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**HYDROREFINING OF PETROLEUM CRUDE OIL
AND CATALYST THEREFOR****John G. Gatsis, Des Plaines, Ill., assignor to Universal Oil
Products Company, Des Plaines, Ill., a corporation of
Delaware****No Drawing. Filed Jan. 2, 1964, Ser. No. 335,353
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The invention herein described is adaptable to a process for the hydrorefining of heavy hydrocarbon fractions and/or distillates for the primary purpose of eliminating or reducing the concentration of various contaminants therein. More particularly, the present invention is directed toward a catalytic hydrorefining process for effecting, in a single operation, the substantial removal of various types of impurities from heavy hydrocarbon charge stocks, and is especially advantageous in treating 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 other heavy hydrocarbon fractions and/or distillates including black oils, heavy cycle stocks, visbreaker liquid effluent, etc., are contaminated by the presence of excessive concentrations of various non-metallic and metallic impurities which detrimentally affect various processes to which such heavy hydrocarbon mixtures may be subjected. Among the non-metallic impurities are nitrogen, sulfur and oxygen which exist as heteroatomic compounds in relatively large quantities. Nitrogen is probably most undesirable because it effectively poisons various catalytic composites which may be employed in the conversion of petroleum fractions; in particular, nitrogen and nitrogenous compounds are known to be extremely effective hydrocracking suppressors. Therefore, it is particularly necessary that nitrogenous compounds be removed substantially completely from all catalytic hydrocracking charge stocks. Nitrogenous and sulfurous compounds are further objectionable because combustion of fuels containing these impurities results in the release of nitrogen and sulfur oxides which are noxious, corrosive and present a serious problem with respect to pollution of the atmosphere. In regard to motor fuels, sulfur is particularly objectionable because of odor, gum and varnish formation and significantly decreased lead susceptibility.

In addition to the foregoing described contaminating influences, petroleum crude oils and other heavy hydrocarbonaceous material contain high molecular weight asphaltenic compounds. These are non-distillable, oil-insoluble coke precursors which may be complexed with sulfur, nitrogen, oxygen and various metals. Generally, the asphaltenic material is colloiddally dispersed within the crude oil, and, when subjected to heat, as in a vacuum distillation process, have the tendency to flocculate and polymerize whereby the conversion thereof to more valuable oil-soluble products becomes extremely difficult. Thus, in the heavy bottoms from a crude oil vacuum distillation column, the polymerized asphaltenes exist as solid material even at ambient temperatures; such a product is generally useful only as road asphalt, or as an extremely low grade fuel when cut with distillate hydrocarbons such as kerosene, light gas oil, etc.

Of the metallic contaminants, those containing nickel and vanadium are most common although other metals including iron, copper, lead, zinc, etc., are often present. These metallic contaminants, as well as others, may be present within the hydrocarbonaceous material in a variety of forms; they may exist therein as metal oxides or sulfides, introduced into the crude oil as metallic scale or particles; they may be in the form of soluble salts of such metals; usually, however, the metallic contaminants are

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found to exist as organo-metallic compounds of relatively high molecular weight, such as metallic porphyrins and the various derivatives thereof. Where the metallic contaminants are present as oxide or sulfide scale, they may be removed, at least in part, by a relatively simple filtering technique, the water-soluble salts being removable by washing and subsequent dehydration of the crude oil. A considerable quantity of the organo-metallic complexes, however, are linked with asphaltenic material and become concentrated in the residual fraction; other organo-metallic complexes are volatile, oil-soluble and are, therefore, carried over in the lighter distillate fraction. A reduction in the concentration of the organo-metallic complexes is not easily achieved, and to the extent that the crude oil, reduced crude oil, or other heavy hydrocarbon charge stock becomes suitable for further processing. Notwithstanding that the concentration of these organo-metallic compounds may be relatively small in distillate oils, for example, often less than about 10 p.p.m. (calculated as if the metallic complex existed as the elemental metal), subsequent processing techniques are adversely affected thereby. For example, when a hydrocarbon charge stock containing organo-metallic compounds, such as metal porphyrins, in amounts above about 3.0 p.p.m., is subjected to hydrocracking or catalytic cracking for the purpose of producing lower-boiling components, the metals become deposited upon the catalyst, increasing in concentration as the process continues. Since vanadium and the iron-group metals favor hydrogenation activity, at cracking temperatures, the resulting contaminated hydrocracking or cracking catalyst produces increasingly excessive quantities of coke, hydrogen and light hydrocarbon gases at the expense of more valuable normally liquid hydrocarbon products. Eventually the catalyst must be subjected to elaborate regenerative techniques, or more often be replaced with fresh catalyst. The presence of excessive quantities of organo-metallic complexes adversely affects other processes including catalytic reforming, isomerization, hydrodealkylation, etc. With respect to a process for hydrorefining, or treating of hydrocarbon fractions and/or distillates, the presence of large quantities of asphaltenic material and organo-metallic compounds interferes considerably with the activity of the catalyst with respect to the destructive removal of the nitrogenous, sulfurous and oxygenated compounds, which function is normally the easiest for the catalytic composite to perform to an acceptable degree. Therefore, it is highly desirable to produce a hydrocarbon mixture substantially free from asphaltenic material and organo-metallic compounds, and which mixture is substantially reduced with respect to nitrogen and sulfur concentration.

The necessity for the removal of the foregoing contaminating influences is well known to the possessing skill within the art of petroleum refining processes. Heretofore, in the field of catalytic hydrorefining, 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, into a fixed-bed or slurry of subdivided catalyst; although perhaps effective in removing at least a portion of oil-soluble organo-metallic complexes, this type process is relatively ineffective with respect to oil-insoluble asphaltenes which are colloiddally dispersed within the charge, with the consequence that the probability of effecting simultaneous contact between catalyst particle and asphaltene molecule is remote. Furthermore, since the hydrogenation reaction zone is generally maintained at an elevated temperature, the retention of unconverted asphaltenes, suspended in a free liquid phase oil for an extended period of time, will result in flocculation making conversion thereof substan-

tially more difficult. The rate of diffusion of the oil-insoluble asphaltenes is substantially lower than that of dissolved molecules of the same molecular size; for this reason, the fixed-bed processes, in which the oil and hydrogen are passed in a downwardly direction, are virtually precluded. The asphaltenes, being neither volatile nor dissolved in the crude, are unable to move to the catalytically active sites, the latter being obviously immovable. Furthermore, the efficiency of hydrogen to oil contact obtainable 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 expanded-bed system at temperatures substantially above about 950° F.; while this obviates to a certain extent the drawbacks of liquid-phase hydrogenation, it is not entirely well-suited to treating crude and heavy hydrocarbon fractions due to the high production of coke and carbonaceous material, with the result that the catalytic composite succumbs to relatively rapid deactivation; this requires high capacity catalyst regeneration equipment in order to implement the process on a continuous basis.

Selective hydrocracking of a full boiling range charge stock is not easily obtained, and excessive amounts of light gases are produced at the expense of the more valuable normally liquid hydrocarbon product; also, when processing a petroleum crude oil, an indeterminate minimum quantity of cracked gasoline production is unavoidable, and such a result is not desirable where the object is to maximize the production of middle and heavy distillates such as jet fuel, diesel oil, furnace oils, and gas oils.

A wide variety of heavy hydrocarbon fractions and/or distillates may be treated, or decontaminated effectively through the utilization of the process of the present invention. Such heavy hydrocarbon fractions include full boiling range crude oils, topped or reduced crude oils, atmospheric distillates, visbreaker bottoms product, heavy cycle stocks from thermally or catalytically-cracked charge stocks, heavy vacuum gas oils, etc. The present process is particularly well adaptable to the process of hydrorefining of petroleum crude oil, and topped or reduced crude oil, containing large quantities of pentane-insoluble asphaltenic material and organo-metallic compounds. A full boiling range crude oil is a preferred charge stock since the oil-insoluble asphaltenic material, being in its native environment, is colloiddally dispersed, and thus more readily converted to oil-soluble hydrocarbons. The asphaltenic material in a reduced or topped crude oil has become agglomerated to a certain extent by reason of the reboil temperature of fractionation, and is, therefore, more difficult to convert. For example, a Wyoming sour crude oil, having a gravity of 23.2° API at 60° F., not only is highly contaminated by the presence of 2.8% by weight of sulfur, 2,700 p.p.m. of total nitrogen, approximately 100 p.p.m. of metallic complexes, computed as elemental metals, but also contains a high boiling, pentane-insoluble asphaltenic fraction in an amount of 8.4% by weight. Similarly, and a much more difficult charge stock to convert into useful liquid hydrocarbons is a crude tower bottoms product having a gravity, °API at 60° F., of 14.3, and contaminated by the presence of 3.0% by weight of sulfur, 3,830 p.p.m. of total nitrogen, 85 p.p.m. of total metals and about 10.93% by weight of asphaltenic compounds. Asphaltenic material is a high molecular weight hydrocarbon mixture having the tendency to become immediately deposited within the reaction zone and other process equipment, and onto the catalytic composite in the form of a gummy, high molecular weight residue. Since this in effect constitutes a large loss of charge stock, it is economically desirable to convert such asphaltenic material into pentane-soluble liquid hydrocarbon fractions. Furthermore, the presence of excessive quantities of asphaltenes and organo-metallic contaminants appear to inhibit the activity of the catalyst

in regard to the destructive removal of sulfur and nitrogen.

In addition to the foregoing described contaminating influences, the heavier hydrocarbon fractions and or distillates contain excessive quantities of unsaturated compounds consisting primarily of high molecular weight mono- and di-olefinic hydrocarbons. At the operating conditions normally employed to effect successful hydrorefining, as well as a suitable degree of hydrocracking, the mono- and di-olefinic hydrocarbons have the tendency to polymerize and co-polymerize, thereby causing deposition of additional high molecular weight, gummy polymerization products within the process equipment and onto the catalytic composite. Similarly, in processes for effecting the catalytic hydrocracking of such heavier hydrocarbon fractions into lower-boiling hydrocarbon products, the catalytic composite becomes deactivated through carbonization effected as a result of the deposition of agglomerated pentane-insoluble asphaltenes, whereby the catalytically active centers and surfaces of the catalyst are effectively shielded from the material being processed.

The object of the present invention is, therefore, to provide a process for hydrorefining heavy hydrocarbonaceous material, and particularly full boiling range crude oils, and topped or reduced crude oils, utilizing a catalytic composite prepared in a manner which makes it particularly adaptable to the hydrorefining of such charge stocks. The present invention affords the utilization of a fixed-bed hydrorefining process, which, as hereinbefore set forth, has not been considered feasible due to the deposition of coke and other gummy carbonaceous material. Although the difficulties encountered in a fixed-bed catalytic process are at least partially solved by a moving-bed or slurry operation wherein the finely-divided catalytic composite is intimately admixed with the hydrocarbon charge stock, the mixture being subjected to the desired operating conditions, the slurry process tends to result in a high degree of erosion, thereby causing plant maintenance and replacement of process equipment to be difficult and expensive. Furthermore, the slurry operation has the disadvantage of having relatively small amounts of catalyst being admixed with relatively large quantities of asphaltenic material, since it is difficult to suspend more than a small percentage of catalyst within the crude oil. In other words, too few catalytically active sites are made available for immediate reaction, with the result that the asphaltenic material has the tendency to undergo thermal cracking which results in large quantities of light gases and coke. These difficulties are in turn at least partially avoided through the utilization of a fixed-fluidized process in which the catalytic composite is disposed within a confined reaction zone, being maintained, however, in a fluidized state by exceedingly large quantities of a fast-flowing hydrogen-containing gas stream. Difficulties attendant the fixed-fluidized type process reside in a large loss of catalyst, removed from the reaction zone with the hydrocarbon product effluent, the relatively large quantities of catalyst necessary to effect proper contact between the asphaltenic material and active catalyst sites, etc. The process of the present invention makes use of a particularly prepared hydrorefining catalyst utilizing a refractory inorganic oxide carrier material, which catalyst permits effecting the process in a fixed-bed unit without incurring the deposition of exceedingly large quantities of coke and other heavy hydrocarbonaceous material. The present process and catalyst yields a liquid hydrocarbon product which is more suitable for further processing at more severe conditions required to produce a virtually complete contaminant-free hydrocarbon product. The process of the present invention is particularly advantageous in effecting the removal of organo-metallic compounds, while simultaneously converting pentane-insoluble material into pentane-soluble liquid hydrocarbons.

In a broad embodiment, therefore, the present invention relates to a method of preparing a hydrorefining cata-

lyst which comprises the steps of: (a) initially forming a refractory inorganic oxide carrier material, and calcining said carrier material at a temperature above about 300° C.; (b) impregnating the calcined carrier material with a decomposable organo-metallic complex of a metal selected from the group consisting of the metals of Groups V-B, VI-B and VIII of the Periodic Table; (c) drying the impregnated carrier at a temperature below about 150° C. and at which temperature the decomposition of said complex is avoided; and, (d) thereafter decomposing said complex in the presence of a hydrocarbon.

Another embodiment of the present invention provides a method for preparing a hydrorefining catalyst which comprises the steps of: (a) initially forming an alumina-containing refractory inorganic oxide carrier material, and calcining said carrier material at a temperature above about 300° C.; (b) impregnating the calcined carrier material with a decomposable organo-metallic complex of a metal selected from the group consisting of the metals of Group V-B, VI-B and VIII of the Periodic Table; (c) drying the impregnated carrier material at a temperature within the range of from about 100° C. to about 150° C., and at which temperature the decomposition of said complex is avoided; and, (d) thereafter decomposing said complex at a temperature within the range of from about 150° C. to about 310° C., and in the presence of a hydrocarbon boiling at a temperature above about 650° F.

As hereinbefore set forth, the catalytic composite, prepared in accordance with the method of the present invention, is particularly advantageous in a process for hydrorefining petroleum crude oils and the heavy hydrocarbon fractions usually derived therefrom. Therefore, the present invention encompasses a process for hydrorefining a hydrocarbon charge stock, which process comprises the steps of: (a) initially contacting said charge stock with a catalytic composite of a refractory inorganic oxide and at least one decomposable organo-metallic complex of a metal selected from the group consisting of the metals of Groups V-B, VI-B and VIII of the Periodic Table; (b) decomposing said complex in the presence of hydrogen sulfide and said charge stock at a temperature above about 150° C.; (c) increasing said temperature to a level above about 310° C., and reacting said charge stock with hydrogen at a pressure greater than about 500 p.s.i.g.; and, (d) separating the total product effluent to provide a hydrorefined normally liquid product.

A more limited embodiment of the present invention affords a process for hydrorefining an asphaltene-containing crude oil which comprises the steps of: (a) initially preparing an uncalcined catalytic composite of an alumina-silica carrier material and at least one decomposable organo-metallic complex of a metal selected from the group consisting of the metals of Groups V-B, and VI-B and VIII of the Periodic Table; (b) decomposing said complex in the presence of hydrogen sulfide and said crude oil, and at a temperature within the range of from about 150° C. to about 310° C.; (c) increasing said temperature to a level of from about 310° C. to about 500° C. and reacting said crude oil with hydrogen in an amount of from about 5,000 to about 50,000 standard cubic feet per barrel and at a pressure of from about 500 to about 5,000 p.s.i.g.; and, (d) recovering a hydrorefined liquid product substantially completely free from pentane-insoluble asphaltenes.

From the foregoing embodiments, it will be noted that the process of the present invention makes use of catalytically active metallic components which are composited with a refractory inorganic oxide carrier material. It has been found that a catalyst comprising a porous, refractory inorganic oxide carrier material, having a well-developed pore structure, has the ability to absorb a substantial quantity of the high-boiling asphaltenes while maintaining its activity with respect to the removal of organo-metallic compounds and the substantial reduction in the concentration of nitrogen and sulfur. It has further

been found that converted asphaltenes, that is, asphaltenes which have been hydrorefined under mild hydrogenative-cracking conditions, are an excellent solvent for the untreated asphaltenes which are, in and of themselves, pentane-insoluble and colloiddally dispersed within the crude oil. The untreated asphaltene material is much more readily converted when initially dissolved in such a solvent than when directly treated in a dispersed phase suspended in a liquid carrier. Thus, by maintaining the fixed catalyst bed at mild hydrogenative-cracking conditions, or those which preclude the thermal cracking of asphaltene material, converted asphaltenes will dissolve the incoming unconverted asphaltenes, thereby making the latter more accessible to the catalytically active sites. This high degree of charge stock to catalyst contact is at least in part achieved through the use of a fixed-fluidized catalyst bed as hereinbefore set forth. However, as previously stated, there exists the need for relatively large volumes of catalyst, in addition to great quantities of fast-flowing hydrogen in order to maintain the catalyst in the proper fluidized state. Through the use of the catalyst of the present invention, the need for relatively large volumes of catalyst, with respect to the volume of charge stock, and exceedingly large volumes of fast-flowing hydrogen are substantially avoided. The catalyst preparation method, encompassed by the present invention, results in additional catalytically active sites being made available not only for the conversion of the incoming asphaltenes through absorption into the catalyst, but also for the destructive removal of nitrogenous and sulfurous compounds.

As above noted, the present invention broadly involves contacting a mixed phase heavy oil charge with hydrogen in the presence of an absorptive hydrogenation catalyst under comparatively mild hydrogenation-hydrocracking conditions. The mild conditions, as herein expressed, are intended to be those operating conditions which minimize the production of light gaseous hydrocarbons, coke, polymerization products, other heavy carbonaceous material, etc. Thus, the catalytic composite is disposed as a fixed bed in a reaction zone, being maintained therein at a temperature in the range of from 725° F. to about 785° F., and under an imposed pressure of from about 500 to about 5,000 pounds per square inch gauge. At these operating conditions, the thermal cracking of asphaltene material is inhibited and suppressed to the extent that the loss of liquid hydrocarbon product to gaseous waste material is significantly decreased, as is the deposition of coke and other heavy carbonaceous material. The particularly preferred operating conditions include a temperature within the range of about 750 to about 785° F. and a pressure of from about 1,000 to about 3,000 p.s.i.g. Hydrogen is employed in admixture with the charge stock in an amount of from about 5,000 to about 50,000 s.c.f./bbl. The hydrogen-containing gas stream, herein sometimes designated as "recycle hydrogen," since it is conveniently recycled externally of the hydrorefining zone, fulfills a number of various functions: it serves as a hydrogenating agent, a heat carrier, and particularly a means for stripping converted asphaltene material from the catalytic composite, thereby making still more catalytically active sites available for the incoming, unconverted asphaltene material. Furthermore, the relatively high hydrogen to hydrocarbon mol ratio decreases the partial pressure of the oil vapor and increases vaporization of the oil at temperatures significantly below those at which thermal cracking of asphaltenes is effected. The liquid hourly space velocity, herein defined as the volumes of hydrocarbon charge per hour per volume of catalyst disposed within the reaction zone, will be at least partially dependent upon the physical and chemical characteristics of the charge stock; however, the liquid hourly space velocity will normally lie within the range of from about 0.5 to about 10.0, and preferably from about 0.5 to about 3.0.

The total product effluent from the hydrorefining zone is passed into a high-pressure separator maintained at about room temperature. Normally liquid hydrocarbons are recovered from the separator, while the hydrogen-rich gaseous phase is returned to the hydrorefining zone in admixture with additional external hydrogen required to replenish and compensate for the net hydrogen consumption which may range from about 200 to about 3,000 s.c.f./bbl. of charge, the precise amount being dependent upon the characteristics of the charge stock. The recycled hydrogen-rich gas stream may be treated by any suitable means to effect the removal of ammonia and hydrogen sulfide resulting from the conversion of nitrogenous and sulfurous compounds contained within the charge stock. Furthermore, the normally liquid hydrocarbon product, removed from the high-pressure separator, may be introduced into a stripping or fractionating column, or otherwise suitably treated for the purpose of removing dissolved normally gaseous hydrocarbons, hydrogen sulfide and ammonia.

An essential feature of the present invention resides in the method employed in the preparation of the catalytic composite disposed within the reaction zone. This hydrogenation catalyst can be characterized as comprising a metallic component having hydrogenation activity, which component is composited with a refractory inorganic oxide carrier material of either synthetic, or natural origin, and which carrier material has a medium to high surface area and a 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 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., and preferably within the range of from about 0.10 to about 0.30 gram/cc. Suitable metallic components having hydrogenation activity, are those selected from the group consisting of the metals of Groups V-B, VI-B and VIII of the Periodic Table as indicated in the Periodic Chart of the Elements, Fischer Scientific Company (1953). Thus, the catalytic composite may comprise one or more metallic components from the group of vanadium, niobium, tantalum, molybdenum, tungsten, chromium, iron, cobalt, nickel, platinum, palladium, iridium, osmium, rhodium, ruthenium, and mixtures thereof. The catalyst may comprise any one or combination of any number of such metals, an essential feature being the means by which the metallic component is ultimately combined with the refractory inorganic oxide carrier material. The concentration of the catalytically active metallic component, or components, is primarily dependent upon the particular metal as well as the characteristics of the charge stock. For example, the metallic components from Groups V-B and VI-B are preferably present in an amount within the range of about 1.0% to about 20.0% by weight, the iron-group metals in an amount within the range of about 0.2% to about 10.0% by weight, whereas the platinum-group metals are preferred to be present in an amount within the range of about 0.1% to about 5.0% by weight, all of which are calculated as if the metallic component existed within the finished composite as the elemental metal.

The refractory inorganic oxide carrier material may comprise alumina, silica, zirconia, magnesia, titania, boria, strontia, hafnia, 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, magnesia-titania, silica-alumina-zirconia, silica-alumina-magnesia, silica-alumina-titania, silica-magnesia-zirconia, alumina-silica-magnesia, 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 material may comprise

equimolar quantities 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 phosphate. In particular instances, the catalytic composite may comprise additional components including combined halogen, and particularly fluorine and/or chlorine, boric and/or phosphoric acid, etc. The refractory inorganic oxide carrier material 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, coprecipitation or successive precipitation from hydrosols; these 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 ambient or elevated temperature, or by gelling the carrier at a critical pH or by treating the carrier with various inorganic or organic reagents. An absorptive hydrogenation catalyst adaptable for utilization in 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 0.35 gram/cc.

The catalyst is prepared by initially forming an alumina-containing refractory inorganic oxide material having the foregoing described characteristics. For example, an alumina-silica composite containing about 63.0% by weight of alumina is prepared by the well-known coprecipitation of the respective hydrosols. The precipitated material, generally 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 composite is then subjected to a 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 chemically-bound water.

The calcined carrier material is combined with the catalytically active metallic component, or components, through an impregnation technique whereby 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 are employed. Suitable organo-metallic compounds include molybdenum blue, molybdenum hexacarbonyl, phosphomolybdic acid, molybdiyl acetylacetonate, nickel acetylacetonate, dinitrito diamino platinum, dinitrito diamino palladium, silicomolybdic acid, tungsten hexacarbonyl, phosphotungstic acid, tungsten acetylacetonate, silicotungstic acid, tungsten ethyl xanthate, vanadium carbonyl, vanadyl acetylacetonate, phosphovanadic acid, vanadyl ethyl xanthate, vanadium esters of alcohols, vanadium esters of mercaptans, nickel formate, various other carbonyls, heteropoly acids, beta-diketone 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 about 100° C. to about 150° C. An essential feature of the catalyst preparation technique is that the impregnation and subsequent drying be carried out in a manner such that no decomposition of the organo-metallic complex occurs; in other words, the dry, impregnated carrier material will have distributed therein the decomposable organo-metallic compound.

The uncalcined, but dried, impregnated composite may

be stored indefinitely until such time as it will be utilized in the hydrotreating process, or it may be placed immediately in the reaction zone. After the 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 is introduced into the reaction zone. Thus, decomposition of the organo-metallic compound, selected as the source of the catalytically active metallic components, 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 hydrotreating conditions during the course of the process. It is further advantageous to conduct the decomposition of the organo-metallic compound in the presence of hydrogen sulfide or a compound which yields hydrogen sulfide at a temperature within the aforesaid range. Thus, a mercaptan such as tertiary butyl mercaptan may be introduced into the reaction zone in admixture with the charge stock, or the hydrogen sulfide may be supplied as such in admixture with an inert gas including nitrogen, carbon dioxide, argon, etc. The quantity of hydrogen sulfide, or mercaptan, is such that the concentration of sulfur lies 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 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 metallic component forms a new complex with the higher-boiling asphaltenic compounds and the refractory inorganic oxide components of the catalyst. 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 hydrotreating conditions hereinbefore set forth. A decomposition temperature less than about 310° C. must necessarily be observed in order to prevent an undue degree of premature thermal cracking of the catalytic composite.

Following the decomposition of the organo-metallic compound, hydrogen is introduced at a predetermined rate within the range of about 5,000 to about 50,000 s.c.f./bbl. of hydrocarbon charge stock, and the temperature is increased to a level within the range of from about 310° C. to about 500° C., the pressure being increased to a level within the range of about 500 to about 5,000 p.s.i.g. The quantity of charge stock passing through the reaction zone during the decomposition of the organo-metallic complex 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 beneficial to operate at conditions which inhibit or totally suppress the thermal cracking of asphaltenic material.

As hereinbefore set forth, the asphaltenic material which has been hydrotreated under mild hydrogenative conditions, precluding the thermal cracking thereof, is an excellent solvent for untreated asphaltenic material which, in and of itself, is pentane-insoluble and colloiddally

dispersed within the crude oil charge. At least a portion of the hydrotreated asphaltenic material will be absorbed within the catalyst structure, and will function as a solvent for unconverted asphaltenic material introduced along with the hydrocarbon charge stock. The heavier liquid phase portion of the raw charge is absorbed into the catalyst particles, dissolved in the particle-held solvent, thereby accelerating the conversion by selective hydrocracking to additional solvent. Since a significantly greater number of catalytically active sites have been made available to the charge stock, a significantly greater proportion of the incoming pentane-insoluble asphaltenic material will be converted into the more valuable pentane-soluble hydrocarbons. The recycle hydrogen stream, as hereinbefore set forth, serves to strip the converted asphaltenes from the catalyst particles virtually immediately upon the formation thereof. Thus, the pentane-soluble hydrocarbons, resulting from the conversion of the asphaltenic material, are rapidly removed from the reaction zone, thereby eliminating the danger of an accumulation of free liquid phase therein.

The following example is given for the purpose of illustrating the method by which the process, encompassed by the present invention is effected. The charge stocks temperatures, pressures, catalyst, rates, 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.

Example

The charge stock utilized in illustrating the process of the present invention is a "topped" Wyoming sour crude oil. This sour crude oil, having a gravity of 23.2° API at 60° F., is contaminated by the presence of 2.8% by weight of sulfur, approximately 2,700 p.p.m. of total nitrogen, 100 p.p.m. of metallic porphyrins (computed as if the metallic component existed as elemental nickel and vanadium), and contains a high-boiling, pentane-insoluble asphaltenic fraction in an amount of 8.39% by weight of the total crude oils. The "topped" crude oil indicates a gravity, ° API at 60° F., of 19.5, and contains 3.0% by weight of sulfur, 2,900 p.p.m. of total nitrogen, 105 p.p.m. of nickel and vanadium, the pentane-insoluble asphaltenic fraction being about 8.5% by weight.

The catalytic composite 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 aluminum chloride hydrosol, with ammonium hydroxide. The resulting hydrogel 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 utilizing isopropyl alcohol solutions of nickel 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 as the elements. 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 temperature rises to a level above about 150° C., at which temperature the complex would decompose, is avoided.

The dried catalyst, having a particle size ranging from 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, and in an amount of about 220 grams. The pressure within the reaction zone is increased to a level of 2,000 p.s.i.g., utilizing a stream of nitrogen having been heated to a temperature of about 150° C. When these conditions are reached, the nitrogen stream is admixed with the topped

crude oil and hydrogen sulfide in an amount of about 1.0 mole percent, based upon the nitrogen stream. The normally liquid hydrocarbon effluent, during this period of operation in which the nickel and molybdenum acetylacetonate are being decomposed, is recycled to combine with fresh feed, 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 of about 1.0 mole percent. After a period of about two hours, the hydrogen stream replaces the mixture of nitrogen and hydrogen sulfide, while the temperature is increased to a level of about 350° 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./bbl. of liquid charge, the temperature has attained the desired operating level within the range of about 310° C. to about 500° C., 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 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./bbl. For approximately one-half of its effective, acceptable life, the catalytic composite will promote the necessary hydrogenation/hydrocracking reactions to produce a normally liquid product substantially free from pentane-insoluble asphaltene, organo-metallic contaminants, sulfurous and nitrogenous compounds. Thus, the normally liquid product effluent will contain less than 0.5% by weight of pentane-insoluble asphaltenic material, less than 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 0.50% by weight of sulfur, the gravity, ° API at 60° F., of the liquid product effluent being within the range of about 30.0 to about 32.0. As hereinbefore set forth, the presence of excessive quantities of pentane-insoluble asphaltenes as well as organo-metallic compounds, interferes with the capability of the catalyst to effect the destructive removal of nitrogenous and sulfurous compounds. Therefore, 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 be within the previously determined range of less than 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 is 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 adapted to a multiple-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 method of preparing a hydrorefining catalyst which comprises the steps of:

- (a) initially forming a refractory inorganic oxide carrier material, and calcining said carrier material at a temperature above about 300° C.;
- (b) impregnating the calcined carrier material with a decomposable organo-metallic complex of a metal selected from the group consisting of the metals of Groups V-B, VI-B and VIII of the Periodic Table;
- (c) drying the impregnated carrier at a temperature below about 150° C., and at which temperature the decomposition of said complex is avoided;
- (d) thereafter decomposing said complex in the presence of a hydrocarbon.

2. The method of claim 1 further characterized in that said complex is decomposed at a temperature within the range of from about 150° C. to about 310° C., and in the presence of a hydrocarbon boiling at a temperature above about 650° F.

3. The method of claim 1 further characterized in that said decomposable organo-metallic complex comprises an organo-molybdenum compound.

4. The method of claim 1 further characterized in that said decomposable organo-metallic complex comprises an organo-vanadic compound.

5. The method of claim 1 further characterized in that said organo-metallic complex comprises an organo-tungstic compound.

6. A method of preparing a hydrorefining catalyst which comprises the steps of:

- (a) initially forming an alumina-containing refractory inorganic oxide carrier material, and calcining said carrier material at a temperature above about 300° C.;
- (b) impregnating the calcined carrier material with a decomposable organo-metallic complex of a metal selected from the group consisting of the metals of Groups V-B, VI-B and VIII of the Periodic Table;
- (c) drying the impregnated carrier material at a temperature within the range of from about 100° C. to about 150° C., and at which temperature the decomposition of said complex is avoided;
- (d) thereafter decomposing said complex at a temperature within the range of from about 150° C. to about 310° C., and in the presence of a hydrocarbon boiling at a temperature above about 650° F.

7. The method of claim 6 further characterized in that said decomposable organo-metallic complex comprises a carbonyl.

8. The method of claim 6 further characterized in that said decomposable organo-metallic complex comprises a heteropoly acid.

9. The method of claim 6 further characterized in that said decomposable organo-metallic complex comprises a beta diketone.

10. The method of claim 6 further characterized in that said complex is decomposed in a hydrogen sulfide-containing atmosphere.

11. The hydrorefining catalyst prepared by the method of claim 1.

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DELBERT E. GANTZ, *Primary Examiner*.

S. P. JONES, *Assistant Examiner*.