculated as the elemental metal, 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, the metals become deposited upon the cracking catalyst utilized, 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 catalytic composite, which is closely controlled with respect to the nature of the charge stock being processed and to the desired product quality and quantity, is changed considerably as the result of the deposition of the metallic contaminants thereupon, the changed composite resulting inherently in changed catalytic characteristics. Such an effect is undesirable with respect to the cracking process, since the deposition of metallic contaminants upon the catalyst tends to result in a lesser quantity of valuable liquid product, and large amounts of hydrogen and coke, the latter producing relatively rapid catalyst deactivation. The presence of organometallic compounds, particularly as metal porphyrins, affects deleteriously other processes including catalytic reforming, isomerization, hydrodealkylation, etc., and exhibits an adverse influence toward the activity of hydrorefining catalysts with respect to the destructive conversion of sulfurous and nitrogenous compounds also contained in the petroleum crude oil. In addition to the foregoing described contaminating influences, crude oils and other heavier hydrocarbon fractions generally contain large quantities of pentane-insoluble material. For example, the Wyoming sour crude described above consists of about 8.3% by weight of pentane-insoluble asphaltenes; asphaltenes are hydrocarbonaceous compounds considered as coke precursors having the tendency to become immediately deposited within the reaction zone and onto the catalytic composite in the form of a heavy gummy residue. Since this constitutes a large loss of charge stock and affects product yield, it is economically desirable to convert such asphaltenes into useful hydrocarbon oil fractions.

The object of the present invention is to provide a much more efficient process for hydrorefining such petroleum crude oils, than those processes currently in use. As hereinabove set forth, metals are generally removed from the charge stock by deposition of the same onto the catalyst, and the pentane-insoluble asphaltenes, as coke-precursors, become immediately deposited upon the catalyst in the form of a gummy hydrocarbonaceous residue. This two-fold effect increases the quantity of catalyst employed in the cracking process and actively shields the catalytically active surfaces and centers from the material being processed, thereby precluding extensive utilization of a fixed-bed catalyst system. Various moving-bed processes, employing catalytically active metals deposited upon silica and/or alumina, are extremely erosive, causing plant maintenance to become difficult and expensive. The present invention teaches the preparation of a colloidally dispersed, unsupported catalyst useful in a continuous or batch-type slurry process, and which will not create extensive erosion and/or corrosion of the reaction system. Furthermore, the present invention affords more

efficient use of the catalyst as well as an extended period of time during which the catalyst may be employed without necessity for frequent, external regeneration. As hereinafter indicated in greater detail, the present process permits autogeneration of the colloidally dispersed catalyst; autogeneration is intended to connote internal regeneration and production of catalyst within the system, without the necessity of utilizing excessive quantities of reagents from an external source. 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 described contaminants. The process is particularly advantageous in converting the organo-metallic compounds without significant product yield loss, while simultaneously converting pentane-insoluble material into pentane-soluble liquid hydrocarbons.

In a broad embodiment, the present invention relates to a process for hydrorefining a hydrocarbon charge stock which comprises the steps of: (*a*) admixing said hydrocarbon charge stock with at least one organo-metallic compound selected from the metals of Group VI–B having an atomic number greater than 24, Group V–B and the Iron-group; (*b*) decomposing said organo-metallic compound in said charge stock and sulfiding the resulting colloidal suspension to form the sulfide of said metal; (*c*) reacting the metal sulfide-containing colloidal suspension with hydrogen at a temperature above about 225° C. and at a pressure greater than 500 pounds per square inch gauge; (*d*) separating the reaction product to provide a gaseous phase containing hydrogen sulfide, a hydrorefined liquid product substantially free from catalytic solids and a catalyst-containing sludge; (*e*) sulfiding at least a portion of said catalyst-containing sludge, admixing the sludge with said hydrocarbon charge stock and reacting the resulting colloidal suspension as aforesaid.

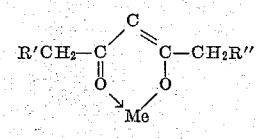
Other embodiments of the present invention involve the utilization of carbonyls and/or beta-diketone complexes of the metals of group VI–B having an atomic number greater than 24, Group V–B and the Iron-group, and reacting the colloidal suspension of said charge stock and sulfided, decomposed organo-metallic compound with hydrogen 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. Reference to Group V–B and VI–B metals is made herein with respect to the Periodic Chart of the Elements as found on pages 448 and 449 of the 43rd edition of the Handbook of Chemistry and Physics.

A more specific embodiment of the present invention encompasses a process for hydrorefining a hydrocarbon charge stock which comprises the steps of: (*a*) admixing said hydrocarbon charge stock with at least one organo-metallic compound selected from the metals of Group VI–B having an atomic number greater than 24, Group V–B and the Iron-group; (*b*) heating the resulting mixture at a temperature less than about 310° C. and for a time sufficient to decompose said organo-metallic compound, and sulfiding the resulting colloidal suspension to form the sulfide of said metal; (*c*) reacting the sulfided colloidal suspension with hydrogen at a temperature within the range of from about 225° to about 500° C. and at a pressure of from about 500 to about 5000 pounds per square inch gauge; (*d*) separating the reaction product to provide a gaseous phase containing hydrogen sulfide, a hydrorefined liquid product substantially free from catalytic solids and a catalyst-containing sludge; (*e*) sulfiding at least a portion of said catalyst-containing sludge at a temperature less than about 200° C., admixing the sludge with said hydrocarbon charge stock and reacting the resulting colloidal suspension as aforesaid.

As hereinabove set forth, the present invention affords particular advantages to the processing of petroleum crude oils containing detrimental quantities of pentane-insoluble asphaltenes. Therefore, a more specific embodiment of

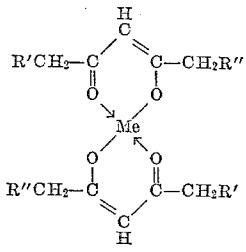
the present invention involves a process for hydrorefining a petroleum crude oil containing pentane-insoluble asphaltenes which process comprises the steps of: (*a*) admixing said crude oil with molybdenum hexacarbonyl, heating the resulting mixture at a temperature less than about 310° C., in a non-reducing atmosphere and for a time sufficient to decompose said molybdneum hexacarbonyl, sulfiding the resulting colloidal suspension to form molybdenum sulfide; (*b*) reacting the sulfided colloidal suspension with hydrogen 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; (*c*) separating the reaction product to provide a hydrorefined liquid product substantially free from pentane-insoluble asphaltenes and a molybdenum-containing catalyst sludge; (*d*) adding from about 0.1% to about 1.0% of said molybdenum hexacarbonyl, calculated as elemental molybdenum, to said petroleum crude oil; (*e*) removing from about 0.1% to about 1.0% by weight of molybdenum, calculated as the element, from said molybdenum-containing catalyst sludge, and combining the remainder of said sludge with said petroleum crude oil and added molybdenum hexacarbonyl; (*f*) decomposing said added molybdenum hexacarbonyl in said crude oil and sulfiding the colloidal suspension as aforesaid thereafter reacting the sulfided colloidal suspension with hydrogen as aforesaid.

From the foregoing embodiments, it will be readily ascertained that the method of the present invention involves the preparation of an unsupported catalyst utilizing metals which are selected from Group VI–B, Group V–B and the Iron-group of the Periodic Table. The catalyst, prepared in accordance with the method of the present invention, may, therefore, comprise one or more metals selected from the group of vanadium, niobium, tantalum, molybdenum, tungsten, iron, cobalt, nickel, and mixtures of two or more. It is noted that the metals selected from Group VI–B, namely molybdenum and/or tungsten, have an atomic number greater than 24. It has been found that organic chromium complexes, upon decomposition, requiring a temperature above about 310° C. do not yield results comparable to molybdenum and tungsten upon subsequent reaction with hydrogen particularly with respect to the conversion of the pentane-insoluble material, and the destructive removal of the organo-metallic contaminants such as nickel and/or vanadium porphyrins. Furthermore, temperatures above about 310° C. result in premature cracking of the charge stock. The catalyst is prepared by initially dissolving an organic complex of the selected metal, or metals, preferably a carbonyl and/or beta-diketone complex of the metal, in the hydrocarbon charge stock containing the pentane-insoluble fraction which is to be converted into soluble hydrocarbons. The quantity of the organo-metallic compound employed is such that the colloidal suspension, or dispersion, which results when the organo-metallic compound is decomposed within the hydrocarbon charge stock, comprises from about 1.0% to about 10.0% by weight thereof, calculated as the elemental metal. Suitable organo-metallic compounds include molybdenum hexacarbonyl, tungsten hexacarbonyl, iron pentacarbonyl, moylbdenum hexacarbonyl in combination with tungsten hexacarbonyl, vanadium carbonyl, various cobalt complexes, nickel acetylacetonate, molybdyl acetylacetonate, tungsten acetylacetonate, the molybdenum complex of 4,6-nonanedione, tantalum acetylacetonate, niobium acetylacetonate, mixtures of two or more, etc. Suitable beta-diketone complexes may be represented by the following structural formula:



(I)

In the above structural formula, Me denotes a metal selected from the group of iron, nickel, and/or cobalt; R' and R'' may be hydrogen, a methyl group, an ethyl group, or other alkyl group containing up to about 10 carbon atoms; R' and R'' may also be an aryl group, or an alkyl-substituted aryl group, and R'' may or may not be of the same chemical character as R'. When molybdenum, tungsten, or metals from Group V–B are employed, the structural formula is represented as shown below:



(2)

In the above formula, Me may be MoO_2, WoO_2, V=O, V, Nb, Ta, etc.

The process is effected, as hereinabove set forth, by initially dissolving the desired quantity of the organo-metallic compound, such as molybdenum hexacarbonyl and/or molybdyl acetylacetonate, in the hydrocarbon charge stock. To facilitate dissolution of the organo-metallic compound within the petroleum crude oil, the same may be initially admixed with a suitable solvent such as methanol, isopropyl alcohol, etc. The resulting mixture is then heated, preferably in a non-reducing atmosphere, and particularly in the absence of free hydrogen, at a temperature less than about 310° C. and for a time sufficient to effect the decomposition of the molybdenum hexacarbonyl, thereby resulting in a colloidal suspension, or dispersion, of the metallic component within the hydrocarbon charge stock. The presence of free hydrogen during the decomposition of the organo-metallic compound has the tendency to affect detrimentally the activity of the catalyst with respect to the conversion of the pentane-insoluble fraction as well as the removal of organo-metallic contaminants; this deleterious effect is hereinafter illustrated by a specific example. The colloidal dispersion is then subjected to a sulfiding technique utilizing a suitable sulfur-containing compound such as carbon disulfide, hydrogen sulfide, tertiary butyl mercaptan, etc., and at a temperature less than about 200° C. for a time sufficient to convert the colloidally dispersed material into the sulfide thereof. The 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. In order to maintain the catalyst in its sulfided, decomposed form, it is necessary that the reaction zone be maintained substantially, completely free from carbon monoxide. Following the decomposition of the moylbdenum hexarcarbonyl, for example, some carbon monoxide will be present in the gaseous phase; this is readily removed upon venting prior to passing the mixture into the reaction zone. If some of the carbon monoxide becomes dissolved in the liquid phase, it is preferred to remove the same by suitable stripping means. 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 product effluent by any suitable means, for example, through the use of a centrifuge, or settling tanks, the resulting catalyst-containing sludge being recycled, at least in part, to combine with additional fresh hydrocarbon charge. The ammonia and hydrogen sufide, resulting from the destructure conversion of sulfurous and nitrogenous compounds contained within the hydrocarbon charge stock, are removed, along with any light paraffinic hydrocarbons including methane, ethane and propane, in a gaseous phase. In one embodiment of the present invention, this gaseous phase, containing substantial quantities of hydrogen sulfide, is utilized to sulfide the decomposed organo-metallic compound within the hydrocarbon charge stock being processed. Prior to combining the catalyst-containing sludge with additional, fresh hydrocarbon charge, the latter is admixed with additional molybdenum hexacarbonyl and/or molybdyl acetylacetonate, in an amount of from about 0.1% to about 1.0%, calculated as elemental molybdenum. Consequently, from about 0.1% to about 1.0% by weight of moylbdenum, or other catalytic metals is withdrawn from the catalyst-containing sludge prior to combining the latter with the fresh hydrocarbon charge stock. In this manner, the desired concentration of the catalytically active metal is readily maintained within the range of from about 1.0% to about 10.0% by weight of the hydrocarbon charge stock. The metals withdrawn from the catalyst-containing sludge, existing as the element or in a combined form, may be converted back to the original organo-metallic compound by any of the well-known chemical means found in the prior art relating thereto. This catalyst-containing sludge will contain, in addition to the metal employed as the catalytically active dispersed material, quantities of nickel and vanadium resulting from the destructive conversion of nickel and vanadium porphyrins contained within the charge stock. Such nickel and/or vanadium may be converted, as about set forth, into suitable organo-metallic compounds for subsequent utilization in the process of the present invention. The nickel and vanadium remaining in that portion of the catalyst-containing sludge which is to be combined with the fresh hydrocarbon charge stock, will be converted to the sulfides thereof, and will, therefore, supply at least a portion of the necessary catalytic action within the reaction zone.

It is seen, therefore, that the autogeneration feature of the process of the present invention utilizes, as at least a portion of the catalyst, those metals originally existing in the form of contaminating influences, and makes use of the hydrogen sufide-containing gaseous phase, removed from the total reaction zone effluent, for the purpose of continually sulfiding such metals. Thus, the hydrorefining reaction is initiated with freshly-prepared catalyst, new catalyst being continuously furnished for the reaction by the destruction of the nickel and vanadium porphyrins contained within the hydrocarbon charge stock, and ultimately sulfided by inclusion within the catalyst-containing sludge being combined with fresh charge stock.

Although the process of the present invention is conducted in the presence of hydrogen, the decomposition of the organo-metallic compound, such as molybdyl acetylacetone, is effected in the absence thereof. If present, for example during the decomposition of molybdyl acetylacetonate, hydrogen will reaction with carbon monoxide, resulting in the formation of water, methane and particularly carbon. It is further preferred that the decomposition to form the colloidal suspension be conducted in the substantial absence of other well-known reducing agents. Depending upon the particular organo-metallic compound selected as the catalyst source, the dispersed material will initially be the elemental metal or a lower oxide form thereof. Following the sulfiding technique, in which the colloidal suspension is treated with a suitable sulfur-containing compound, the metal exists as a colloidal dispersion of the sulfide form. In any event, it is understood that the stated concentrations are calculated on the basis of the elemental metal. The decomposition of the organo-metallic compound is conducted at a temperature less than about 310° C. in order to avoid initial cracking of the petroleum crude oil prior to effecting complete decomposition and sulfiding of the

decomposed compound. The quantity of hydrogen present in the reaction zone, in admixture with the colloidal suspension, is determined by the pressure imposed upon the reaction zone; as hereinabove set forth, this pressure will be within the range of from about 500 to about 5000 pounds per square inch gauge.

The following examples are given to illustrate the process of the present invention and the effectiveness thereof in removing nickel and vanadium porphyrins from a petroleum crude oil, and in converting pentane-insoluble asphaltenes while simultaneously effecting the conversion of sulfurous and nitrogenous compounds into sulfur and nitrogen-free hydrocarbons. It is not intended that the present invention be unduly limited to the catalyst, charge stock and/or operating conditions employed in these illustrations. The concentration of the nickel and vanadium porphyrins, remaining in the reaction zone liquid product effluent, following the separation thereof from the catalyst-containing sludge, was determined through the utilization of spectrographic emission.

The crude oil employed was Wyoming sour crude having a gravity of 23.2° API at 60° F., and contained 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 on the basis of the elemental metal. In addition, the sour crude consisted of 8.3% by weight of pentane-insoluble asphaltenes. As hereinafter indicated, the process of the present invention results in the conversion of a significant proportion of such asphaltenes, and to the degree that the same no longer exert a detrimental effect upon further processing.

Example I

This example is presented for the purpose of illustrating the comparison of the results obtained through the utilization of decomposed vanadyl acetylacetonate, and a colloidal suspension of decomposed vanadyl acetylacetonate which had been sulfided at a temperature less than about 200° C.

An alcohol solution of vanadyl acetylacetonate, in an amount of 16.6 grams, was added to 100 grams of the previously described Wyoming sour crude, the mixture being heated to a temperature of about 255° C. for a period of about 30 minutes to decompose the vanadyl acetylacetonate, thereby resulting in a colloidal suspension. The colloidal suspension was charged into a rotating autoclave, pressured to 100 atmospheres with hydrogen and heated to a temperature of 400° C., thus increasing the pressure within the autoclave to about 200 atmospheres. The autoclave was maintained at these conditions for a period of 8 hours. The total product effluent was subjected to centrifugal separation, the resulting normally liquid hydrocarbons indicating a gravity, ° API at 60° F., of 31.5, 965 p.p.m. of nitrogen, 0.40% by weight of sulfur, 0.91% by weight of pentane-insoluble asphaltenes, 0.6 p.p.m. of nickel and 2.0 pp.m. of vanadium, the latter existing as metallic porphyrins.

42 grams of vanadyl acetylacetonate were dissolved in 500 grams of normal amyl alcohol, the mixture being added to 250 grams of the Wyoming sour crude, heated and maintained at a temperature of 150° C. throughout the addition during which time the amyl alcohol was removed. The vanadyl acetylacetonate was decomposed within the Wyoming crude at a temperature of 180° C. The resulting colloidal suspension was maintained at a temperature of 180° C. for a period of 30 minutes while hydrogen sulfide was bubbled therethrough, 130 grams of the resulting sulfided colloidal suspension being placed in the rotating autoclave, pressured to 100 atmospheres with hydrogen and heated to 400° C. for a period of 8 hours, the final pressure being about 200 atmospheres. The total autoclave product effluent was subjected to centrifugal separation employing an angle centrifuge at 3500 r.p.m. for a period of 30 minutes. The analysis of the normally liquid hydrocarbon product, having an API gravity of 42.4° at 60° F., indicated 0.308% by weight of pentane-insoluble asphaltenes, 0.19% by weight of sulfur, 139 p.p.m. of nitrogen, less than 0.03 p.p.m. of nickel. This example clearly indicates the substantial improvement resulting from the use of an unsupported, sulfided vanadium catalyst, and as a finely dispersed, colloidal suspension within the petroleum crude oil.

Example II

This example is presented to indicate the detrimental effects resulting when the organo-metallic compound is decomposed within the petroleum crude oil in the presence of hydrogen. Molybdyl acetylacetonate, in an amount of 33.0 grams, and 5.0 grams of nickel acetylacetonate were admixed with 300 grams of the Wyoming sour crude, the mixture being heated at a temperature of 300° C. for a period of 1 hour. The resulting colloidal suspension, in an amount of 200 grams, was charged to the rotating autoclave, pressured to 100 atmospheres with hydrogen and then heated to a temperature of 400° C., thereby increasing the pressure to about 200 atmospheres. These conditions were maintained for a period of 4 hours, the resulting liquid product, following the removal of the catalyst sludge by centrifugal separation, indicated less than about 0.01% by weight of sulfur, 51 p.p.m. of nitrogen, 0.1 p.p.m. of nickel and less than 0.5 p.p.m. of vanadium A significant degree of conversion to lower-boiling hydrocarbon products was effected since the liquid product effluent indicated a gravity, ° API, of 317.

Molybdyl acetylacetonate, in an amount of 21.7 grams, and 3.5 grams of nickel acetylacetonate were admixed with 200 grams of the Wyoming sour crude. The total mixture was charged into the rotating autoclave, pressured to 100 atmospheres with hydrogen and heated to 400° C., raising the pressure to about 200 atmospheres. Through this procedure, the decomposition of the molybdyl and nickel acetylacetonate was effected in situ, in the presence of hydrogen. The foregoing conditions were maintained for a period of 4 hours, the final liquid product indicating 1404 p.p.m. of nitrogen as compared to 51 p.p.m. resulting when the decomposition was effected in the absence of hydrogen.

Example III

The molybdenum-containing catalyst sludge from the foregoing Example II is admixed with fresh Wyoming sour crude in an amount of about 200 grams. 1.0% by weight of the catalytic solids, calculated as elemental molybdenum, is removed from the catalyst-containing sludge prior to being admixed with the petroleum hydrocarbon charge. About 1.0% by weight of molybdenum acetylacetonate, calculated as elemental molybdenum, is then added to the mixture of fresh Wyoming sour crude and the catalyst-containing sludge. The resulting mixture is subjected to heating at a temperature of about 255° C. for the purpose of decomposing the added molybdenum acetylacetonate within the Wyoming sour crude, the resulting colloidal suspension being treated with gaseous hydrogen sulfide at a temperature of about 180° C. for a period of about 30 minutes. The resulting sulfided colloidal suspension is placed within the rotating autoclave, pressured to 100 atmospheres with hydrogen, and heated to a temperature of 400° C. for a period of about 8 hours, the final pressure being about 200 atmospheres. The total reaction zone effluent is subjected to centrifugal separation, as hereinabove described, the normally liquid hydrocarbons indicating less than about 0.2% by weight of pentane-insoluble asphaltenes, less than 0.05 p.p.m. of nickel, less than 0.05 p.p.m. of vanadium, less than about 150 p.p.m. of nitrogen, and less than 0.1% by weight of sulfur.

The foregoing examples and specification clearly indicate the process of the present invention and the benefits to be afforded through the utilization thereof. The advantages of the autogeneration process described herein, utilizing the hydrogen sulfide-containing gaseous phase and the nickel and vanadium metals resulting from the

decomposition of the metallic porphyrins, will be readily recognized by those possessing skill within the art of petroleum processing.

We claim as our invention:

1. A process for hydrorefining a hydrocarbon charge stock which comprises the steps of:
(a) admixing said hydrocarbon charge stock with an organo-metallic compound in which the metal is selected from the group consisting of vanadium, niobium, tantalum, molybdenum, tungsten, iron, cobalt and nickel;
(b) decomposing said organo-metallic compound in said charge stock and sulfiding the resulting colloidal suspension to form the sulfide of said metal;
(c) reacting the metal sulfide-containing colloidal suspension with hydrogen at a temperature above about 225° C. and at a pressure greater than 500 pounds per square inch gauge;
(d) separating the reaction product to provide a gaseous phase containing hydrogen sulfide, a hydrorefined liquid product substantially free from catalytic solids and a catalyst-containing sludge;
(e) sulfiding at least a portion of said catalyst-containing sludge, admixing the sludge with said hydrocarbon charge stock and reacting the resulting colloidal suspension as aforesaid.

2. The process of claim 1 further characterized in that said organo-metallic compound is a beta-diketone complex of said metal.

3. The process of claim 1 further characterized in that said organo-metallic compound is a carbonyl of said metal.

4. The process of claim 1 further characterized in that said sulfided colloidal suspension is reacted with hydrogen 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.

5. The process of claim 1 further characterized in that the decomposition of said organo-metallic compound is effected in a non-reducing atmosphere.

6. A process for hydrorefining a hydrocarbon charge stock which comprises the steps of:
(a) admixing said hydrocarbon charge stock with an organo-metallic compound in which the metal is selected from the group consisting of vanadium, niobium, tantalum, molybdenum, tungsten, iron, cobalt and nickel;
(b) heating the resulting mixture at a temperature less than about 310° C. and for a time sufficient to decompose said organo-metallic compound, and sulfiding the resulting colloidal suspension to form the sulfide of said metal;
(c) reacting the sulfided colloidal suspension with hydrogen 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;
(d) separating the reaction product to provide a gaseous phase containing hydrogen sulfide, a hydrorefined liquid product substantially free from catalytic solids and a catalyst-containing sludge;
(e) sulfiding at least a portion of said catalyst-containing sludge at a temperature less than about 200° C., admixing the sludge with said hydrocarbon charge stock and reacting the resulting colloidal suspension as aforesaid.

7. The process of claim 6 further characterized in that said organo-metallic compound is vanadyl acetylacetonate.

8. The process of claim 6 further characterized in that said organo-metallic compound comprises molybdyl acetylacetonate.

9. The process of claim 6 further characterized in acetylacetonate.

10. A process for hydrorefining a hydrocarbon charge stock which comprises the steps of:
(a) admixing said hydrocarbon charge stock with an organo-metallic compound in which the metal is selected from the group consisting of vanadium, niobium, tantalum, molybdenum, tungsten, iron, cobalt and nickel;
(b) decomposing said organo-metallic compound in said charge stock and sulfiding the resulting colloidal suspension to form the sulfide of said metal;
(c) reacting the sulfided colloidal suspension with hydrogen at a temperature above about 225° C. and at a pressure greater than 500 pounds per square inch gauge;
(d) separating the resulting reaction mixture to provide a gaseous phase containing hydrogen sulfide, a hydrorefined liquid product substantially free from catalytic solids and a catalyst-containing sludge;
(e) adding from about 0.1% to about 1.0% of said organo-metallic compound, calculated as the elemental metal, to said hydrocarbon charge and combining at least a portion of said catalyst-containing sludge therewith;
(f) decomposing said added organo-metallic compound as aforesaid, sulfiding the resulting colloidal suspension, and reacting the sulfided colloidal suspension with hydrogen as aforesaid.

11. The process of claim 10 further characterized in that said hydrocarbon charge stock is a petroleum crude oil containing pentane-insoluble asphaltenes and said organo-metallic compound is a beta-diketone complex of said metal.

12. The process of claim 11 further characterized in that said beta-diketone complex is vanadyl acetylacetonate.

13. The process of claim 11 further characterized in that said beta-diketone complex comprises molybdyl acetylacetonate.

14. The process of claim 11 further characterized in that said beta-diketone complex comprises nickel acetylacetonate.

15. The process of claim 10 further characterized in that said hydrocarbon charge stock is a petroleum crude oil containing pentane-insoluble asphaltenes and said organo-metallic compound is a carbonyl of said metal.

16. A process for hydrorefining a petroleum crude oil containing pentane-insoluble asphaltenes which comprises the steps of:
(a) admixing said crude oil with molybdenum acetylacetonate, heating the resulting mixture at a temperature less than about 310° C., in a non-reducing atmosphere and for a time sufficient to decompose said molybdenum acetylacetonate (sulfiding the resulting colloidal suspension to form molybdenum sulfide;
(b) reacting the sulfided colloidal suspension with hydrogen 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;
(c) separating the reaction product to provide a hydrorefined liquid product substantially free from pentane-insoluble asphaltenes and a molybdenum-containing catalyst sludge;
(d) adding from about 0.1% to about 1.0% of said molybdenum acetylacetonate, calculated as elemental molybdenum, to said petroleum crude oil;
(e) removing from about 0.1% to about 1.0% by weight of molybdenum, calculated as the element, from said molybdenum-containing catalyst sludge, and combining the remainder of said sludge with said petroleum crude oil and added molybdenum acetylacetonate;
(f) decomposing said added molybdenum acetyl-

acetonate in said crude oil, sulfiding the colloidal suspension as aforesaid, and reacting the sulfided colloidal suspension with hydrogen as aforesaid.

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