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PROCESS FOR HYDROREFINING PETROLEUM CRUDE OIL

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The present application is a continuation-in-part of my copending application Serial Number 286,477, filed June 10, 1963, now abandoned, all the teachings of which application are incorporated herein by specific reference thereto.

The present invention involves a novel catalytic composite which is especially adaptable for utilization in a process for hydrorefining petroleum crude oils, heavy vacuum gas oils, heavy cycle stocks, black oils, white oils, etc., as well as the heavier hydrocarbon fractions which may be derived therefrom. More specifically, the present invention affords a process for hydrorefining heavy hydrocarbon charge stocks for the primary purpose of effecting the elimination of nitrogenous and sulfurous compounds, and provides additional, unexpected advantages through the effective removal of organo-metallic contaminants, and in the conversion of the pentene-insoluble portion of such heavy hydrocarbon charge stocks into more valuable pentane-soluble hydrocarbon oils.

Petroleum crude oils, and the heavier hydrocarbon fractions and/or distillates which may be derived therefrom, generally contain nitrogenous and sulfurous compounds in relatively large quantities. In addition, petroleum crude oil is contaminated by the inclusion therein of detrimental quantities of organo-metallic contaminants having the tendency to exert deleterious effects upon a catalytic composite which is employed in various processes to which the crude oil or heavy hydrocarbon fraction may be subjected. The most common metallic contaminants are nickel and vanadium, although other metals including iron, copper, etc., may be present. These metals may occur within the crude oil in a variety of forms: they may exist as metal oxides or sulfides, introduced as metallic scale or particles; they may be present in the form of soluble salts of such metals; generally, however, they exist in the form of organo-metallic compounds, such as metal porphyrins and various derivatives thereof. Although those metallic contaminants existing in the form of oxide and/or sulfide scale, may be removed by a relatively simple washing-filtering procedure, and the water-soluble salts are at least in part removable by water-washing followed by a subsequent dehydration technique, a much more severe treatment is required to remove the organo-metallic compounds, and to the extent that the resulting crude oil or heavy hydrocarbon fraction becomes suitable for further, subsequent processing. In addition to the organo-metallic compounds, petroleum crude oils contain greater quantities of sulfurous and nitrogenous compounds than are found in the lighter hydrocarbon fractions including gasoline, kerosene, middle-distillate gas oils, etc. For example, a Wyoming sour crude having a gravity of about 23.2° API at 60° F., will contain up to about 2.8% by weight of sulfur and 2700 p.p.m. of total nitrogen. The nitrogenous and sulfurous compounds may be at least in part converted, on being subjected to a treating or hydrorefining process, into hydrocarbons, ammonia, and hydrogen sulfide, the latter being readily removed from the system in a gaseous phase. The reduction in the concentration of the organo-metallic compounds is not as easily achieved, and to the extent that the crude oil may be subjected to acceptable, further processing, particularly in a system which utilizes a catalytic composite. Notwithstanding that the total concentration of such organo-metallic compounds is relatively small, for example, often less than about 10 p.p.m., calculated as elemental metals, subsequent processing techniques will be adversely affected thereby. For example, when a topped petroleum crude oil having a concentration of organo-metallic compounds in excess of about 3.0 p.p.m., is subjected to a catalytic cracking process for the primary purpose of producing lower-boiling components, the metals become deposited upon the catalyst employed, steadily increasing in quantity until such time as the composition of the catalytic composite is changed to the extent that undesirable results are obtained. Similarly, the catalytic composite which may be utilized in a hydrorefining process, for the purpose of effecting the destructive removal of the nitrogenous and sulfurous compounds within the crude oil, experiences a composition change with a net result that the catalyst loses its required degree of activity to convert the sulfurous and nitrogenous compounds into hydrogen sulfide, ammonia and hydrocarbons. That is to say, the composition of the catalytic composite, which is closely controlled with respect to the nature of the charge stock being processed and to the desired product quality and quantity, is changed considerably as a result of the deposition of the metallic contaminants onto the catalyst; the changed composite inherently results in different catalytic characteristics, and the desired object is virtually impossible to achieve. Such an effect is undesirable with respect to the catalytic cracking process, or other processes in which a catalytic composite performs an intended function, since the deposition of metallic contaminants on such catalyst tends to result in a lesser quantity of valuable liquid product and large quantities of hydrogen and coke, the latter producing a relatively rapid degree of catalyst deactivation. The presence of organo-metallic compounds in lighter hydrocarbon charge stocks, will affect deleteriously other processes including catalytic reforming, isomerization, hydrodealkylation, hydrorefining, etc.

In addition to the organo-metallic compounds, and sulfurous and nitrogenous compounds, petroleum crude oils consist of a particular fraction which is predominantly pentane-insoluble material. For example, the Wyoming sour crude oil previously described consists of about 8.37% by weight of pentane-insoluble asphaltenes. These compounds are of a heavy hydrocarbonaceous nature, and function as coke-precursors having the tendency to become immediately deposited within the reaction zone, and onto the catalytic composite employed therein, in the form of a gummy hydrocarbonaceous residue. The deposition of this material may be considered as constituting a relatively large loss of charge stock, and it is, therefore, economically desirable to convert such asphaltenes into useful hydrocarbon oil fractions. In addition to effecting a high degree of removal of nitrogenous compounds, sulfurous compounds and virtually eliminating the organo-metallic compounds, the process of the present invention, hereinafter described in greater detail, affords the additional advantage of converting pentane-insoluble material into pentane-soluble material without incurring the relatively rapid deposition of coke and other heavy hydrocarbonaceous material. It will be readily recognized that the overall effect is to increase the volumetric yield of liquid product by the amount of insoluble asphaltenes which are converted into the more valuable pentane-soluble hydrocarbon products.

The object of the present invention is, therefore, to provide a useful process for hydrorefining heavy hydrocarbonaceous material, and particularly petroleum crude oils, through the utilization of a catalytic composite having particular physical characteristics and composition. The

process of the present invention affords the opportunity to utilize a fixed-bed hydrorefining process, 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. On the other hand, slurry processes, employing catalytically active metals deposited on a refractory inorganic oxide, suffer from the effect of having the composition changed as a result of the deposition of the metallic contaminants, and tend to result in a high degree of erosion whereby plant maintenance and replacement of process equipment becomes difficult and expensive; the present invention makes possible the use of an acceptable slurry-type process.

The present invention involves the preparation of a particular hydrorefining catalytic composite, utilizing a refractory inorganic oxide as the carrier material for the catalytically active metallic components, which catalytic composite permits effecting the hydrorefining process as a fixed-bed system, as a moving-bed process, or a slurry-type process. Through the use of this particular catalyst, the present process yields a liquid hydrocarbon product significantly more suitable for further processing without experiencing the degree of difficulties otherwise resulting from the presence of the foregoing described contaminating influences. The process of the present invention is particularly advantageous for effecting the removal of organo-metallic compounds without significant product yield loss, and simultaneously converts pentane-insoluble material into pentane-soluble liquid hydrocarbon product; the catalyst of the present invention effects a degree of removal of nitrogenous compounds heretofore unobtainable due to the difficulty which present-day hydrorefining catalysts exhibit with respect to this particularly desired function when the charge stock also contains metallic contaminants and a significant amount of asphaltenes. Furthermore, the process of the present invention results in a greater degree of conversion to lighter-boiling hydrocarbon products.

Therefore, in a broad embodiment, the present invention relates to a hydrorefining catalyst comprising at least one metallic component selected from the group consisting of the metals of Groups VI-B and VIII of the Periodic Table and compounds thereof, composited with a refractory inorganic oxide containing boron phosphate, said catalyst having an apparent bulk density less than about 0.35 gram/cc.

The catalyst described herein affords particular advantages for effecting the removal of contaminating influences from heavy hydrocarbonaceous material, and, therefore, the present invention encompasses a process for hydrorefining a hydrocarbon charge stock, which process comprises reacting said charge stock and hydrogen in contact with a catalytic composite of at least one metallic component selected from the group consisting of the metals of Groups VI–B and VIII of the Periodic Table and compounds thereof, composited with a silica-alumina carrier containing boron phosphate, said catalytic composite having an apparent bulk density less than about 0.35 gram/cc., and at a temperature above about 225° C. and at a pressure greater than about 500 p.s.i.g., and recovering a hydrorefined liquid product.

A more limited embodiment of the present invention affords a process for hydrorefining a petroleum crude oil containing pentane-insoluble asphaltenes, which process comprises reacting said crude oil and hydrogen in contact with a catalytic composite of from about 1.0% to about 6.0% by weight of nickel and from about 4.0% to about 30.0% by weight of molybdenum composited with a silica-alumina carrier, containing from about 13.0% to about 35.0% by weight of boron phosphate, said catalytic composite having an apparent bulk density less than 0.35 gram/cc., said crude oil and hydrogen being reacted at a temperature above about 225° C. and at a pressure in the range of from about 500 to about 5000 p.s.i.g., and recovering said crude oil substantially free from pentane-inosluble asphaltenes.

From the foregoing embodiments, it will be noted that the method of the present invention involves the preparation of a catalytic composite having a particular composition, utilizing those metals selected from Groups VI–B and VIII of the Periodic Table. Metals from Groups VI–B and VIII of the Periodic Table are intended to include those indicated on the Periodic Chart of the Elements published by Fisher Scientific Company, 1953, and therefore, the catalyst of the present invention may comprise one or more metals from the group of molybdenum, tungsten, chromium, iron, nickel, cobalt, the platinum-group metals, etc. As hereinafter indicated in a specific example, the preferred hydrorefining catalyst comprises at least one decomposed beta-diketone complex of particular metals from Groups VI–B and VIII. When the beta-diketone complex comprises metals from Group VI–B, it is limited to those metals having an atomic number greater than 24; beta-diketone complexes of chromium, such as chromium acetylacetonate, decompose at temperatures greater than 310° C. the maximum decomposition temperature utilized when the source of active metallic components is one or more beta-diketone complexes. Other beta-ketone complexes decompose at lower temperatures to yield a more uniform and thoroughly-impregnated catalytic composite. When the metal is selected from Group VIII of the Periodic Table, such metals will include decomposed beta-diketone complexes selected from the metals of the iron-group, and, therefore, include iron, cobalt and nickel. Notwithstanding that the process of the present invention is conducted in the presence of hydrogen, the decomposition of the beta-diketone complex, such as molybdenum acetylacetonate, is effected in the absence thereof. Depending upon the particular beta-diketone complex selected as the source of the catalytically active metallic component, the carrier material will be impregnated with such metallic component either as the elemental metal, or as a lower oxide form thereof. In any event, it is understood that the stated concentrations are computed on the basis of the elemental metals. The decomposition of the beta-diketone complex is conducted at a temperature less than about 310° C. in order to avoid initial rupture of the catalyst structure during the decomposition, and to provide thorough, uniform penetration.

An essential feature of the inventive concept embodied by the present invention resides in the physical and chemical characteristics of the hydrorefining catalytic composite. Briefly, the catalytic composite is prepared by initially forming a carrier material comprising one or more refractory inorganic oxides including alumina, silica, thoria, boria, strontia, hafnia, zirconia, etc. The preferred carrier material comprises a composite of alumina and from about 10.0% to about 90.0% by weight of silica, based upon the dry weight of alumina and silica, to which composite boron phosphate is subsequently combined. The alumina-silica carrier material may be prepared by coprecipitating the silica and alumina at a pH in the range of about 8.0 to about 10.0, or more. That is, for example, an aqueous solution of water glass may be intimately commingled with an aluminum chloride hydrosol, or other aluminum salt solution, the resulting mixture being added to a suitable alkaline precipitant, such as ammonium hydroxide, or hexamethylenetetramine, to coprecipitate the hydrogel composite of alumina and silica. The gel is subjected to a water-washing, filtering technique for the purpose of removing sodium ions, and chloride ions if the initial hydrosol comprises aluminum chloride. The hydrogel is then reslurried in an aqueous solution of phosphoric and boric acids, the latter being utilized in a mol ratio of approximately 1:1, and in a total amount to yield a finished carrier material containing from about 13.0% to about

35.0% by weight of boron phosphate, on a dry basis. Following a drying technique at a temperature within the range of about 200° F. to about 400° F., or a spray drying procedure at a higher temperature level, the boron phosphate-containing carrier material is formed into the particularly desired size and/or shape and subsequently calcined in an atmosphere of air at a temperature within the range from about 800° F. to about 1400 °F., or higher.

It has been found that a more suitable carrier material, for utilization in the preparation of a catalytic composite especially adaptable to a process for hydro-refining petroleum crude oils, is afforded when the coprecipitative reaction mixture is maintained at a pH within the range of about 8.0 to about 10.0, or higher. Although the precise change in the carrier material, as compared to that resulting from coprecipitation effected at a pH below about 8.0, and even at an acidic pH level below 7.0, is not known with accuracy, it is believed that the physical structure of the composite is more adaptable for the thorough penetration and even distribution of the catalytically active metallic components. The stated pH range may be maintained in any manner which achieves the desired result, either by commingling the entire mixture, for example, of water glass and the aluminum-containing hydrosol or solution with an excess quantity of ammonium hydroxide such that the final pH is above 8.0, or by the simultaneous, controlled addition of each stream to a vessel, the contents of which are initially in the stated pH range, the rates of each stream being controlled to maintain the pH within said range.

It has been found further that an alumina-silica carrier material, coprecipitated at a higher pH level, within the range of from about 8.0 to about 10.0 or higher, is made more effective as an integral component of a hydrorefining catalytic composite when the same has surface area characteristics indicating relatively large pore volume and pore diameter. In conjunction with high pore volume and high pore diameter, and as evidence thereof, is a relatively low apparent bulk density, expressed as grams/cc. I have now found that an unusually active hydrorefining catalyst is obtained, through the utilization of a boron phosphate-containing carrier material, when the finished catalyst has a low apparent bulk density. In the preparation of this carrier material, it is believed that the boron phosphate is best incorporated into the structure prior to the high-temperature calcination thereof and in such a manner that aluminum polyorthophosphates are formed. Thus, as hereinabove set forth, the hydrogel of alumina and silica is subjected to a filtering technique for the purpose of removing excess, physically-held water, and immediately thereafter reslurried in an aqueous solution of phosphoric and boric acids in the desired concentrations. As hereinafter indicated in a specific example, a degree of criticality appears to be attached to the quantity of boron phosphate within the final carrier materials; that is, if the boron phosphate is present in an amount either less than 13.0%, or more than 35.0% by weight, the resulting catalytic composite is less effective for the removal of contaminating influences than that catalyst in which the carrier material contains boron phosphate within the aforesaid range.

Therefore, the catalytic composite of the present invention is characterized by a carrier material containing a particular quantity of boron phosphate and has an apparent bulk density less than about 0.35 gram/cc. following the deposition of the catalytically active metallic components. As hereinabove stated, the coprecipitated alumina-silica composite affords advantages as a component of the hydrorefining catalyst when coprecipitation is effected at a pH above about 8.0, compared to a composite which has been precipitated at an acidic pH below about 7.0. However, the high-pH precipitated material results in a final catalytic composite having an apparent bulk density of about 0.65 gram/cc., and, for the purposes of the present invention, the apparent bulk density of the alumina-silica material must be at a level below about 0.35 gram/cc. This may be accomplished either during the formation of the coprecipitated reaction mixture, or after the same has been subjected to an initial drying technique for the purposes of removing the excess water of formation. For example, the apparent bulk density of the coprecipitative reaction mixture may be decreased from a level of about 0.65 gram/cc. to about 0.28 gram/cc. through the utilization of a water-extraction technique rather than the standard drying technique at a temperature within the range of 200° F. to about 400° F. The excess water is extracted from the coprecipitated material with a suitable oxygen-containing organic compound such as methanol, acetone, ethyl alcohol, propyl alcohol, iso-propyl alcohol, etc. Following the water-extraction technique, the hydrogel may then be dried at a temperature within the range of about 200° F. to about 400° F. Through the proper selection of the aluminum-containing compound utilized as the source of alumina in the formation of the coprecipitative reaction mixture, the apparent bulk density thereof will be within the desired limits. For example, the use of an aqueous solution of aluminum nitrate, in conjunction with water glass, results in a final catalytic composite having an apparent bulk density of about 0.33 gram/cc.

The catalytically active metallic components may be composited with the carrier material in any suitable manner resulting in the deposition of the desired quantity of the chosen metals. For example, combining the metallic components, with the carrier, by way of the well-known impregnating technique, results in a very effective catalyst, provided, however, that the apparent bulk density is less than 0.35 gram/cc. following the deposition of the metallic components. The impregnation of the carrier material is most readily effected through the utilization of suitable water-soluble compounds of the desired metal or metals, and such suitable compounds include, although not by way of limitation, molybdic acid, ammonium molybdate, ammonium tugnstate, nickel nitrate hexahydrate, cobalt nitrate hexahydrate, nickel chloride, cobalt chloride, etc. Where two or more metallic components are utilized, they may be incorporated in a single, or a successive impregnation with or without intermediate high-temperature calcination. The final catalytic composite will contain from about 4.0% to about 30.0% by weight of a Group VI–B metal, and from about 1.0% to about 6.0% by weight of a Group VIII metal, calculated as if the metallic components existed within the composite as the elements thereof. As previously stated, and as hereinafter indicated by specific example, a more effective catalyst results when the catalytically active metallic components are combined with the carrier material through the use of beta-diketone complexes.

The process is effected, as hereinabove defined, by reacting the petroleum crude oil, or other heavy hydrocarbon mixture, and hydrogen in contact with a catalytic composite prepared as hereinafter set forth. The charge stock and hydrogen mixture is heated to the operating temperature within the range of from about 225° C. to about 500° C., and contacts the catalyst under an imposed pressure of from about 500 to about 5000 p.s.i.g. The total reaction zone product effluent is passed into a suitable high-pressure, low-temperature separator from which a gaseous phase rich in hydrogen is removed and recycled to combine with fresh hydrocarbon charge. The remaining normally liquid product effluent is then introduced into a suitable fractionator or stripping column for the purpose of removing hydrogen sulfide and light paraffiic hydrocarbons including methane, ethane and propane. Although the normally gaseous phase from the high-pressure separator may be treated for the purpose of removing the ammonia formed as a result of the destructive removal of nitrogenous compounds, a more convenient method involves the introduction of water upstream from the high-pressure separator, removing said

water and absorbed ammonia via suitable liquid level control means disposed in said high-pressure separator.

The following examples are presented for the purpose of illustrating the beneficial effects afforded a process for the hydrorefining of petroleum crude oils, through the utilization of a catalytic composite prepared in accordance with the method hereinbefore set forth. It is understood that the present invention is not intended to be limited, beyond the scope and spirit of the appended claims, to the operating conditions, reagents and/or concentrations as utilized within the examples. The petroleum crude oil utilized was a sour Wyoming crude having a gravity, °API at 60° F., of 22.0, and contained about 2700 p.p.m. of total nitrogen, about 2.8% of sulfur (calculated as the element) and 100 p.p.m. total metals (nickel and vanadium), the pentane-insoluble asphaltenes portion being in an amount of about 8.37% by weight.

Example I

The two catalysts designated as catalysts A and B in the following Table I were evaluated, with respect to the hydrorefining of a petroleum crude oil, in an 1850 milliliter rocker-type autoclave. The tests were conducted by initially preparing a slurry of 20 grams of 60-mesh catalyst and 200 grams of the sour Wyoming crude oil, placing the mixture in the autoclave and the same to 100 atmospheres of hydrogen at room temperature. The hydrogen pressure increased to 200 atmospheres while the temperature was increased to a level of 400° C., being maintained at this level for a period of four hours. The total product effluent was subjected to centrifugal separation, the liquid portion being analyzed for the concentration of sulfurous and nitrogenous compounds remaining, and the quantity of nickel and vanadium.

Catalyst B, was prepared by commingling 3260 grams of aluminum chloride hexahydrate dissolved in 3260 milliliters of water, with 354 grams of acidified N-brand water glass diluted with 354 grams of water. The mixture was added with virgorous stirring to 3400 milliliters of ammonium hydroxide, the final pH of the precipitated mixture being 8.2. The resultant hydrogel was filtered and washed free of sodium ions at a temperature of about 190° F. The filter cake was reslurried with a phosphoric acid-boric acid solution consisting of 136 grams of boric acid in 750 milliliters of water, and 245 grams of an 87.0% by weight solution of phosphoric acid. The hydrogel slurry was then dried at a temperature of about 300° F. The surface area characteristics indicated a pore volume of 1.23 grams/cc., a pore diameter of about 125 Angstrom units and an apparent density of about 0.28 gram/cc. This carrier material consisted of 68.0% by weight of alumina, 12.0% by weight of silica and 22.0% by weight of boron phosphate. An impregnating solution was prepared utilizing 270 grams of an 85.0% by weight solution of molybdenum oxide dissolved in one liter of water and 225 milliliters of ammonium hydroxide; 95 grams of nickel nitrate hexahydrate dissolved in 85 milliliters of ammonium hydroxide completed the impregnating solution. The solution was utilized to impregnate 900 grams of the boron phosphate-containing alumina-silica carrier material hereinabove described, the resulting slurry being dried at a temperature of 250° F. and calcined in an atmosphere of air for a period of one hour at a temperature of 1100° F. The final apparent bulk density of the calcined, impregnated catalyst, containing 16.0% by weight of molybdenum and 2.0% by weight of nickel, calculated as the elements thereof, was 0.34 gram/cc.

Catalyst A was prepared in the same manner as catalyst B, with but a single exception. The source of alumina was an aluminum chloride-containing hydrosol obtained by the hydrochloric acid digestion of aluminum metal, and having the same alumina equivalent as the aluminum chloride hexahydrate employed in the preparation of catalyst B. The boron phosphate-containing carrier material indicated an apparent bulk density greater than 0.35 gram/cc., and following an impregnating procedure resulting in a catalytic composite containing 16.0% by weight of molybdenum and 2.0% by weight of nickel, calculated as the elements thereof, the apparent bulk density increased to a level of 0.73 gram/cc.

Both catalysts were subjected individually to the rocker-type autoclave test procedure hereinabove set forth. The results obtained with respect to the elimination of the contaminating influences are indicated in the following Table I:

TABLE I.—APPARENT BULK DENSITY COMPARISON

Catalyst Designation	A	B
Apparent Bulk Density, grams/cc	0.73	0.34
Liquid Product, °API at 60° F	34.5	36.8
Sulfur, wt. percent	0.06	0.10
Nitrogen, p.p.m	88.0	7.0
Nickel, p.p.m	0.12	0.04
Vanadium, p.p.m	0.16	0

Upon reference to the data presented in Table I, it will be readily ascertained that the catalyst prepared in accordance with the method of the present invention affords a much more attractive process for the hydrorefining of petroleum crude oils. The concentration of nitrogenous compounds was decreased from 88 p.p.m. to 7 p.p.m., while the total quantity of metals (nickel and vanadium) was decreased from 0.28 p.p.m. to 0.04 p.p.m. Of further significance is the fact that the liquid product effluent exhibited an API gravity, at 60° F., of 36.8 as compared to the 34.5 resulting from the utilization of catalyst A. This is indicative of the production of a greater quantity of lower-boiling hydrocarbon products, and particularly the conversion of pentane-insoluble asphaltenes into pentane-soluble hydrocarbon products.

Example II

The additional catalysts were prepared utilizing an aluminum chloride salt solution prepared from aluminum chloride hexahydrate dissolved in water and N-brand water glass, the mixture being coprecipitated with ammonium hydroxide, filtered and subjected to a washing technique to remove sodium ions. The resulting hydrogel was dried at a temperature of 250° F. for a period of about 12 hours, the dried hydrogel being separated into three individual portions. Each portion of the hydrogel was then reslurried with a phosphoric acid-boric acid crystal solution of a concentration such that catalyst C contained 12.0% by weight of boron phosphate, catalyst D contained 22.0% by weight of boron phosphate and catalyst E contained 36.0% by weight thereof. Each portion of the boron phosphate-containing carrier material was impregnated with a solution of molybdic acid and nickel nitrate hexahydrate of sufficient quantity to result in the deposition of 16.0% by weight of molybdenum and 2.0% by weight of nickel, calculated as the elements thereof, within each of the three catalyst portions. Each of the impregnated carrier materials was dried for a period of two hours at a temperature of 250° F., and thereafter oxidized in an atmosphere of air for a period of one hour at a temperature of 1100° F.

Each catalyst portion was individually subjected to the rocker-type autoclave test procedure previously described with respect to the foregoing Example I. The results of the analyses performed on the liquid product effluent are given in the following Table II:

TABLE II.—CONCENTRATION OF BORON PHOSPHATE

Catalyst Designation	C	D	E
Boron Phosphate, wt. percent	12.0	22.0	36.0
Liquid Product Gravity, °API	35.3	35.8	33.9
Sulfur, wt. percent	0.06	0.06	0.11
Total Nitrogen, p.p.m	78.0	34.0	152.0
Pentane-insolubles, wt. percent	0.18	0.10	0.21

As noted in the foregoing Table II, the three catalysts portions contain varying quantities of boron phosphate; catalyst C, containing 12.0% by weight of boron phosphate resulted in a total nitrogen content of 78 p.p.m., and catalyst E a total nitrogen content of 152 p.p.m. Both of these catalysts contain quantities of boron phosphate outside the limits imposed on the concentration thereof within the alumina-silica composite. Catalyst D, containing 22.0% by weight of boron phosphate within the carrier material, resulted in a liquid product effluent having a total nitrogen content significantly less than either of the other catalysts. Furthermore, catalyst D, produced a liquid product having fewer pentane-insoluble asphaltenes and, as evidenced by the increased gravity in °API, a greater concentration of lower-boiling hydrocarbon products. The seeming discrepancy between the total nitrogen concentrations with respect to catalysts B and D results from the use of boric acid crystals in the preparation of the latter, whereas boric acid powder was used to prepare the former. However, the comparison of catalysts C, D and E is valid since all three were prepared using the crystals of boric acid.

The foregoing specification and specific examples indicate clearly the inventive concept embodied by the present invention, and the unusual benefits afforded a process for the hydrorefining of petroleum crude oils and the heavier hydrocarbon fractions derived therefrom.

I claim as my invention:

1. A process for hydrorefining a hydrocarbon charge stock containing organo-metallic and asphaltene contaminants for the removal of such contaminants therefrom, which comprises reacting said charge stock and hydrogen at a temperature above about 225° C. and a pressure greater than about 500 p.s.i.g. in contact with a catalytic composite of boron phosphate and at least one metallic component selected from the group consisting of the metals of Groups VI–B and VIII of the Periodic Table and compounds thereof, composited with alumina and silica coprecipitated at a pH of at least about 8.0 from aqueous water glass and aluminum salt solutions, said catalytic composite having an apparent bulk denisty less than about 0.35 gram/cc., and recovering a hydrorefined liquid product.

2. The process of claim 1 further characterized in that said charge stock and hydrogen are reacted at a temperature within the range of from about 225° C. to about 500° C. and under an imposed pressure of from about 500 to about 5000 p.s.i.g.

3. The process of claim 1 further characterized in that said boron phosphate is in the amount of from about 13.0% to about 35.0% by weight of the coprecipitated alumina and silica.

4. The process of claim 1 further characterized in that said metallic component comprises from about 1.0% to about 6.0% by weight of nickel and from about 4.0% to about 30.0% by weight of molybdenum.

5. The process of claim 1 further characterized in that said catalytic composite has an apparent bulk density of from about 0.15 to about 0.35 gram/cc.

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