The invention herein described is adaptable to a process for hydrorefining heavy hydrocarbon fractions and/or distillates for the primary purpose of effecting the removal of, or a reduction in the concentration of various contaminating influences. More specifically, the present invention relates to a novel method for effecting the catalytic hydrorefining of a heavy hydrocarbon charge stock utilizing a fixed-bed reaction zone. The process is especially advantageous in treating full boiling range petroleum crude oils, and topped or reduced crude oils for the removal of organo-metallic contaminants and the conversion of pentane-insoluble asphaltenic material.

Petroleum crude oils, and topped or reduced crude oils, as well as various heavy hydrocarbon fractions and/or distillates which may be derived therefrom, including black oils, heavy cycle stocks, visbreaker liquid effluent, etc., are generally contaminated through the inclusion of excessive concentrations of various oxygen-metallic and metallic impurities which detrimentally affect various processes to which these heavy hydrocarbon mixtures may be subjected. Among the non-metallic impurities are nitrogen, sulfur and oxygen which normally exist as heteroatomic compounds in relatively large quantities. Nitrogen is probably the most undesirable of the impurities since it effectually poisons various catalytic compositions employed in a multitude of processes for the conversion of petroleum fractions; in particular, nitrogenous compounds are known to be extremely effective hydrocracking suppressors. Therefore, it is particularly desirable to have nitrogenous compounds substantially completely removed from the charge stocks used in catalytic hydrocracking processes. Nitrogenous and sulfurous compounds are further objectionable because combustion of fuels containing these impurities results in the release of noxious and poisonous oxides which are noxious, corrosive and present, therefore, a serious problem with respect to atmospheric pollution. The presence of sulfur in motor fuels and various fuel oils is particularly objectionable because of odor, gum and varnish formation, and significantly decreased lead susceptibility.

In addition to the foregoing described contaminating influences, crude oil and heavier hydrocarbon fractions contain quantities of metallic contaminants which can exert detrimental effects upon the catalyst utilized in various processes to which crude oil may be ultimately subjected. Of the metallic contaminants, those containing nickel and vanadium are most prevalent although other metals, including iron, copper, lead, zinc, etc., are often present. Such metals may occur as suspended metal oxides or sulfides, or water-soluble salts which may be removed, at least in part, by filtration, water washing, desalting or other relatively simple physical means; generally, however, the metals occur as thermally stable organo-metallic complexes such as metallic porphyrins and the various derivatives thereof. A considerable quantity of the organo-metallic complexes are linked within the pentane-insoluble asphaltenic fraction, and become concentrated in the residual portion of the hydrocarbon charge stock. Some of the organo-metallic complexes are volatile, oil-soluble and are, therefore, carried over in the lighter distillate fractions. A reduction in the concentration of the organo-metallic complexes is not easily achieved, and to the extent that the crude oil or other heavy hydrocarbon charge stock becomes suitable for further processing. Notwithstanding that the concentration of these organo-metallic complexes may be relatively small in distillate oils, for example, often less than about 10 p.p.m. (calculated as if the complex existed as the elemental metal), subsequent processing techniques are often adversely affected thereby. For example, when a hydrocarbon charge stock containing organo-metallic complexes, such as the metallic porphyrins in an amount above about 3.0 p.p.m., is subjected to cracking, for the purpose of producing low-volume normally liquid components, the metals become deposited upon the catalyst, increasing in concentration as the process continues. Since vanadium and the iron-group metals tend to favor hydrogenation reactions, at the temperatures experienced in the cracking operation, the resulting contaminated cracking catalyst produces increasing excessive quantities of coke, hydrogen, and light hydrocarbon gases at the expense of more valuable liquid product. Eventually, the catalyst must be subjected to elaborate regenerative techniques, or more often be replaced with fresh catalysts.

In addition to sulfurous and nitrogenous compounds, as well as the organo-metallic complexes, petroleum crude oils, and other heavy hydrocarbonaceous material, contain high molecular weight asphaltenic compounds. These non-dissolvable, oil-insoluble coke precursors which may contain sulfur, nitrogen, oxygen and various metals. They are generally colloidal dispersed within a crude oil, and when subjected to elevated temperature, as in a vacuum distillation process, have the tendency to flocculate and polymerize, thereby making their conversion to more valuable oil-soluble products extremely difficult. Thus, in the heavy bottoms from a reduced vacuum distillation column, the polymerized asphaltenes existed as solid material even at ambient temperatures; such a product is generally useful only as road asphalt or as a low-grade fuel oil when cut back with middle-distillate hydrocarbons such as kerosene, light gas oil, etc. Furthermore, these high molecular weight asphaltenic compounds have the tendency to become immediately deposited within the reaction zone and onto the catalytic composite employed therein, in the form of a heavy hydrocarbonaceous residue. Not only does the deposition of this residue result in the relatively rapid deactivation of the catalytic composite, but constitutes a large loss of charge stock; it is, therefore, economically desirable to convert such asphaltenes into useful hydrocarbon oil fractions. With respect to the hydrorefining, or hydrotreating of hydrocarbon fractions and/or distillates, the presence of large quantities of asphaltenic compounds interferes considerably with the activity of the catalytic composite in regard to the destructive removal of the nitrogenous, sulfurous and oxygenated compounds. Therefore, it is highly desirable to produce a hydrocarbon mixture of reduced sulfur and nitrogen concentration, however, being substantially completely free from asphaltene material and organo-metallic compounds. Such a mixture is then more readily subject to further hydrorefining at sufficiently severe conditions required for a product virtually completely free from sulfur and nitrogen.

The desirability of removing the foregoing described contaminating influences from hydrocarbon mixtures is well known within the art of petroleum refining. Herefore, in the field of catalytic hydrotreating, two principal approaches have been advanced: liquid-phase hydrogenation and vapor-phase hydrocracking. In the former type of process, the oil is passed upwardly in liquid phase and in admixture with hydrogen through a fixed bed or slurry of sub-divided catalysts. Although perhaps effective in removing oil-soluble organo-metallic complexes, this type of process is relatively ineffective with respect to oil-insoluble asphaltenes which are colloiodally dispersed with-
in the charge, with the consequence that the probability of effecting simultaneous contact between the asphaltene molecule and the catalytically active sites, is remote. Furthermore, since the hydrogenation zone is maintained at an elevated temperature, the retention of unconverted asphaltenes, suspended in a liquid phase oil, in their native state, for an extended period of time, will result in flocculation and deposition upon the catalytic particles, thereby causing conversion of the remaining portion of the charge stock to become substantially more difficult and virtually impossible. The rate of diffusion of the insoluble asphaltenes is significantly lower than that of dissolved molecules of the same molecular size, as well as the other components of the hydrocarbon charge stock; for this reason, a fixed-bed process in which the oil and hydrogen are passed in a downwardly direction, is virtually precluded. The asphaltenes, being neither volatile, nor dissolved, are incapable of movement into the inner catalytically active sites, these being obviously immovable, as a result of which the asphaltenes tend to agglomerate upon the surface of the catalytic particles. Furthermore, the efficacy of hydrogen to oil contact, obtained by bubbling hydrogen through an extensive liquid body, is relatively low. On the other hand, vapor phase hydrocracking is carried out either with a fixed-bed, or an expanded-bed system at temperatures substantially above 950° F. While this technique obviates some extent the drawbacks of liquid-phase hydrogenation, it is not entirely well-suited to treating crude oil and heavy hydrocarbon fractions due to the production of coke and carbonaceous material with the result that the catalytic composite succumbs to a relatively rapid degree of deactivation; selective hydrocracking of a wide boiling range charge stock is not easily obtained, and excessive amounts of light gases are produced at the expense of an acceptable yield of the more valuable normally liquid hydrocarbons. Also, when processing a petroleum crude oil, a minimum limit on cracked gasoline production is unattainable; this is not always desirable where the end result is to maximize the production of middle and heavy distillates such as jet fuel, diesel oils, furnace oils and gas oils.

The object of the present invention is to provide a process for the hydrotreating, or hydrorefining of petroleum crude oils and other heavy hydrocarbon fractions and/or distillates of this process be conducted on a continuous basis without incurring the detrimental effects suffered by present-day methods. The process of the present invention is a combination process, and affords the opportunity to utilize a fixed-bed catalytic reaction zone, which type of process was heretofore not considered feasible due to the virtually immediate deposition of coke, the rapid deactivation of the catalytic composite employed, and the inability to convert pentane-insoluble asphaltenes.

Therefore, in a broad embodiment, the present invention relates to a process for hydrorefining a hydrocarbon charge stock, which process comprises the steps of:

(a) Admixing said charge stock with a thermally decomposable compound of a metal selected from the group consisting of the metals of Groups V-B, VI-B and the iron-group, heating the resulting mixture at a temperature less than about 310° C. and for a time sufficient to decompose said compound;

(b) Reacting the resultant colloidal suspension with hydrogen and in contact with a solid catalytic composite containing at least one metallic component selected from the metals of Groups V-B, VI-B and VIII, and.compound thereof

(c) Separating the total reaction product effluent to provide a hydrogen-rich gaseous phase and a normally liquid phase containing a sludge, recycling at least a portion of said gaseous phase to combine with said colloidal suspension; and,

(d) Separating said sludge from said liquid phase, combining a portion of said sludge with said charge stock and recovering the remainder of said liquid phase.

A more limited embodiment of the present invention involves a process for hydrorefining a hydrocarbon charge stock containing pentane-insoluble asphaltenes, which process comprises the steps of:

(a) Admixing said charge stock with from about 250 p.p.m. to about 2,500 p.p.m. of a decomposable compound of a metal selected from the group consisting of the metals of Groups V-B, VI-B, and the iron-group, and from about 1.0% to about 15.0% hydrogen sulfide, heating the resulting mixture in the absence of hydrogen, at a temperature less than about 310° C. and for a time sufficient to decompose said compound;

(b) Reacting the resulting colloidal suspension with hydrogen in a reaction zone containing a solid catalytic composite of a siliceous refractory inorganic oxide carrier material and at least one metallic component selected from the metals of Groups V-B, VI-B and VIII and compounds thereof;

(c) Separating the resulting reaction product effluent into a hydrogen-rich gaseous phase and a sludge-containing hydrorefining liquid phase, recycling a portion of said gaseous phase to combine with said colloidal suspension; and,

(d) Separating said sludge from said liquid phase, combining a portion thereof with said charge stock and hydrogen sulfide, and recovering the remainder of said hydrorefined liquid phase substantially free from pentane-insoluble asphaltenes.

In a specific embodiment, the present invention affords a process for hydrorefining an asphaltene-containing petroleum crude oil, which process comprises the steps of:

(a) Admixing said charge stock with from about 250 p.p.m. to about 2,500 p.p.m. of a decomposable organo-molybdenum compound and from about 1.0% to about 15.0% hydrogen sulfide, heating the resulting mixture in the absence of hydrogen, at a temperature less than about 310° C. and sufficient to decompose said organo-molybdenum compound;

(b) Reacting the resulting colloidal suspension with hydrogen in a reaction zone containing a catalytic composite of an alumina-silica carrier material, from about 10.0% to about 30.0% by weight of molybdenum and from about 1.0% to about 6.0% by weight of nickel, calculated as the elemental metals, at hydrorefining conditions including a temperature of from 225° C. to about 500° C. and a pressure within the range of 500 to about 5,000 pounds per square inch;

(c) Separating the resulting reaction zone effluent into a hydrogen-rich gaseous phase and a hydrorefined liquid phase containing a sludge, recycling at least a portion of said gaseous phase to combine with said colloidal suspension; and,

(d) Further separating said hydrorefined liquid phase to remove said sludge, recycling the portion of the latter to combine with said crude oil and recovering the remainder of said hydrorefined liquid phase substantially free from pentane-insoluble asphaltenes.

From the foregoing embodiments, it will be recognized that, for all intents and purposes, the present process is a two-stage process. In the first stage of the process, a minor quantity of a decomposable compound selected from the metals of Groups V-B, VI-B and the iron-group of the Periodic Table is admixed with the hydrocarbon charge stock to be processed. As the metallic compound is decomposed within the hydrocarbon charge stock, a colloidal suspension or dispersion is formed which the decomposed compound forms a complex with the asphaltene material. In the second stage of the process, the resulting colloidal suspension is brought to the desired reaction conditions, admixed with hydrogen, and passed into a fixed-bed catalytic reaction zone in which is disposed a catalytically composite of a siliceous carrier material
and metallic components selected from the metals of Groups V-B, VI-B and VII-B of the Periodic Table, and compounds thereof. A wide variety of heavy hydrocarbon fractions and/or distillates may be treated effectively through utilization of the process of the present invention. These heavy hydrocarbon oils include full boiling range crude oils, topped or reduced crude oils, atmospheric distillates, visbreaker bottoms product, tar sand oils, heavy cycle oil from thermally cracked or coker units, coker stocks, light and heavy vacuum gas oils, etc. The present process is particularly well adaptable for the hydrotreating of petroleum crude oil, and topped or reduced crude oil containing large quantities of pentane-insoluble asphaltic material and organo-metallic compounds. Exemplary of the heavy hydrocarbon fraction which may be hydrotreated in accordance with the present invention is a Wyoming sour crude oil having a gravity, *API* at 60 °F., of 23.2, and containing about 2.8% by weight of sulfur, 2,700 p.p.m. of total nitrogen, approximately 100 p.p.m. of organo-metallic compounds (calculated as if existing as the elemental metals), and about 8.4% by weight of pentane-insoluble asphaltenes. Similarly, a crude tower bottoms product, having a gravity, *API* at 60 °F., of 14.3, is contaminated by the presence of 3.1% by weight of sulfur, 3,380 p.p.m. of nitrogen, 185 p.p.m. of metals, and consists of about 10.5% by weight of pentane-insoluble asphaltic material.

Under normal circumstances, a hydrotreating process for the primary purpose of effecting the destructive removal of nitrogenous and sulfurous compounds is readily achieved; the degree of success is, of course, dependent to some extent upon the concentration of these contaminating influences. However, where the hydrocarbon charge stock is further contaminated by the inclusion therein of excessive quantities of asphaltenic compounds, the activity of the catalytic composite, especially with respect to the removal of nitrogen and sulfur, is severely hampered by the presence of the latter. Thus, it is of primary importance to convert the pentane-insoluble asphaltenes into pentane-soluble liquid hydrocarbons, while removing substantially completely all the organo-metallic contaminants, and at least partially reducing the concentration of sulfur and nitrogen.

The process is effected, as hereinabove set forth in the several embodiments, by initially dissolving the desired quantity of the decomposable compound in the hydrocarbon charge stock. An organo-metallic compound, for example molybdenum hexacarbonyl, upon admixture with the petroleum hydrocarbon charge stock, contacts the asphaltenes therein and, upon being decomposed at a temperature of from 150 °C. to about 300 °C., forms a complex therewith. Following the removal of an off-gas stream, hereinafter described, the colloidal suspension is introduced into a fixed-bed catalytic hydrotreating reaction zone wherein the asphaltenes are converted to pentane-soluble liquid hydrocarbons as a result of the unsupported catalyst component complexed therewith, the remainder of the charge stock being free to react with hydrogen upon contact with the fixed-bed of supported catalyst. The process of the present invention is readily understood upon reference to the accompanying drawing which illustrates an embodiment thereof. In the drawing, various valves, heaters, compressors, control mechanisms, etc., have been greatly reduced or entirely eliminated as not being necessary to a complete and clear understanding of the present invention. It is understood that the present invention is not limited to the embodiment so illustrated.

With reference now to the drawing, a petroleum crude oil, containing pentane-insoluble asphaltenes as well as sulfuriferous and nitrogenous materials, enters the process through line 1, and is admixed therein with a non-decomposable compound in an amount of about 250 p.p.m. to about 2,500 p.p.m. based upon the quantity of the crude oil. Prior to being raised to a temperature within the range of about 150 °C. to less than about 310 °C., and preferably below 300 °C., for the purpose of decomposing the organo-metallic compound and thereby forming a complex with the asphaltenes in the crude oil, the mixture is combined with a recycle sludge stream, entering via line 3, the source of which is hereinafter described, and hydrogen sulfide entering via line 4. The hydrogen sulfide is employed in an amount of about 1.0% to about 15.0%, based upon the concentration of asphaltenic compounds, and appears to facilitate the formation of the asphaltene complex upon decomposition of the organo-metallic compound. In any event, the mixture of crude oil, decomposable compound, recycle sludge and hydrogen sulfide continues through line 1 and heater-exchanger 5 into stripper 6. The purpose of the heat-exchanger 5 is to raise the temperature of the mixture to a temperature of about 150 °C. to about 310 °C. at which temperature the organo-metallic compound decomposes within stripper 6.

The decomposition of the organo-metallic compound should be effected 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 organo-metallic compound. The presence of free hydrogen during the decomposition has the tendency to affect detrimental the activity of the organo-metallic compound for the conversion of the pentane-insoluble asphaltenes with which it is complexed. Furthermore, in order to maintain the metallic component in its decomposed form, as a complex with the asphaltenes, it is necessary that the subsequent reaction zone be maintained substantially completely free from carbon monoxide. For example, following the decomposition of molybdenum hexacarbonyl, as well as various beta-diketone complexes, some carbon monoxide will be present in a gaseous phase. This carbon monoxide, along with excess hydrogen sulfide, is removed from the colloid suspension or dispersion in stripper 6 via line 7. The colloid suspension is then passed through heater 9, through line 10 into hydrotreating reactor 12. Heater 9 serves the purpose of raising the temperature of the charge stock containing the colloidal suspension to the operating level desired within reactor 12. The catalyst disposed in reactor 12 is maintained at a temperature within the range of from about 225 °C. to about 500 °C., and preferably at an elevated temperature within the range of about 300 °C. to about 500 °C.; the operating pressure within reactor 12, being maintained by compressive recycle of hydrogen in an amount of from about 5,000 to about 50,000 s.c.f./b. of liquid hydrocarbon charge, lies within the range of from about 500 to about 5,000 pounds per square inch. Prior to being introduced into reactor 12, the colloidal suspension in line 10 is admixed with the aforesaid quantity of hydrogen in line 11. In some instances, it may be desirable to combine the recycle hydrogen in line 11 with the colloidal suspension in line 8, in which case the mixture will pass through heater 9 in line 10 into reactor 12.

The total reaction zone effluent is removed from reactor 12 via line 13, at least a portion thereof passing through heat-exchanger 5 to raise the temperature of the fresh petroleum crude oil to the temperature at which the organo-metallic compound, added thereto via line 5, is decomposed, continuing through line 13 into separator 14. Separator 14 is operated at substantially the same pressure as reactor 12, however, at a lower temperature of about 100 °F. or below. A hydrogen-rich recycle gas stream is removed from separator 14 via line 15, is com-
bine with make-up hydrogen entering the process via line 19, and is recycled through line 11, via compressor 18, to combine with the colloidal suspension. At least a portion of the gaseous phase in line 15 is removed from the process via line 16 containing valve 17, not only for the purpose of providing pressure control over reactor 12, but also to prevent an undue accumulation of gaseous components other than hydrogen in this recycle gas stream.

The remaining portion of the total effluent from reactor 12 is removed from separator 14 via line 20, and introduced into settling tank 21. Although illustrated as a settling tank, it is understood that vessel 21 may comprise any suitable means for removing the sludge from the normally liquid product effluent entering through line 20. Thus, the liquid portion of the process effluent may be passed into a series of centrifugal separators, filters, or any combination of these with settling tanks. In any event, the metal-containing sludge is removed from settling tank 21 via line 3, at least a portion of which continues through line 3 to be combined with the fresh petroleum crude oil. It is preferred that from about 1.0% to about 20.0% by weight of the sludge be removed via lines 22 prior to recycling the remainder through line 3. Since that portion of the sludge which is removed from the process will contain a portion of the metallic component resulting from the decomposable compound originally entering via line 2, as well as some of the metallic compounds originally present in the crude, an additional quantity of the decomposable catalytic component should be recombined with the fresh crude oil in order to compensate for that quantity being removed. It will be readily ascertained that recycling the metal-containing sludge tends to decrease the total quantity of the decomposable catalyst employed, and permits recycling the asphaltenic components to extinction within the process. The metals contained in that portion of the sludge removed from the process via line 22 may also be recovered by any suitable means well known in the art, and at least a portion of those metals can be utilized in forming the complex with the asphaltic material in the fresh petroleum crude oil.

Following the sludge removal the supernatant liquid is withdrawn from settling tank 21 via line 23, and passes into fractionator 24 containing a center well 25. In the illustrated embodiment, fractionator 24 serves to further separate the hydrotreated liquid product into three main streams. Due to the character of the solid catalytic component, as well as a fixed-bed reactor 12, at least a portion of the crude oil will be converted into lower-boiling hydrocarbon products. In many instances, various select fractions of the total reaction zone product will be substantially free from all the foregoing described contaminating influences, and in other instances substantially decreased in the concentration thereof. In the illustrated embodiment, the fraction of fractionator 24 is to separate the hydrotreated liquid product effluent, following the removal of the metal-containing sludge, into a naphtha fraction containing gasoline boiling range hydrocarbons boiling at temperatures below about 425°F. to about 450°F., and leaving via line 26, a middle-distillate boiling range fraction containing those hydrocarbons boiling at temperatures within the range of from about 425°F. to about 650°F. or 700°F., and a heavier, gas oil fraction containing that portion of the product effluent which boils above a temperature of about 650°F. to about 700°F. Depending upon the precise character of the fresh hydrocarbon charge stock, as well as the desired end result, the select fractions removed from fractionator 24 via lines 2628 and 29 can be adjusted accordingly.

The decomposable compound serving as the catalytic agent which becomes complexed with the asphaltenes in the hydrocarbon charge stock, is employed in an amount of from 250 p.p.m. to about 2,500 p.p.m., based upon the weight of the charge stock. It has been found that the decomposition is facilitated in the presence of hydrogen sulfide, however, in the absence of hydrogen or other reducing atmosphere. The hydrogen sulfide is utilized in an amount within the range of from about 1.0% to about 15.0%, based upon the weight of the asphaltene material. Suitable decomposable compounds, for forming the colloidal suspension, or dispersion, are selected from the metals of Groups VI-B and VII-B of the Periodic Table. In this regard, the metals intended are those shown in the Periodic Chart of the Elements, Handbook of Physics and Chemistry, 43rd edition. Thus, suitable compounds for utilization in forming the asphaltic complex, include heteropolyacids such as phosphomolybdic acid, silicotungstic acid, phosphovanadic acid, silicomolybdic acid, phosphotungstic acid and siliconovanadic acid, organo-metallic compounds such as molybdenum blue, various carboxyls including molybdenum hexacarbonyl, tungsten hexacarbonyl, iron pentacarbonyl, molybdenum hexacarbonyl in combination with nickel formate and tungsten hexacarbonyl in combination with iron carbonyl, beta-diketone complexes including vanadium acetylacetonate, tungsten acetylacetonate, nickel acetylacetonate, molybdenum ethyl xanthate, vanadium ethyl xanthate, and various ayl-substituted and alkyl-substituted beta-diketones, various thioheteropolyacids including thiophosphoric acid, thiovanadic acid and thiotungstic acid, as well as organo-metallic sulfides of the above compounds, etc.

It is also contemplated that the catalytic agent may be the decomposition product of a combination of any two or more of the aforesaid compounds, such as molybdenum and vanadium, vanadium and nickel, molybdenum and iron, etc.

The process is effected, as hereinafter set forth, by initially dissolving the desired quantity of the organo-metallic compound in the hydrocarbon charge stock. The resulting mixture, including the added hydrogen sulfide and the recycled metal-containing sludge, is then heated at a temperature less than about 310°C. or even for a time sufficient to effect the decomposition of the organo-metallic compounds, thereby resulting in a colloidal suspension, or dispersion, of the asphaltic complex within the hydrocarbon charge stock. It is particularly preferred to carry out the decomposition in a non-reducing atmosphere, and particularly in the absence of free hydrogen, and at a temperature not above about 300°C. At higher temperatures premature cracking reactions are effected, causing an undesirable sudden increase in temperature, as well as the production of coke and light paraffinic gaseous hydrocarbons. In order to maintain the catalyst in its decomposed form, it is necessary that carbon monoxide be removed from the system. Therefore, the colloidal suspension is passed into a stripping column, or other suitable separating means, whereby the carbon monoxide may be vented from the system along with other gaseous constituents including hydrogen sulfide, nitrogen, oxygen, etc.

The mixture is then raised to the desired temperature at which the initial portion of the catalyst bed, disposed in the subsequent reaction zone, is maintained. Although the process may be effected at a catalyst bed inlet temperature within the range of from about 225°C. to about 500°C., it is preferred to employ temperatures above about 300°C., maintaining the upper limit of about 500°C. Either before or after heating the mixture to the desired temperature, the same is admixed with recycle hydrogen in an amount of from about 5,000 to about 50,000 s.c.f/b. of liquid charge, the mixture then passing into the reaction zone which is maintained under a pressure of from about 500 to about 1,000 psig, via line 20. The liquid hourly space velocity (defined as volumes of liquid hydrocarbon charge per hour per volume of catalyst disposed within the reaction zone), will lie within the range of from about 0.25 to about 5.0, the precise rate being dependent upon the physical and chemical characteristics of the charge stock.
With respect to the solid catalytic composite disposed within the fixed-bed reaction zone, it may be characterized as comprising a metallic component having hydrogenation activity, which component is combined with a refractory inorganic oxide carrier material of either synthetic or natural origin, and which carrier material has a medium to high surface area as well as well-developed pore structure. The precise composition and method of manufacturing the carrier material is not considered to be an essential feature of the present invention, although the particularly preferred carrier material, in order to have the most advantageous pore structure will have an apparent bulk density less than about 0.35 gram/cc. Suitable methods of having the requisite hydrogenation activity, are those selected from the group consisting of the metals, and compounds thereof, of Groups V–B, VI–B and VIII of the Periodic Table as indicated in the Periodic Chart of the Elements, Handbook of Physics and Chemistry, 43rd edition. Thus, the catalytic composite may comprise one or more metallic components from the group consisting of niobium, tantalum, molybdenum, tungsten, chromium, iron, cobalt, nickel, platinum, palladium, iridium, osmium, rhodium, and mixtures thereof. The catalyst may comprise any one or combination of any number of such metals, and they may exist in some combined form, such as the oxide, sulfide, element, or as a complex with the various other components of the catalytic composite. The concentration of the catalytically active metallic component, or components, is primarily dependent upon the particular metal as well as the characteristics of the charging stock. For example, the metallic components which are selected from Groups V–B and VI–B are preferably present in an amount within the range of from about 6.0% to about 30.0% by weight, and preferably from about 10.0% to about 30.0%, the iron-group metal in an amount within the range of from about 0.2% to about 10.0% by weight, and preferably from about 1.0% to about 6.0%, whereas the platinum-group metals are preferred to be present in an amount within the range of from about 0.1% to about 5.0% by weight, all of which are calculated as if the metallic components existed within the composite as the elemental metal regardless of the fact that they may be present in some combined form.

The refractory inorganic oxide carrier material may comprise alumina, silica, zirconia, magnesia, titanias, boria, sibunita, and mixtures of two or more including silica-alumina, silica-zirconia, silica-magnesia, silica-titania, alumina-zirconia, alumina-magnesia, alumina-titania, magnesia-zirconia, titania-zirconia, titania-titania, alumina-zirconia, silica-alumina-magnesia, silica-alumina-titania, silica-magnesia-zirconia, alumina-silica, magnesia-titania, etc. It is preferred to utilize a carrier material containing at least a portion of alumina, and preferably a composite of alumina and silica, with alumina being in the greater proportion. By way of specific examples, a satisfactory carrier may comprise equimolar concentrations of alumina and silica, or 63.0% by weight of alumina and 37.0% by weight of silica, or a carrier of 68.0% by weight of alumina, 10.0% by weight of silica, and 22.0% by weight of boron oxide and/or boron phosphate. In particular instances, the catalytic composite may comprise additional components including combined halogen, and particularly fluoride and/or chlorine, phosphoric and/or boric acid, etc.

The carrier material, comprising one or more refractory inorganic oxides, may be formed by any of the numerous techniques which are rather well-defined in the prior art relating thereto. Such techniques include the acid-treating of a natural clay, sand or earth, co-precipitation or successive precipitation of hydrosols to form hydrogels, which techniques are frequently coupled with one or more activating treatments including hot oil aging, steaming, drying, oxidizing, reducing, calcining, etc. The pore structure of the carrier, commonly defined in terms of surface area, pore diameter and pore volume, may be developed to specified limits by any suitable means, for example by aging the hydrosol and/or hydrogel under controlled acidic or basic conditions at any reasonable temperature, or by gelling the carrier at a particularly selected pH, or by treating the carrier with various inorganic or organic reagents. A suitable adsorbent hydrogenation catalyst adaptable for utilization in the fixed-bed reaction zone of the process of the present invention, will have a surface area of about 50 to about 700 square meters per gram, a pore diameter of about 20 to about 300 Angstroms, a pore volume of about 0.10 to about 0.80 milliliter per gram and an apparent bulk density within the range of from about 0.10 to about 0.035 gram/cc.

The catalytic composite, to be disposed in reactor 12, is prepared by initially forming an alumina-containing refractory inorganic oxide carrier material having the foregoing described characteristics. For example, an alumina-silica composite containing about 63.0% by weight of alumina is prepared by the precipitation of the respective hydrosols. The precipitated material is dried and calcined, in the form of a hydrogel is dried at a temperature of about 100°C and for a time sufficiently long to remove substantially all of the physically-held water. The dried composite is then subjected to high-temperature calcination technique in an atmosphere of air, for a period of about one hour at a temperature above about 300°C, which technique serves to remove the greater proportion of the chemically-bound water. The calcined carrier material is combined with the catalytically active metallic component, or components, through the preferred impregnation technique, either through the use of solutions of decomposable organo-metallic complexes of the metals selected from the group of the metals of Groups V–B, VI–B and VIII of the Periodic Table, or through the use of suitable water-soluble salts of these metals. Thus, the catalyst will comprise at least one metallic component selected from the group consisting of chromium, molybdenum, tungsten, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, and mixtures of two or more, etc. The preferred catalytic composite comprises molybdenum and at least one component from the metals of the iron-group. A particularly preferred catalytic composite comprises from about 10.0% to about 30.0% of weight of molybdenum and from about 1.0% to about 6.0% by weight of nickel, calculated as the elemental metals.

When utilizing water-soluble salts of the foregoing metals, suitable impregnating solutions may be prepared from molybdenum acid, ammonium molybdate, cobalt nitrate hexahydrate, cobalt chloride hexahydrate, nickel chloride hexahydrate, platonic chloride, platinosium chloride, etc. When utilizing decomposable compounds, suitable impregnating solutions include molybdenum blue, molybdenum hexacarbonyl, phosphomolybdic acid, molybdyl acetylacetonate, siliconomolybdic acid, tungsten hexacarbonyl, phosphotungstic acid, tungsten acetylacetonate, silicon tungstic acid, tungsten xanthate, nickel formate, various other carboxyls, heterocyclic material, generally in the form of organo-metallic complexes, etc. In those instances where the organo-metallic complex is not water-soluble at the desired impregnation temperature, other solvents may be employed, and include alcohols, esters, ketones, aromatic hydrocarbons, etc. The impregnated carrier material is then dried at a temperature less than about 150°C and preferably within the range of from about 100°C to about 150°C. Since there are advantages in effecting the decomposition of the decomposable organo-metallic compound in the presence of a hydrocarbon, it is preferred that the solid catalyst preparation technique involve impregnation and subsequent drying in a manner such that no decomposition of the decomposable organo-metallic compound occurs; in other words, the dry, impregnated carrier ma-
The uncalked, but dried, impregnated composite may be stored indefinitely until such time as it will be utilized in the hydrorefining process, or it may be placed immediately within the fixed-bed reaction zone. After the solid catalytic composite, containing the decomposable organo-metallic component, or components, has been placed within the reaction zone, the temperature thereof is increased to a level within the range of from about 150 °C. to about 310 °C. as the hydrocarbon charge stock, containing the colloidally dispersed catalytic material is introduced into the reaction zone. Thus, decomposition of the organo-metallic compound within and throughout the carrier material, is effected in situ in the presence of a hydrocarbon. It is preferred that the decomposition be effected in the presence of a hydrocarbon boiling substantially completely above a temperature of about 650 °F., and it is particularly preferred to utilize the charge stock which will ultimately be subjected to hydrorefining conditions during the course of the process. Since it is further advantageous to conduct the decomposition of the organo-metallic compound in the presence of hydrogen sulfide, hydrogen sulfide is supplied in an amount within the range of from about 0.01% to about 1.0% by weight, based upon the total weight of the catalytic composite disposed within the reaction zone. Notwithstanding that the process is conducted in the presence of large quantities of recycle hydrogen, it is preferred to conduct the decomposition of the organo-metallic compound in the absence of hydrogen and other well-known reducing agents. Although the precise character of the solid catalytic composite, following the decomposition in the presence of the hydrocarbon charge stock and hydrogen sulfide, is not known with accuracy, it is believed that the metal component forms a new complex with the refractory inorganic oxide components of the catalysts. In any event, this particular method of effecting the decomposition of the organo-metallic compound results in a catalytic composite having more catalytically active sites available to the partially vaporized charge stock when the process is thereafter conducted at the hydrorefining conditions hereinafter set forth.

Following the decomposition of the organo-metallic compound, hydrogen is introduced at a predetermined rate of from 5,000 to about 50,000 s.c.f./b. of hydrocarbon charge stock, and the temperature is increased to a level within the range of from about 150 °C. to about 500 °C., the pressure being increased to a level within the range of about 500 to about 5,000 pounds per square inch. The quantity of charging stock passing through the reaction zone during the decomposition of the organo-metallic complex within the refractory inorganic oxide carrier material, is not wasted, but may be recycled and introduced in the same manner as fresh hydrocarbon charge stock. The precise operating temperature and pressure, at any given instant, is at least partially dependent upon the physical and chemical characteristics of the hydrocarbon charge stock, the length of the period during which the catalyst has previously been functioning, and the desired end result. In any event, it has been found to be beneficial to operate at conditions which inhibit or totally suppress the thermal decomposition of asphaltenic material.

So the asphaltenic material enters the fixed-bed reaction zone in the form of a collooidally dispersed complex with the decomposable organo-metallic compound originally admixed with the hydrocarbon charge stock, it undergoes virtually immediate conversion into pentane-soluble, normally liquid hydrocarbons. This asphaltenic material will not, therefore, have the opportunity to become absorbed within the solid catalyst structure, thereby precluding the remaining portion of the raw charge from coming into contact with the catalytically active sites. Thus, a significantly greater number of these active sites are made available to the liquid phase portion of the charge stock, and a correspondingly greater proportion will be converted into lower-boiling, normally liquid hydrocarbons. Thus, the solid catalytic composite disposed within the reaction zone effects a dual function, the advantages of which will be readily recognized. That is, the catalytic composite effects the destructive removal of nitrogenous and sulfur compounds by converting the gas into hydrogen sulfide and ammonia and normally liquid hydrocarbons, while simultaneously producing lower-boiling hydrocarbon products which are substantially contaminant-free, and suitable for immediate use and/or direct subsequent processing. Thus, from a charge stock which boils entirely above the middle-distillate boiling range of 650 °F. to about 700 °F., there will be produced a significant quantity of both gasoline boiling range hydrocarbons having an end boiling point of about 425 °F., and middle-distillate boiling range hydrocarbons having an end point of about 650 °F., both of which fractions are substantially completely free from the contaminating in-flux of sulfurous and nitrogenous compounds. Any residual nitrogenous and sulfurous compounds, remaining in the liquid product effluent following the removal of the metal-containing sludge therefrom, will be concentrated in the higher-boiling, or gas oil fraction. This heavy gas oil fraction, generally comprising those hydrocarbons having boiling points above about 650 °F. to about 700 °F., may be subjected to further hydrorefining on one or more additional fixed-bed reaction zones. Additional advantages arise, however, when the gas oil fraction is recycled to combine with the fresh hydrocarbon charge stock either before or after the formation therein of the collooidally dispersed complex of the organo-metallic compound with asphaltenic material.

The following examples are given for the purpose of illustrating the method by which the process, encompassed by the present invention, is effected. The charge stock, temperatures, pressures, the various catalysts, range, etc., are herein presented as being exemplary only, and are not intended to limit the present invention to an extent greater than that defined by the scope and spirit of the appended claims.

The charge stock utilized for the purpose of illustrating the means by which the process of the present invention is effected, is a "topped" sour crude oil. This charge stock was obtained from the Wyoming sour crude oil previously described. The "topped" crude oil, comprising those hydrocarbons boiling above the middle-distillate boiling range, that is above a temperature of 700 °F., has a gravity, API at 60 °F., of 14.5 and contains about 3.0% by weight of sulfur, 3,900 p.p.m. of total nitrogen, and 185 p.p.m. of metallic porphyrins (calculated as elemental nickel and vanadium), the pentane-insoluble asphaltenic fraction being about 12.5% by weight. The concentration of the nickel and vanadium metals in the charge stock, and remaining in the reaction zone normally liquid product effluent, following separation of the metal-containing sludge, is determined through the utilization of spectrographic emission.

**Example 1**

This example is presented to show that the unsupported, decomposable composite admixed with the hydrocarbon charge stock forms a complex with the asphaltenic compounds contained therein. The hydrocarbon fraction utilized in this illustration was a "white oil" virtually completely devoid of organo-nickel and organo-nickel and organo-vanadium compounds, and containing less than 0.1% by weight of asphaltenic compounds. This white oil has a gravity, API at 60 °F., of 28.4, an initial boiling point of 690 °F., and a 90.0% volumetric distillation temperature of 862 °F. Phosphomolybdc acid, in an amount of 1.0 grams, was dissolved in 15.0 grams of isopropl alcohol. The resulting solution was
added dropwise to 500 grams of the white oil, accompanied by vigorous stirring with a vibromixer, and removal of the alcoholic solvent by distillation. The concentration of the phosphomolybdic acid was 0.2% by weight, or 2,000 p.p.m. As the solution was added to the white oil, the resulting mixture developed an opaque blue color; furthermore, the catalyst particles began settling virtually immediately and were easily separated from the white oil by centrifugal methods employed. These observations indicate that the white oil-phosphomolybdic acid mixture originally consisted of about 0.1% by weight of molybdenum, as if existing as the elemental metal, and that substantially all of the molybdenum appeared in the solid material which immediately settled out of the white oil.

Phosphomolybdic acid, in an amount of 25.4 grams was dissolved in 200 grams of isopropyl alcohol, the resulting solution being added dropwise to 1,000 grams of the full boiling range sour Wyoming crude oil previously described. An analysis of the resulting colloidal dispersion indicated a concentration of about 1.46% by weight of molybdenum, calculated as the elemental metal, and there was no indication of settling of solid material from the mixture. 200 grams of the crude oil-phosphomolybdic acid dispersion were subjected to centrifugal separation over a period of thirty minutes on an angle centrifuge at 3,500 r.p.m. The supernatant liquid was decanted from the centrifuged solids, the latter being treated with benzene to remove the benzene-soluble portion, then pentane washed. A total of about 2.0 grams of insoluble solids remain, which, on analysis, were found to contain 59.8% carbon and 16.5% molybdenum, indicating that the significantly greater proportion of the molybdenum, in the form of the asphaltenic complex, remained as a highly dispersed material within the crude oil. This is in direct contrast to the removal of the molybdenum component, by virtue of immediate settling, from the white oil in which no asphaltenic material was originally present.

Example II

The charge stock utilized in this example is the "topped" sour Wyoming crude oil previously described. Molybdenum hexacarbonyl, in an amount of 2.0 grams, or 2,000 p.p.m., is added with 10.0 grams of tertiary butyl mercaptan, the resulting mixture being added to 1,000 grams of the topped crude oil. In order to form the colloidal suspension in the topped crude oil, the temperature thereof is increased to a level of about 250° C., and passed into an enclosed vessel maintained at a pressure of about 1,500 p.s.i. An off gas containing carbon monoxide, hydrogen sulfide and a minor amount of light olefinic and paraffinic hydrocarbons, is vented. The resulting colloidal dispersion is admixed with hydrogen in an amount of about 25,000 s.c.f./b., the rate of the crude oil charge stock being about 100 grams per hour. The mixture is heated to a temperature of about 500° C., and passes into a reaction zone containing a fixed-bed of a catalytic composite comprising alumina, silica, nickel and molybdenum.

The catalytic composite disposed in the fixed-bed reaction zone, is a spray-dried alumina-silica carrier material comprising about 63.0% by weight of alumina. The carrier material is prepared by initially precipitating, at a constant acidic pH of about 8.0, a blend of acidulated water glass and an aluminum chloride hydrate, with ammonium hydroxide. The resulting hydrate is washed free of sodium ions, chloride ions and ammonium ions, and spray-dried. The spray-dried composite is oxidized, or calcined, in an atmosphere of air for a period of about one hour at a temperature of about 550° C. An impregnating solution is prepared by utilizing isopropyl alcohol solutions of nickel acetylacetonate and molybdenum acetylacetonate and molybdenum acetylacetonate in amounts required to produce a final catalytic composite comprising 2.0% by weight of nickel and 16.0% by weight of molybdenum, calculated as if existing within the catalytic composite as the elemental metal. The alumina-silica carrier material is impregnated with the alcoholic solution of the nickel and molybdenum complexes, and dried at a temperature of about 100° C. for a period of about two hours. The drying temperature is controlled such that sudden temperatures rises to a level above about 150° C., at which temperature the nickel and molybdenum acetylacetonates would decompose, is avoided.

The dried catalyst, having a particle size ranging from about 20 to about 150 microns, approximately 99.0% by weight thereof having a particle size less than 150 microns, is disposed as a fixed bed in a reaction zone in an amount of about 220 grams. The pressure within the reaction zone is increased to a level of about 2,000 p.s.i., utilizing a stream of nitrogen which has been heated to a temperature of about 150° C. When these conditions are reached, a nitrogen stream is admitted with the colloidal suspension of the topped crude oil and the molybdenum hexacarbonyl-asphaltene complex, and hydrogen sulfide is added in an amount of about 1.0 mole percent, based upon the nitrogen stream. The product effluent, during this period of operation in which the nickel and molybdenum acetylacetonate are being decomposed, is recycled to combine with fresh topped crude oil, while the gaseous stream from the high-pressure separator is recycled after the addition thereto of sufficient hydrogen sulfide to maintain the concentration to a level about 1.0 mole percent. After about two hours, a hydrogen stream replaces the mixture of nitrogen and hydrogen sulfide, while the temperature is increased to a level of 500° C. The normally liquid product effluent from the high-pressure separator is continuously recycled to combine with fresh feed until such time as the quantity of hydrogen being recycled is about 25,000 s.c.f./b. of liquid charge, the temperature has attained the desired operating level, and the recycle gas stream is substantially free from nitrogen.

The reaction products from the reaction zone are continuously cooled and passed into a high-pressure separator from which the liquid hydrocarbon product is removed to a receiver, the hydrogen-rich gas being removed through a water-scrubber and recycled to the reactor. In order to compensate for the quantity of hydrogen consumed within the process, and absorbed by the normally liquid product effluent, fresh hydrogen sulfide is added to the recycle gas as determined by the operating pressure within the reaction zone, in this instance, being in an amount of about 2,000 s.c.f./b.

Following the removal of the hydrogen-rich gaseous phase for internal recycle from the high-pressure separator to combine with the colloidal suspension, the remaining portion of the total reaction zone effluent is passed into a settling tank. A metal-containing sludge, consisting of about 1.0% by weight of unreacted asphaltenes as well as a portion of the metals resulting from the conversion of the high molecular weight organometallic contaminants is removed, at least in part, to combine with fresh hydrocarbon charge stock. The supernatant liquid is withdrawn and introduced into a fractionator for the purpose of recovering the desired product fractions having particular boiling ranges.

For approximately one-half of its effective, acceptable life, the alumina-silica catalytic composite will produce the necessary hydrogenation/hydrocracking reactions to produce a normally liquid product substantially free from pentane-insoluble asphaltenes, organo-metallic contaminants, and sulfuriferous and nitrogenous compounds. Thus, the normally liquid product effluent will contain less than about 0.5% by weight of pentane-insoluble asphaltene material, less than about 0.5 p.p.m. of organo-metallic compounds (calculated as elemental metals), less than about 50 p.p.m. of total nitrogen and less than about 0.5% by weight of sulfur, the gravity, ° API at 60° F., of this normally liquid product effluent being within the range.
of from about 30.0 to about 35.0. Upon separation into various boiling range fractions, it will be found that the naphtha and middle-distillate boiling range fractions are substantially completely free from the asphaltene material and organo-metallic compounds. Eventually, however, the catalyst will indicate an activity decline through an increase in the concentration of residual sulfurous and nitrogenous compounds in the normally liquid product effluent. However, since the pentane-insoluble asphaltenes and organo-metallic compounds will continue to be less than the aforesaid amounts of 0.5% by weight and 0.5 p.p.m., respectively, the operation may be continued on an economic basis notwithstanding a comparatively high concentration of residual nitrogenous and sulfurous compounds. In this situation, the normally liquid product effluent may be subjected to a second stage operation at significantly more severe conditions for the purpose of effecting the complete destructive removal of the remaining sulfurous and nitrogenous compounds. Thus, the method of the present invention is readily adaptable to a multi-stage process which, as will be recognized by those possessing skill within the art of petroleum refining, leads directly to clean gasoline and diesel oil, the latter being sufficiently decontaminated to be used immediately as diesel, jet or fuel oil.

I claim as my invention:

1. A process for hydrorefining a hydrocarbon charge stock containing asphaltenes which comprises the steps of:
   (a) admixing said charge stock with a decomposable compound of a metal selected from the group consisting of the metals from Groups V–B, VI–B and the iron-group, heating the resulting mixture, in the absence of free hydrogen, at a temperature less than about 310°C, and for a time sufficient to decompose said compound and form a colloidal suspension of said metal complexed with said asphaltenes;
   (b) reacting the resultant colloidal suspension with hydrogen and in contact with a fixed bed of a solid catalytic composite containing at least one metallic component selected from the metals of Groups V–B, VI–B and VIII, and compounds thereof, combined with a refractory inorganic oxide carrier material;
   (c) separating the total reaction product effluent to provide a hydrogen-rich gaseous phase and a hydrorefined liquid phase containing a sludge, recycling at least a portion of said gaseous phase to combine with said colloidal suspension; and,
   (d) separating said sludge from said hydrorefined liquid phase, combining at least a portion of said sludge with said charge stock and recovering the remainder of said hydrorefined liquid phase.

2. A process for hydrorefining a hydrocarbon charge stock containing pentane-insoluble asphaltenes which comprises the steps of:
   (a) admixing said charge stock with from about 250 p.p.m. to about 2500 p.p.m. of a decomposable compound of a metal selected from the group consisting of the metals of Groups V–B, VI–B, and the iron-group and from about 1.0% to about 15.0% hydrogen sulfide, heating the resulting mixture in the absence of free hydrogen, at a temperature less than about 310°C, and for a time sufficient to decompose said compound and form a colloidal suspension of said metal complexed with said asphaltenes;
   (b) reacting the resulting colloidal suspension with hydrogen in a reaction zone in contact with a fixed bed of a solid catalytic composite of a siliceous refractory inorganic oxide carrier material and at least one metallic component selected from the metals of Groups V–B, VI–B and VIII, and compounds thereof;
   (c) separating the resulting reaction product effluent into a hydrogen-rich gaseous phase and a sludge-containing hydrorefined liquid phase, recycling at least a portion of said gaseous phase to combine with said colloidal suspension; and,
   (d) separating said sludge from said liquid phase, combining a portion thereof with said charge stock and hydrogen sulfide, and recovering the remainder of said hydrorefined liquid phase substantially free from asphaltenes.

3. The process of claim 2 further characterized in that said decomposable compound is a carbonyl.

4. The process of claim 2 further characterized in that said decomposable compound is a beta-diketone complex.

5. The process of claim 2 further characterized in that said decomposable compound is a heteropoly acid.

6. The process of claim 2 further characterized in that said solid catalytic composite is an alumina-silica carrier material containing molybdenum and an iron-group metallic component.

7. A process for hydrorefining an asphaltene-containing crude oil which comprises the steps of:
   (a) admixing said charge stock with from about 250 p.p.m. to about 2500 p.p.m. of a decomposable organo-molybdenum compound and from about 1.0% to about 15.0% hydrogen sulfide, heating the resulting mixture, in the absence of free hydrogen, at a temperature less than about 310°C and sufficient to decompose said organo-molybdenum compound and form a colloidal suspension of molybdenum complexed with asphaltenes;
   (b) reacting the resulting colloidal suspension with hydrogen in a reaction zone in contact with a fixed bed of a catalytic composite of an alumina-silica carrier material, from about 10.0% to about 30.0% by weight of molybdenum and from about 1.0% to about 6.0% by weight of nickel, calculated as the elemental metals, at hydrorefining conditions including a temperature of from 225°C to about 500°C, and a pressure within the range of 500 to about 5,000 pounds per square inch;
   (c) separating the resultant total reaction zone effluent into a hydrogen-rich gaseous phase and a hydrorefined liquid phase containing a sludge, recycling at least a portion of said gaseous phase to combine with said colloidal suspension; and,
   (d) further separating said hydrorefined liquid phase to remove said sludge, recycling a portion of the latter to combine with said crude oil and recovering the remainder of said hydrorefined liquid phase substantially free from asphaltenes.

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