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HYDROREFINING OF PETROLEUM CRUDE OIL AND CATALYST THEREFOR

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The invention herein described is adaptable to a process for hydrorefining heavy hydrocarbon fractions and/or distillates for the primary purpose of eliminating or reducing the concentration of various contaminants contained therein. More particularly, the present invention is directed toward a fixed-bed catalytic hydrorefining process for effecting the substantially complete removal of various types of impurities from hydrocarbon charge stocks boiling above a temperature of about 650° F.; the method is especially advantageous in treating petroleum crude oils, topped or reduced crude oils, and atmospheric and vacuum tower bottoms product for the removal of sulfur and nitrogen, notwithstanding the presence therein of excessively large quantities of pentane-insoluble asphaltenic material and organo-metallic complexes.

Petroleum crude oils, and topped or reduced crude oils, as well as other heavy hydrocarbon fractions and/or distillates boiling at a temperature above about 650° F., including black oils, heavy cycle stocks, atmospheric tower bottoms, visbreaker liquid effluent, vacuum tower bottoms, etc., are contaminated by the inclusion therein of large quantities 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 generally exist as heteroatomic compounds. Of these, nitrogen is probably the 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 very effective hydrocracking suppressors. Therefore, it is particularly necessary that nitrogenous compounds be removed substantially completely from all charge stocks which are intended for hydrocracking processes. 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 as a result of pollution of the atmosphere. In regard to motor fuels, and various burner oils, sulfur is especially 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 consist in part of a high molecular weight asphaltenic fraction. The asphaltenic compounds are non-distillable, oil-insoluble coke precursors which may be complexed with sulfur, nitrogen, oxygen and various metals. Generally, the asphaltenic material is colloidally dispersed within the crude oil and, when subjected to heat as in a vacuum distillation process, has the tendency to flocculate and polymerize whereby the conversion thereof to more valuable oil-soluble hydrocarbon products becomes extremely difficult. Thus, in the heavy bottoms from a crude oil vacuum or atmospheric distillation column, the polypmerized asphaltenes exist as a semi-solid material.

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 exist

within the hydrocarbonaceous material in a variety of forms; they may appear 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 found to exist as organometallic compounds of relatively high molecular weight, such as metallic porphyrins and the various derivatives thereof. Nothwithstanding that the concentration of the organometallic 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 adversely affected thereby. When a hydrocarbon charge stock, containing organo-metallic compounds, is subjected to a hydrocracking or catalytic cracking process, for the purpose of producing lower-boiling hydrocarbon products, the metals become deposited upon the catalyst, increasing in concentration as the process continues. At elevated cracking temperatures, the resulting contaminated 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 regeneration techniques, or more often be replaced with fresh catalyst. 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 in regard 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.

The necessity for the removal of the foregoing contaminating influences is well known to those 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. However, since the hydrogenation and/or hydrocracking zones are generally maintained at an elevated temperature, above about 600° F., the retention of the uncovered asphaltenes, suspended in a free liquid-phase oil for an extended period of time, will result in flocculation making conversion thereof substantially 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, fixed-bed processes in which the oil and hydrogen are passed in a downwardly direction, have been considered virtually impractical. The asphaltenes, being neither volatile nor dissolved in the crude, are unable to move to the catalytically active sites, the latter being obviously immovable. Selective hydrocracking of a full boiling range charge stock, at temperatures substantially above 900° F. is not easily obtained, and excessive amounts of light gases are produced at the expense of the more valuable normally liquid hydrocarbon product. Also, there exists the virtually immediate deposition of coke and other heavy carbonaceous material onto the catalytic composite, thereby shielding the active surfaces and centers thereof from the material being processed.

The object of the present invention is to provide a fixed-bed process for hydrorefining heavy hydrocarbonaceous material, and particularly a full boiling range crude oil and topped or reduced crude oils, utilizing a catalyst which is particularly adaptable to the hydrorefining of such charge stocks. 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 sub-

jected to reaction and conversion at 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, this type operation has the disadvantage of having relatively small amounts of catalyst being intimately 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 resulting 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 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, and 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 system without incuring the deposition of exceedingly large quantities of coke and other heavy hydrocarbonaceous material. The present process and catalyst yields a hydrocarbon liquid product which is more suitable for further processing at more severe conditions required to produce a virtually complete contaminant-free liquid hydrocarbon product. The process of the present invention is particularly advantageous in effecting the removal of nitrogenous and sulfurous compounds, notwithstanding the presence of exceedingly large quantities of pentane-insoluble asphaltenes and organo-metallic compounds.

In a broad embodiment, the present invention relates to a hydrorefining catalytic composite comprising a refractory inorganic oxide, an absorbed hydrocarbon, and a heteropoly acid.

Another broad embodiment of the present invention involves a hydrorefining catalytic composite comprising alumina, an adsorbed hydrocarbon boiling above a temperature of about 650° F. and a heteropoly acid.

The present invention affords a method of preparing a hydrorefining catalyst, which method comprises initially forming an alumina-containing refractory inorganic oxide, adsorbing a hydrocarbon boiling above a temperature of about 650° F. therein, and thereafter impregnating said inorganic oxide with a heteropoly acid.

A more limited embodiment of the present invention involves a process for hydrorefining a crude oil which comprises reacting said crude oil with hydrogen at a temperature within the range of from about 225° C. to about 500° C. and under a pressure of from about 500 to about 5,000 p.s.i.g., in contact with a catalyst prepared by initially adsorbing a portion of said crude oil onto alumina and thereafter impregnating said alumina with a heteropoly acid.

A wide variety of heavy hydrocarbon fractions and/or distillates may be treated, or decontaminated effectively, through the utilization of the process encompassed by the present invention. Such heavy hydrocarbon fractions include full boiling range crude oils, topped or reduced crude oils, atmospheric and vacuum tower bottoms product, visbreaker bottoms product, heavy cycle stocks from thermally or catalytically-cracked charge stocks, heavy vacuum gas oils, etc. The present process is especially well adaptable to the hydroefining of a petroleum crude oil, and topped or reduced crude oils, 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 colloidally dispersed, and thus is more readily converted into oil-insoluble hydrocarbons; furthermore, the full boiling range crude does not exert as detrimental an effect upon the ability of the catalyst to remove nitrogenous and sulfurous compounds. The asphaltenic material in a reduced or topped crude oil, or atmospheric or crude tower bottoms product, has become agglomerated to a certain extent by reason of the reboil temperature of fractionation and is, therefore, more difficult to convert into pentane-insoluble hydrocarbon products. For example, a Wyoming sour crude oil, having a gravity of 23.2° API at 60° F., not only is contaminated by the presence of 2.8% by weight of sulfur, 2,700 p.p.m. of total nitrogen, and 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 about 8.4% by weight. A much more difficult charge stock to process into useful liquid hydrocarbons is a crude tower bottoms product having a gravity of 14.3° API at 60° F., contaminated by 3.0% by weight of sulfur, 3,830 p.p.m. of total nitrogen, 105 p.p.m. of total metals, and about 10.9% by weight of asphaltenic compounds. As hereinbefore set forth, 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-insoluble hydrocarbon fractions, while simultaneously effecting the removal of nitrogenous and sulfurous compounds via conversion to ammonia, hydrogen sulfide and hydrocarbons. In addition to the foregoing described contaminating influences, heavier hydrocarbon fractions and/or distillates contain excessively large quantities of unsaturated compounds consisting primarily of high molecular weight mono- and di-olefinic hydrocarbons. At the operating severity 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 the deposition of additional high molecular weight, gummy polymerization product.

As will be noted, the present invention broadly involves contacting a mixed-phase heavy oil charge stock with hydrogen in the presence of an adsorptive hydrogenation catalyst under comparatively mild hydrogenation/hydrocracking conditions. The mild conditions, as herein expressed, are those intended to minimize the production of light gaseous hydrocarbons, coke, polymerization products, other heavy hydrocarbonaceous material, etc. Thus, the catalytic composite is disposed as a fixed-bed in a reaction zone being maintained therein at a temperature within the range of from about 225° C. to about 500° C., and under an imposed pressure of from about 500 to about 5,000 p.s.ig. A preferred temperature range is from about 300° C. to about 400° C., within which the thermal cracking of asphaltenic 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 materials; similarly, the preferred operating range of pressure is from about 1,000 to about 3,000 p.s.i.g. Hydrogen is employed in admixture with the hydrocarbon charge stock in an amount of from about 5,000 to about 100,000 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, serves as a hydrogenating agent, a heat carrier, and means for

stripping converted material from the catalytic composite, thereby causing more catalytically active sites to become available for the incoming charge stock. 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 normally 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/or chemical characteristics of the charge stock; however, the 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 liquid 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 for the purpose of effecting the removal of ammonia and hydrogen sulfide resulting from the conversion of the 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.

As hereinbefore set forth, the operating conditions of the process encompassed by the present invention are selected to convert nitrogenous and sulfurous compounds into hydrocarbons, ammonia and hydrogen sulfide. In general, when processing heavy hydrocarbon charge stocks contaminated to the extent of the foregoing described crude oil and topped crude oil, significantly more severe conditions of temperature and pressure are required. That is, it is known that the destructive removal of nitrogenous compounds by conversion thereof into a hydrocarbon and ammonia is directly proportional to an increase in temperature. Through the use of the catalyst of the present invention, lower severity of operation is afforded which further tends to suppress adverse thermal cracking, and offers economical advantages over that process which is carried out at a higher level of severity. Other advantages attendant low severity operation, as compared to high severity operation, will be readily recognized by those possessing knowledge concerning petroleum refining operations and processes.

An essential feature of the present process resides in the method employed in the preparation of the catalytic composite disposed within the reaction zone. This composite 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 has a medium to high surface area in addition to a well-developed pore structure. The preferred carrier material will have an apparent bulk density less than about 0.35 gram per cc., and preferably within the range of from about 0.10 to about 0.30 gram per cc. Suitable metallic components 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 contain 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, one 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 physical and chemical 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 0.1% 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 catalytic composite as the elemental metal.

The refractory inorganic oxide 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, alumina-silica-zirconia, alumina-silica-magnesia, alumina-silica-titania, silica-magnesia-zirconia, 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, or a carrier consisting solely of alumina. 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, co-precipitation or successive precipitation from hydrosols; these techniques are frequency 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 including 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 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, as hereinabove set forth an apparent bulk density preferably within the range of from about 0.10 to about 0.30 gram/cc. It is understood that the precise physical and/or chemical characteristics of the carrier material are not considered to be limiting upon the scope of the present invention, with the exception that such carrier material have an absorbed hydrocarbon, prior to impregnation with the active metal component.

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 co-precipitation of the respective hydrosols. The precipitate material, generally in the form of a hydrogel, is dried at a temperature of about 100° C. for a time sufficiently long to re-

move 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 organometallic complexes of the metals selected from the group consisting 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, molybdyl 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 complexes are not water-soluble at the desired impregnation temperature, other solvents may be employed, and include alcohols, esters, ketones, aromatic hydrocarbons, etc. It is particularly preferred to use heteropoly acids as the source of the catalytically active metallic components, and especially heteropoly acids selected from the group consisting of phosphomolybdic acid, silicomolybdic acid, phosphotungstic acid, silicotungstic acid, phosphovanadic acid, silicovanadic acid, etc.

Prior to the impregnation of the calcined alumina-containing carried material with the desired heteropoly acid, it is an essential feature of the present invention that said carrier material contain an adsorbed hydrocarbon. As hereinafter indicated by specific example, a catalytic composite comprising an alumina-containing carrier material, initially having a hydrocarbon adsorbed therein prior to impregnation with the heteropoly acid, is significantly more active with respect to the hydrorefining of heavy hydrocarbon fractions, and particularly petroleum crude oils. The absorbed hydrocarbon is preferably one which has a boiling range substantially completely above a temperature of about 650° F. That is, a hydrocarbon fraction and/or distillate of the character of light vacuum gas oils and heavier hydrocarbon mixtures. It is particularly preferred that the absorbed hydrocarbon be substantially identical to that heavy hydrocarbon fraction and/or distillate which is to be ultimately processed in contact with the catalytic composite. Thus, where the process involves the hydroefining of a full boiling range petroleum crude oil, the absorbed hydrocarbon is preferably the crude oil. Similarly, where the hydrocarbon charge stock is a vacuum tower bottoms product, at least a portion thereof is absorbed within the carrier material prior to the impregnation thereof with the heteropoly acid. Upon impregnation, for example with phosphomolybdic acid, it is believed that the heavier components of the absorbed hydrocarbon mixture and phosphomolybdic acid form a pseudo-complex within the carrier material, the greater proportion of which appears on the surface of the catalytic composite. Conversely, impregnation of a carrier material not having an absorbed hydrocarbon, results in a more uniformly impregnated catalyst. Since asphaltenic compounds do not readily diffuse into the catalyst particle, too few catalytically active sites are available to convert the asphaltenic material into pentane-soluble hydrocarbons. In effect, not all the available catalytically active components are utilized. When the carried material is first impregnated with, or has absorbed therein, for example an atmospheric tower bottoms, the oil serves to increase the concentration of metals near the outer surface of the catalyst, where the reaction with the asphaltenes, as hereinbefore set forth, must necessarily take place. Vacuum tower bottoms product, atmospheric tower bottoms product, catalytically-cracked recycle stocks and full boiling range crude oils are preferred since they contain a sufficient quantity of high molecular weight substances required to form pseudo-complexes with the heteropoly acid near the surface of the catalytic composite. Thus, as hereinabove set forth, the preferred hydrocarbon, for absorption onto the carrier material, comprises a hydrocarbon boiling substantially completely above a temperature of about 650° F.

Following the impregnation of the carrier material with the heteropoly acid, the composite is dried at a temperature less than about 150° C. and preferably within the range of about 100° C. to about 150° C. The dried, impregnated composite may be stored indefinitely until such time as it will be utilized in the hydroening process, or it may be placed immediately within the reaction zone. After the catalytic composite 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. to effect decomposition of the heteropoly acid, selected as the source of the catalytically active metallic component thereby forming the pseudo-complex with the heavy hydrocarbon material previously absorbed within the refractory inorganic oxide. It appears to be advantageous to conduct the decomposition of the heteropoly acid 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. For this purpose, only a minor quantity of hydrogen sulfide, or mercaptan, is required, and 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. Although the precise character of the catalytic composite, following the decomposition of the organo-metallic compounds serving as the source of the catalytically active metallic component, is not known with accuracy, it is believed, as hereinbefore set forth, that the metallic component forms a pseudo-complex with the higher-boiling, high molecular weight compounds in the crude oil or other heavy hydrocarbon charge stock. In any event, the particular method of effecting the decomposition of the organo-metallic compound, in the presence of the absorbed hydrocarbon oil, results in a catalytic composite having more catalytically active sites available to the partially vaporized charge stock when the process is thereafter conducted at hydrorefining conditions hereinafter set forth. A decomposition temperature less than about 310° C. is observed in order to prevent the thermal cracking of the absorbed hydrocarbon oil prior to the formation of the complex.

Following the decomposition, hydrogen is introduced at a pre-determined rate within the range of about 5,000 to about 50,000 standard cubic feet per barrel 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 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 results. 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 hydrorefined 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 colloidally dispersed within the crude oil charge. At least a portion of

the hydrorefined asphaltenic material will function as the solvent for the unconverted asphaltenic material introduced along with the hydrocarbon charge stock. The heavier liquid phase portion of the raw charge no longer requires absorption into the catalyst particles, to be dissolved in the particle-held solvent, but is readily converted into pentane-soluble material by the additional catalytically active sites made available on or near the surface of the catalytic composite. 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 any 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 stock, temperatures, pressures, reagents, catalyst, rates, quantities, 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 hydrocarbon charge stock used to illustrate both the preparation of the novel catalytic composite, and the effectiveness thereof in reducing the concentration of pentane-insoluble asphaltenes and nitrogenous compounds, was an atmospheric tower bottoms product derived from a Wyoming sour crude oil. Analyses indicated that the atmospheric tower bottoms, having a gravity of 14.3° API at 60° F. was contaminated by 3.08% by weight of sulfur, 3,830 p.p.m. of total nitrogen, 105 p.p.m. of total metals and 10.93% by weight of pentane-insoluble asphaltenic compounds.

Two catalytic composites were prepared utilizing phosphomolybdic acid as the source of the catalytically active metallic component. The carrier material was alumina, in the form of 1/16 inch spherical particles, having an apparent bulk density of about 0.25 gram/cc. 60 grams of the alumina was placed in an evaporating dish and admixed therein with 40 grams of phosphomolybdic acid dissolved in 200 grams of ethyl acetate. The mixture was placed on a steam bath for the purpose of distilling the ethyl acetate solvent. The second catalyst was prepared in accordance with the method of the present invention, whereby 60 grams of the alumina was placed in the evaporating dish and admixed with 60 grams of the atmospheric tower bottoms dissolved in 120 grams of benzene. The mixture was placed on the steam bath to distill the benzene, after which 40 grams of phosphomolybdic acid, dissolved in 200 grams of ethyl acetate were added to the alumina containing the absorbed oil. The sample was thoroughly mixed and placed on the steam bath to distill the ethyl acetate.

The two catalytic composites were individually evaluated in an 1,800 cc. rocker-type autoclave, to which the catalytic composite and 200 grams of atmospheric tower bottoms were charged. After sealing, the autoclave was pressured to 15 atmospheres with hydrogen sulfide and to 125 atmospheres with hydrogen, thereafter being heated at a temperature of 350° C. for a period of eight hours.

Upon analysis, the liquid product resulting from the catalytic composite prepared in the absence of the absorbed hydrocarbon oil, indicated a gravity, ° API at 60° F., of 25.2, and was found to be contaminated by 896 p.p.m. of residual nitrogen and 1.62% by weight of sulfur; in addition, 1.0 grams of unconverted asphaltenic material was extracted from the used catalyst particles. The catalyst, prepared in accordance with the method of the present invention produced a liquid product having a gravity, ° API at 60° F., of 27.4, containing 78 p.p.m. of residual nitrogenous compounds and 0.51% by weight of sulfur; the quantity of asphaltenes extracted from the catalyst was indicated as a "trace." A visual comparison of the two liquid products indicated that the hydrocarbons resulting from the use of the catalyst of the present invention was virtually colorless, or water-white, whereas the hydrocarbon product resulting from the use of the catalyst prepared in the absence of the absorbed tower bottoms was considerably darker, being of a yellow-brown color. This difference in color is indicative of a significant quantity of residual pentane-insoluble asphaltenic material in the hydrorefined liquid product.

The normally liquid product effluent, resulting from the use of the catalyst of the present invention, may be subjected to a second-stage operation at significantly more severe conditions of temperature and pressure for the purpose of effecting the complete removal of the remaining sulfurous and nitrogenous compounds, in view of the fact that the pentane-insoluble asphaltenic material has been virtually completely eliminated, being less than about 0.5% by weight. 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, can be specifically designed to produce ultra-clean gasoline and diesel oil, the latter being sufficiently decontaminated to be used immediately as jet or fuel oil.

I claim as my invention:

1. A hydrorefining catalytic composite comprising a refractory inorganic oxide having formed on its surface the product resulting from the heating to a temperature of from about 150° C. to about 310° C. an adsorbed hydrocarbon boiling above a temperature of about 650° F. and a heteropoly acid.

2. A hydrorefining catalytic composite comprising alumina having formed on its surface the product resulting from the heating to a temperature of from about 150° C. to about 310° C. an adsorbed hydrocarbon boiling above a temperature of about 650° F. and a heteropoly acid.

3. The catalytic composite of claim **2** further characterized in that said heteropoly acid is phosphomolybdic acid.

4. A method for preparing a hydrorefining catalyst which comprises adsorbing on a refractory inorganic oxide a hydrocarbon boiling above a temperature of about 650° F., impregnating said inorganic oxide with a heteropoly acid and heating the resultant mixture to a temperature of from about 150° C. to about 310° C.

5. A method of preparing a hydrorefining catalyst which comprises adsorbing crude oil on an alumina-containing carrier material, thereafter impregnating said carrier material with from about 0.1% to about 20.0% by weight of a heteropoly acid, calculated as the elemental metal and heating the resultant mixture to a temperature of from about 150° C. to about 310° C.

6. The method of claim **5** further characterized in that said heteropoly acid comprises phosphomolybdic acid.

7. The method of claim **5** further characterized in that said heteropoly acid comprises silicomolybdic acid.

8. The method of claim **5** further characterized in that said heteropoly acid comprises silicotungstic acid.

9. The method of claim **5** further characterized in that said heteropoly acid comprises phosphotungstic acid.

10. A process for hydrorefining a hydrocarbon charge stock which comprises reacting said charge stock with hydrogen in contact with a catalyst prepared by adsorbing a portion of said charge stock on a refractory inorganic oxide, thereafter impregnating said inorganic oxide with a heteropoly acid and heating the resultant mixture to a temperature of from about 150° C. to about 310° C.

11. A process for hydrorefining a crude oil which comprises reacting said crude oil with hydrogen in contact with a catalyst prepared by adsorbing a portion of said crude oil on an alumina-containing carrier material,

thereafter impregnating said carrier material with a heteropoly acid and heating the resultant mixture to a temperature of from about 150° C. to about 310° C.

12. The process of claim 11 further characterized in that said crude oil is reacted with hydrogen at a temperature above about 225° C. and under a pressure of from about 500 to about 5,000 p.s.i.g.

13. A process for hydrorefining a crude oil which comprises reacting said crude oil with hydrogen at a temperature within the range of from about 225° C. to about 500° C. and under a pressure of from about 500 to about 5,000 p.s.i.g., and in contact with a catalyst prepared by initially adsorbing a portion of said crude oil onto alumina, thereafter impregnating said alumina with a heteropoly acid and heating the resultant mixture to a temperature of from about 150° C. to about 310° C.

14. The process of claim 13 further characterized in that said heteropoly acid comprises phosphovanadic acid.

15. The process of claim 13 further characterized in that said heteropoly acid comprises phosphomolybdic acid.

16. The process of claim 15 further characterized in that said heteropoly acid comprises from about 0.1% to about 20.0% by weight of phosphomolybdic acid, calculated as elemental molybdenum.

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