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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 the hydrorefining of heavy hydrocarbon fractions and/or distillates for the primary purpose of eliminating or reducing a concentration of various contaminants. More particularly, the present invention is directed toward a catalytic hydrorefining process for effecting the substantially complete removal of various types of impurities from hydrocarbon charge stocks boiling at a temperature above 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 compounds.

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 excessive quantities of various non-metallic and metallic impurities which detrimentally effect 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 extremely effective hydrocracking suppressors. Therefore, it is particularly necessary that nitrogenous compounds be removed substantially completely from all charge stocks intended for hydrocracking processes. Nitrogenous and sulfurous compounds are further objectionable because combustion of the 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 and various burner oils, 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 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 colloiddally 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 products becomes extremely difficult. Thus, in the heavy bottoms from a crude oil vacuum or atmospheric distillation column, the polymerized asphaltenes exist as a semi-solid material even at ambient temperatures.

Of the metallic contaminants, those containing nickel and vanadium are most common, although other metals including iron, copper, lead, zinc, etc., are often present.

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These metallic contaminants, as well as others, may exist within the hydrocarbonaceous material in a variety of forms; 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 organo-metallic compounds of relatively high molecular weight, such as metallic porphyrins and the various derivatives thereof. A reduction in the concentration of the organo-metallic complexes is not as easily achieved as is a reduction in the quantity of nitrogenous, sulfurous and oxygenated compounds, 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 the organo-metallic complexes may be relatively small in distillate oils, for example often less than about 10 p.p.m. (calculated as if the complex existed as the elemental metal), subsequent processing techniques are adversely affected thereby. When a hydrocarbon charge stock, containing organo-metallic compounds, is subjected to hydrocracking or catalytic cracking, for the purpose of producing lower-boiling hydrocarbon products, 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 elevated 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. 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 unconverted 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 amount 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 proc-

ess for hydrotreating heavy hydrocarbonaceous material, and particularly a full boiling range crude oil and topped or reduced crude oils, utilizing a catalytic composite which is particularly adaptable to the hydrotreating of such charge stocks. The present invention affords the utilization of a fixed-bed hydrotreating process, which, as hereinbefore set forth, has not been considered feasible due to the virtually immediate 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 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 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 hydrotreating catalyst utilizing a refractory inorganic oxide carrier material, which catalyst permits effecting the process in a fixed-bed system without incurring the deposition of exceedingly large quantities of coke and other heavy hydrocarbonaceous material. The present process and catalyst yield a liquid hydrocarbon 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 sulfur compounds, notwithstanding the presence of exceedingly large quantities of pentane-insoluble asphaltenes and organo-metallic compounds.

In a broad embodiment, therefore, the present invention relates to a process for removing sulfur and nitrogen from a heavy hydrocarbon charge stock containing pentane-insoluble asphaltenes, which process comprises reacting said charge stock with hydrogen in the presence of a catalyst containing the decomposition product of a mixture of a heteropoly acid and nickelous sulfate, and at conditions selected to convert nitrogenous and sulfur compounds into hydrocarbons, ammonia and hydrogen sulfide.

Another broad embodiment of the present invention involves a process for removing sulfur and nitrogen from a hydrocarbon charge stock boiling at a temperature above about 650° F. and containing pentane-insoluble asphaltenes, which process comprises reacting said charge stock 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 5,000 p.s.i.g., said conditions selected to convert nitrogenous and sulfur compounds into hydrocarbons, hydrogen sulfide and ammonia; the process further characterized in that said charge stock and hydrogen are reacted in the presence of a catalytic compo-

site of an alumina-containing refractory inorganic oxide and the decomposition product of a heteropoly acid and nickelous sulfate.

A more limited embodiment of the present invention is directed toward a process for removing sulfur and nitrogen from a petroleum crude oil fraction boiling at a temperature above about 650° F., and containing pentane-insoluble asphaltenes, which process comprises reacting said crude oil fraction with hydrogen at a temperature within the range of from about 225° C. to about 500° C. and under a pressure within the range of from about 500 to about 5,000 p.s.i.g., said conditions selected to convert nitrogenous and sulfur compounds into hydrocarbons, ammonia and hydrogen sulfide; the process being further characterized in that said crude oil fraction and hydrogen are reacted in the presence of a catalytic composite of alumina and the decomposition product of phosphomolybdic acid and nickelous sulfate formed at a temperature less than about 310° C.

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 a process of hydrotreating 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 colloidal 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 to remove nitrogenous and sulfur 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-soluble hydrocarbon products. 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 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., and 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-soluble liquid hydrocarbon fractions, in addition to effecting the destructive removal of nitrogenous and sulfur compounds. 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 hydrotreating, as well as a suitable degree of hydrocracking, the mono- and di-olefinic hydrocarbons have the tendency to polymerize and co-

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polymerize, thereby causing the deposition of additional high molecular weight, gummy polymerization products.

As will be 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 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.i.g. 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 products to gaseous waste material is significantly decreased, as is the deposition of coke and other heavy carbonaceous material; 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 hydrotreating zone, serves as a hydrogenating agent, a heat carrier, and a means for stripping converted material from the catalytic composite, thereby creating more catalytically active sites 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 hydrotreating 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 hydrotreating 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 to effect the same degree of decontamination. That is, it is known that the destructive removal of nitrogenous compounds by conversion into a hydrocarbon and ammonia is directly proportional to an increase in temperature.

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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 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 has a medium to high surface area in addition to 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 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. Although the catalyst may contain any one or combination of any number of such metals, an essential feature of the present invention is that the catalytically active metallic component on the finished catalyst comprise the decomposition product of nickelous sulfate and at least one organo-metallic compound of the metals listed above and particularly, as hereinafter specified, a heteropoly acid. 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 Group 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 in the range of 0.1% to about 5% 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 example, 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 material consisting solely of alumina. The 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 are frequently cou-

pled 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 hydrogen under controlled acidic or basic conditions at ambient or elevated temperature, or by gelling the carrier at a critical pH or by treating carrier with various inorganic and organic reagents. An adsorptive 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 per cc.

The catalyst is prepared by initially forming an alumina-containing refractory inorganic oxide having the foregoing described characteristics. For example, an alumina-silica composite containing about 63.0% by weight of alumina may be prepared by 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 the chemically-bound water. Where the carrier material is to consist solely of alumina, the same may be prepared from an aluminum chloride hydrosol by the well-known oil-drop method as set forth in U.S. Patent No. 2,620,314, issued to James Hokestra. The calcined carrier material is combined with the catalytically active metallic component or components through an impregnation technique whereby a solution 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. Heteropoly acids including silicomolybdic acid, silicotungstic acid, silicovanadic acid, phosphomolybdic acid, phosphotungstic acid, phosphovanadic acid, and mixtures thereof, are particularly preferred. As hereinafter indicated by specific example, the impregnating solution, comprising one or more of the foregoing heteropoly acids, is supplemented with from about 5.0% to about 25.0% by weight of nickelous sulfate, based upon the quantity of the heteropoly acid and calculated as the hexahydrate. Following the impregnation technique, the carrier material is dried at a temperature of about 100° C., and thereafter subjected to a calcination treatment at a temperature of from about 100° C. to about 310° C. for the purpose of forming the decomposition product of the heteropoly acid nickelous sulfate. Other suitable organo-metallic compounds, in addition to the heteropoly acids, include molybdenum blue, molybdenum hexacarbonyl, molybdyl acetylacetonate, nickel acetylacetonate, dinitritodiamino platinum, dinitritodiamino palladium, tungsten hexacarbonyl, tungsten acetylacetonate, tungsten ethyl xanthate, vanadium carbonyl, vanadyl acetylacetonate, 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, paraffinic hydrocarbons, etc.

As hereinbefore set forth, the alumina-containing carrier material is impregnated with a solution of nickelous sulfate and a heteropoly acid, for example phosphomolybdic acid. Following the drying of the composite, to remove physically-held water, a calcination treatment, at a temperature less than about 310° C. is effected for the

purpose of forming the decomposition product within and throughout the alumina structure. Although the precise character of the catalytic composite, following the formation of the decomposition product of nickelous sulfate and phosphomolybdic acid, is not known with accuracy, it is believed that the decomposition product forms an involved complex with the alumina structure by displacing at least a portion of the hydroxyl groups thereof. In any event, as hereinafter set forth by specific example, I have found that the utilization of other nickelous salts, in conjunction with the heteropoly acid, do not yield acceptable results. In fact, the difference in results are of such degree as to lead to the conclusion that the decomposition product is not formed, and does not become complexed with the alumina-containing carrier material as when nickelous sulfate is utilized.

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, catalytic composite, 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 was an atmospheric "topped" Wyoming sour crude oil. The "topped" crude oil, upon analysis, indicated a gravity of about 14.5° API at 60° F., and contained about 3.0% by weight of sulfur, 3,830 p.p.m. of total nitrogen, approximately 105 p.p.m. of nickel and vanadium (existing as metallic porphyrins), the pentane-insoluble asphaltenic fraction being about 10.9% by weight.

Four catalysts were prepared, each utilizing 60 grams of a carrier material consisting solely of alumina, and having an apparent bulk density of about 0.25 gram per cc. With the exception of the compounds utilized as the source of the catalytically active metallic component, all the catalysts were prepared in the identical manner. An impregnating solution, containing the desired quantities of the catalytically active metallic components, was initially prepared and admixed with a 60-gram portion of the alumina sphere; the impregnated spheres were dried over a steam bath for the purpose of removing the solvent employed in preparing the impregnating solution, and thereafter calcined at a temperature of about 250° C.

In all cases, the catalyst and 200 grams of the atmospheric tower bottoms hereinabove described, were placed in an 1800 cc. rocker-type autoclave, initially pressured to 15 atmospheres with hydrogen sulfide, then to 125 atmospheres with hydrogen, the contents being heated to a temperature of 350° C., which temperature was maintained for a period of eight hours. The relative activity of each catalyst was determined by the degree to which nitrogenous compounds were removed through conversion to hydrocarbons and ammonia. Since nitrogen removal is a direct function of temperature, the conditions were selected, utilizing a relatively low reaction temperature, in order to emphasize the varying catalytic activity, without incurring an abnormally high degree of thermal cracking. After eight hours in the rocking autoclave, the contents were allowed to cool to room temperature, the autoclave was depressured, and the normally liquid hydrocarbon separated from the catalyst and analyzed to determine the residual concentration of nitrogenous compounds, sulfurous compounds and the gravity, ° API at 60° F.

The first catalyst was prepared by dissolving 40 grams of phosphomolybdic acid in 200 grams of ethyl acetate, the resulting impregnating solution being admixed with 60 grams of 20-mesh alumina. The mixture was placed on a steam bath for drying and removal of the ethyl acetate solvent, and subsequently calcined.

The second catalyst utilized an impregnating solution consisting of 40 grams of phosphomolybdic acid dissolved

in 150 grams of methyl alcohol and 5.2 grams of nickel chloride dissolved in 100 grams of methyl alcohol. The phosphomolybdic acid-nickel chloride solution was added to the 60 grams of alumina, thoroughly mixed therewith and placed on the steam bath to remove the methyl alcohol solvent and physically-held water, and subsequently calcined.

The third catalyst was prepared utilizing an impregnating solution consisting of 40 grams of phosphomolybdic acid dissolved in 200 grams of ethyl acetate and 12.5 grams of nickel iodide dissolved in 250 grams of ethyl acetate. As above, the mixture was placed in an evaporating dish over a steam bath to remove the ethyl acetate solvent, the thus dried composite then being calcined.

The fourth catalyst, comprising phosphomolybdic acid and nickelous sulfate in accordance with the present invention, was prepared by initially forming an impregnating solution containing 40 grams of phosphomolybdic acid dissolved in 150 grams of methyl alcohol and 11 grams of nickelous sulfate hexahydrate dissolved in 100 grams of methyl alcohol. The impregnating solution was thoroughly mixed with 60 grams of the 20-mesh alumina and placed on a steam bath for the purpose of removing the methyl alcohol solvent; the dried, impregnated catalyst was then calcined as hereinbefore set forth.

All four catalyst samples were subjected to the 8-hour rotating-autoclave test utilizing 200 grams of the atmospheric tower bottoms. The results of the analyses performed upon the normally liquid product effluent from each test are presented in the following table.

TABULATED DATA

Catalyst	°API	Nitrogen, p.p.m.	Sulfur, wt. percent
Phosphomolybdic Acid.....	25.2	896	1.62
Nickel Chloride.....	27.0	120	0.55
Nickel Iodide.....	27.6	77	0.51
Nickelous Sulfate.....	30.3	14	0.28

Upon reference to the data indicated in the above table, it will be noted that the catalyst containing only phosphomolybdic acid resulted in a normally liquid product effluent having 896 p.p.m. of residual nitrogen and 1.62% by weight of residual sulfur, notwithstanding an increase in gravity, degrees API at 60° F., to 25.2. Although some improvement resulted through the use of either nickel chloride or nickel iodide, in addition to the phosphomolybdic acid, as indicated by an increase in gravity to 27.0 and 27.6 respectively, a considerable quantity of residual nitrogenous and sulfurous compounds remains in the normally liquid product effluent.

In view of the slight improvement obtained through the use of nickel halides, in conjunction with phosphomolybdic acid, those obtained through the use of a catalyst comprising the decomposition product of phosphomolybdic acid and nickelous sulfate are unexpected. The gravity of the normally liquid product effluent has increased to a level of 30.3, the residual nitrogen has decreased to a level of 14 p.p.m. and the concentration of sulfur has decreased to 0.28% by weight. The significant difference resulting through the use of various nickel salts is believed to be due to the formation of the decomposition product, when utilizing nickelous sulfate, which product becomes complexed with the alumina structure in a manner not obtained when other nickel salts are employed. In other words, it is believed that neither nickel chloride nor nickel iodide form a decomposition product with phosphomolybdic acid, which product becomes complexed within the alumina structure.

The foregoing specification and example illustrate the effectiveness of the catalyst of the present invention in effecting the removal of nitrogenous and sulfurous compounds from a high-boiling hydrocarbonaceous material. Furthermore, the removal of these contaminating influences is to an acceptable degree notwithstanding the

presence of significant quantities of asphaltenic material and organometallic compounds.

I claim as my invention:

1. A process for removing sulfur and nitrogen from a heavy hydrocarbon charge stock containing pentane-insoluble asphaltenes which comprises reacting said charge stock with hydrogen in the presence of a catalyst containing the decomposition product of a mixture of a heteropoly acid and nickelous sulfate, and at conditions selected to convert nitrogenous and sulfurous compounds into hydrocarbons, ammonia and hydrogen sulfide.

2. A process for removing sulfur and nitrogen from a hydrocarbon charge stock boiling at a temperature above about 650° F. and containing pentane-insoluble asphaltenes which comprises reacting said charge stock with hydrogen at conditions selected to convert nitrogenous and sulfurous compounds into hydrocarbons, ammonia and hydrogen sulfide, and in contact with a catalytic composite of a refractory inorganic oxide and the decomposition product of a heteropoly acid and nickelous sulfate.

3. The process of claim 2 further characterized in that said heteropoly acid comprises phosphomolybdic acid.

4. The process of claim 2 further characterized in that said heteropoly acid comprises silicomolybdic acid.

5. The process of claim 2 further characterized in that said heteropoly acid comprises silicotungstic acid.

6. The process of claim 2 further characterized in that said heteropoly acid comprises phosphotungstic acid.

7. A process for removing sulfur and nitrogen from a hydrogen charge stock boiling at a temperature above about 650° F. and containing pentane-insoluble asphaltenes which comprises reacting said charge stock 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., said conditions selected to convert nitrogenous and sulfurous compounds into hydrocarbons, hydrogen sulfide and ammonia; the process further characterized in that said charge stock and hydrogen are reacted in the presence of a catalytic composite of an alumina-containing refractory inorganic oxide and the decomposition product of a heteropoly acid and nickelous sulfate.

8. The process of claim 7 further characterized in that said charge stock is a crude oil.

9. The process of claim 7 further characterized in that said charge stock is a reduced crude oil.

10. The process of claim 7 further characterized in that said charge stock is a crude tower bottoms product.

11. A process for removing sulfur and nitrogen from a crude oil fraction boiling at a temperature above about 650° F., and containing pentane-insoluble asphaltenes, which comprises reacting said crude oil fraction with hydrogen at a temperature of from about 225° C. to about 500° C. and under a pressure within the range of from 500 to about 5,000 p.s.i.g., said conditions selected to convert nitrogenous and sulfurous compounds into hydrocarbons, ammonia and hydrogen sulfide; the process further characterized in that said crude oil fraction and hydrogen are reacted in the presence of a catalytic composite of alumina and the decomposition product of phosphomolybdic acid and nickelous sulfate formed at a temperature less than about 310° C.

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