The invention described herein relates to the hydrotreating of petroleum crude oils and other heavy hydrocarbon fractions and/or distillates for the primary purpose of eliminating, or reducing the concentration of various contaminating influences contained therein. More particularly, the present invention is directed toward an auto-regenerative, single-stage catalytic hydrotreating process for effecting the substantially complete removal of various types of impurities from heavy hydrocarbon charge stocks, and especially from petroleum crude oils.

Petroleum crude oils, topped or reduced crude oils, and other heavy hydrocarbon fractions and/or distillates including black oils, heavy cycle stocks, visbreaker liquid effluent, etc., contain various non-metallic and metallic impurities which detrimentally affect various processes to which such heavy hydrocarbon fractions may be subjected. Included among the non-metallic impurities are large quantities of nitrogen, sulfur and oxygen which exist as heteroatomic compounds. Nitrogen is undesirable because it very effectively poisons various catalytic compositions which may be employed in the conversion of a variety of petroleum fractions; in particular, nitrogenous compounds are known to be effective hydrocracking suppressors and, therefore, must necessarily be removed from all catalytic hydrocracking charge stocks. Nitrogenous and sulfurous compounds are also objectionable since the combustion of fuels containing these impurities causes the release of nitrogen and sulfur oxides which are noxious, corrosive and present a serious problem with respect to pollution of the atmosphere. Sulfur is detrimental with respect to motor fuels because of odor, gum formation and a significantly lower lead susceptibility than sulfur-free gasolines.

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

Of the metallic contaminants, those containing nickel and vanadium are the most common, although other metals, including iron, copper, lead, zinc, etc., are often present. Such metals may occur as suspended metal oxides or sulfides, or water-soluble salts which may be removed, at least in part, by filtration, water washing, desalting or other relatively simple physical means; generally, however, the metals occur as thermally stable organo-metallic complexes, such as metallic porphyrins and the various derivatives thereof. A considerable quantity of the organo-metallic complexes are linked with the asphaltenes and become concentrated in residual fractions; some of the remaining organo-metallic complexes are volatile, oil-soluble and are, therefore, carried over in the lighter distillate fractions. A reduction of the concentration of the organo-metallic complexes is not easily achieved, and to the extent that the crude oil or other heavy hydrocarbon charge stock becomes suitable for further processing. Notwithstanding that the concentration of these organo-metallic complexes may be relatively small in distillate oils, for example, only about 10 p.p.m. (calculated as if the complex existed as the elemental metal), subsequent processing techniques are often adversely affected thereby. For example, when a hydrocarbon charge stock containing organo-metallic compounds, such as metal porphyrins, in an amount above about 3.0 p.p.m. is subjected to hydrocracking or catalytic cracking for the purpose of producing lower-boiling components, the metals become deposited upon the catalyst, increasing in concentration as the process continues. Since vanadium and the iron-group metals favor hydrogenation activity, at cracking temperatures, the resulting contaminated hydrocracking or cracking catalyst produces increasingly excessive quantities of coke, hydrogen and light hydrocarbon gases at the expense of more valuable liquid product. Eventually, the catalyst must be subjected to elaborate regenerative techniques, or more often be replaced with fresh catalyst. The presence of excessive quantities of organo-metallic complexes adversely affects other processes including catalytic reforming, isomerization, hydrodesulfuration, etc. With respect to the hydrotreating, or hydrodetering of hydrocarbon fractions and/or distillates, the presence of large quantities of asphaltic compounds and organo-metallic complexes as in topped or reduced crude oils, interferes considerably with the activity of the catalytic composite with respect to the destructive removal of the nitrogenous, sulfurous and oxygenated compounds. Therefore, it is highly desirable to produce a hydrocarbon mixture of reduced sulfur and nitrogen concentration, however, being substantially free from asphaltic material and organo-metallic compounds. Such a mixture is then subject to fixed-bed hydrotreating at sufficiently severe conditions required for a product virtually completely free from sulfur and nitrogen.

The desirability of removing the foregoing described contaminating influences from hydrocarbon mixtures is well known within the art of petroleum refining. Heretofore, in the field of catalytic hydrodetering, two principal approaches have been advanced: liquid phase hydrogenation and vapor phase hydrocracking. In the former type of process, the oil is passed upwardly in liquid phase and in admixture with hydrogen through a fixed bed or slurry of sub-divided catalyst. Although perhaps effective in removing oil-soluble, organo-metallic complexes, this type of process is relatively ineffective with respect to oil-insoluble asphaltenes, collooidally dispersed within the charge, with the consequence that the probability of effecting simultaneous contact between catalyst particle and asphaltene molecule is remote. Furthermore, the hydrogenation zone is at an elevated temperature, the retention of unconverted asphaltenes, suspended in a free liquid phase oil for an extended period of time will result in flocculation causing conversion thereof to become substantially more difficult. The rate of diffusion of the oil-insoluble asphaltenes is significantly less than that of dissolved molecules of the same molecular size; for this reason, a fixed-bed process in which the oil and hydrogen are passed in a downwardly direction, is virtually precluded. The asphaltenes, being neither volatile, nor dissolved in the crude, cannot move to the active catalyst sites, the latter being obviously immovable. Furthermore, the efficiency of hydrogen to oil contact, obtained
by bubbling hydrogen through an extensive liquid body, is relatively low. On the other hand, vapor phase hydrocracking is carried out either with a fixed-bed, or an expanded-bed system at temperatures substantially above about 950°F. While this technique obviates some extent the drawbacks of liquid phase hydrogenation, it is not suited to treating crude hydrocarbon fractions due to the high production of coke and carbonaceous material with the result that the catalytic composite succumbs to a relatively rapid deactivation; this requires a large capacity catalyst regeneration system in order to implement the process on a continuous basis. Selective hydrocracking of a wide boiling range charge stock is not easily obtained, and excessive amounts of light gases are produced at the expense of the more valuable normally liquid hydrocarbons. Also, when charging a petroleum crude oil, a minimum limit on cracked gasoline production is unavoidable; this is not always desirable where the end result is to maximize the production of middle and heavy distillates such as jet fuel, diesel oil, furnace oils and gas oils.

A primary object of the present invention is to provide a process for the hydrotreating, or hydrorefining of petroleum crude oils and other heavy hydrocarbon fractions and/or distillates, which process may be conducted on a continuous basis without incurring the detrimental effects suffered by present-day methods. A further object of the present invention is to provide a hydrotreating process which, in and of itself, is autoregenerative.

Therefore, in a broad embodiment, the present invention relates to a process for hydrorefining an asphaltic hydrocarbon charge stock containing organo-metallic contaminants, which process comprises the steps of: (a) reacting said charge stock and hydrogen in a reaction zone containing adsorptive hydrogenation catalyst particles, and at hydrorefining conditions including a temperature below that at which thermal cracking of asphaltene's is effected; (b) when said catalyst accumulates unreacted asphaltene's, increasing said temperature to a level above that at which thermal cracking of asphaltene's is effected; (c) when said unreacted asphaltene's are removed from said catalyst, decreasing said temperature to a level below that at which thermal cracking of asphaltene's is effected; and, (d) continually separating the reaction zone effluent to provide a normally liquid hydrocarbon fraction substantially free from asphaltene's and organo-metallic compounds.

Another broad embodiment of the present invention provides a process for hydrorefining an asphaltic hydrocarbon charge stock containing organo-metallic contaminants, which process comprises the steps of: (a) reacting said charge stock and hydrogen in a reaction zone containing adsorptive hydrogenation catalyst particles disposed therein in a fluidized state, and at hydrorefining conditions including a temperature below that at which thermal cracking of asphaltene's is effected; (b) when said catalyst accumulates unreacted asphaltene's, ceasing the flow of said charge stock, maintaining the fluidized state of said catalyst by continuously separating the reaction zone effluent to provide a normally liquid hydrocarbon fraction substantially free from asphaltene's and organo-metallic compounds.

A more limited embodiment of the present invention encompasses a process for hydrorefining an asphaltic hydrocarbon charge stock containing organo-metallic compounds, which process comprises the steps of: (a) reacting said charge stock and hydrogen in a reaction zone containing adsorptive hydrogenation catalyst particles in a fluidized state and at hydrorefining conditions including a temperature within the range of about 725°F. to about 785°F. and below that at which thermal cracking of asphaltene's is effected; (b) when said catalyst accumulates unreacted asphaltene's, ceasing the flow of said charge stock, maintaining the fluidized state of said catalyst by continuously separating the reaction zone effluent to provide a normally liquid hydrocarbon fraction substantially free from asphaltene's and organo-metallic compounds.

Similarly, a crude tower bottoms product, having a gravity API at 60°F., of 14.3, and contaminated by the presence of asphaltene's, is treated with a hydrogenation catalyst and hydrogen in a process which is carried out under conditions substantially similar to that described above, but which also includes the step of introducing hydrogen into the reaction zone in a dissolved state, whereby a substantially higher concentration of hydrogen is available in the reaction zone, resulting in a higher reaction rate and a more rapid removal of asphaltene's.
ence of 3.1% by weight of sulfur, 3,830 p.p.m. of nitrogen and 85 p.p.m. of metals, consists of about 10.9% by weight of pentane-insoluble asphaltenes. Usually, the destructive removal of nitrogen and sulfur is achieved by the conversion of asphaltenes and the removal of metallic contaminants. However, the activity of the catalytic composite with respect to the former, is severely hampered by the presence of excessive quantities of asphaltenic material and metals. Thus, it is of primary importance to remove substantially completely all of the latter contaminants, while at least partially reducing the concentration of sulfur and nitrogen.

In addition to the foregoing described contaminating influences, the heavier hydrocarbon fractions and/or distillates contain excessive quantities of unsaturated compounds consisting primarily of high molecular weight mono- and di-olefinic hydrocarbons. A successful, effective fixed-bed catalytic hydrodewaxing process is virtually precluded as a direct result of these various contaminants. At the operating conditions generally employed to effect successful hydrodewaxing, as well as hydrocracking, the mono- and di-olefinic hydrocarbons have the tendency to polymerize and to aromatize, and to form gum or asphaltene material, gummy polymerization products within the process equipment and onto the catalytic composite. Similarly, in processes for effecting the catalytic hydrocracking of such heavier hydrocarbon fractions into lower-boiling hydrocarbon products, the catalytic composite becomes deactivated through carbon deposition as a result of the deposition of the agglomerated pentane-insoluble asphaltenes, whereby the catalytically active centers and surfaces of the catalytic material are effectively shielded from the material being processed.

The difficulties encountered in a fixed-bed catalytic process are at least partially solved by employing a slurry operation wherein the finely-divided catalytic composite is intimately admixed with the hydrocarbon charge stock, the mixture being subjected to the desired operating conditions. However, the slurry-type of operation has the obvious disadvantage of relatively small amounts of catalyst being mixed with relatively large amounts of asphaltenic material, since it is difficult to suspend more than a small percentage of catalyst in the crude oil. In other words, too few active catalytic sites are made available for immediate reaction, with the result that the asphaltenic material undergoes thermal cracking resulting in quantities of light gases and coke. In accordance with the process encompassed by the present invention, large quantities of catalyst are brought into contact with comparatively small amounts of asphaltenes through the utilization of a fixed-fluidized catalytic bed. This method permits the asphaltenes, which have relatively low rates of diffusion compared to other hydrocarbon molecules, to come into contact with the active catalytic sites. It has been found that a hydrogenation catalyst comprising a porous, refractory inorganic oxide carrier material, having a well-developed pore structure, has the ability to absorb a substantial quantity (up to about 50.0% by weight) of the high-boiling asphaltenes and yet continue to appear ostensibly dry and free-flowing. It has further been found that converted asphaltenes, that is, asphaltenes which have been hydrodewaxed under mild hydrogenative-cracking conditions to yield oil-soluble hydrocarbons comprise an excellent source for the untreated asphaltenes which are themselves pentane-insoluble, and colloidal dispersed within the crude oil. The untreated asphaltenic material is much more readily converted when initially dissolved in such a solvent than one directly treated in a dispersed phase suspended in a liquid carrier. Thus, by maintaining the slurry-catalytic fixed-bed in a fluidized state, through the utilization of fast flow hydrogen in an amount within the range of about 5,000 to about 500,000 standard cubic feet per barrel of liquid charge, the liquid-phase portion of the feed, at a temperature within the range of about 725°F. to about 785°F., exists as a fine mist readily absorbed by the catalyst. This absorbed liquid, mostly asphaltenic in nature, will be converted by the catalytic process of hydrocracking reactions into soluble liquid which can act as a solvent for unconverted asphaltenes. Utilizing this principle permits the catalyst to function in an acceptable manner, and to remain free-flowing, for an extended period of time. However, the catalytic particles will eventually absorb more than about 50.0% by weight of asphaltic material, and when catalyst deactivation begins to take place. That the catalytic composite has absorbed asphaltenic material in an amount above about 50.0% by weight, is indicated, and can be determined by analyses performed on the normally liquid product effluent; that is, when the concentration of organo-metallic compounds, calculated as if the metal existed as the elements, approaches and exceeds 0.5 p.p.m. and/or when the residual pentane-insoluble asphaltenes approaches and exceeds a concentration above about 0.5% by weight. Since the rate at which unconverted asphaltenic material is absorbed by the catalytic composite increases as asphaltenes are absorbed by the catalytic composite, it is preferred to initiate the auto-regeneration procedure hereinafter set forth as the amount of absorbed asphaltenic material approaches and exceeds about 35.0% by weight. Another indication of rapid accumulation of unreacted asphaltenes by the catalytic composite is made available by the concentration of nitrogen and sulfur in the normally liquid product effluent. The present process will effectively eliminate the asphaltenes and metallic contaminants completely, and reduce nitrogen and sulfur about 60.0%, notwithstanding that the destructive removal of the latter is generally more easily performed. As unreacted asphaltenes are accumulated the catalyst loses its capability to remove nitrogen and sulfur at an increasing rate.

As will be noted from the foregoing embodiments, the hydrodewaxing process of the present invention is effected at a temperature below that temperature at which thermal cracking of asphaltenes is effected. At such time as the catalyst accumulates unconverted asphaltenes, for example, above about 35.0% by weight, the operating temperature is increased to a level at which thermal cracking of asphaltenes is effected, and maintained at such elevated level until the unconverted and removed from the catalytic composite. In order to minimize the cracking of hydrocarbonaceous material into light gaseous waste products, it is preferred to cut off the flow of hydrocarbons to the catalyst bed, continuing, however, the flow of hydrogen therethrough when the operating temperature is increased to a level above about 785°F.

As the asphaltenic material is being removed from the catalytic composite, by way of hydrogenation-cracking reactions, normally liquid hydrocarbonaceous material will appear in the effluent stream from the reaction zone. When normally liquid hydrocarbons no longer appear in the product effluent stream, it may be presumed that the catalytic composite is substantially completely free from absorbed unconverted asphaltenic material. At such time, fresh hydrocarbon charge stock may be re-introduced into the reaction zone and in admixture with the fast-flowing hydrogen stream. As above noted, this invention broadly involves contacting a mixed phase heavy oil charge with hydrogen in the presence of a finely-divided hydrogenation catalyst maintained in a fixed-fluidized state, and under conditions specifically designed to suppress or inhibit the thermal cracking of asphaltenic material. Thus, the catalytic composite is maintained at an elevated temperature of from about 725°F. to about 785°F., the mixture of hydrogen and hydrocarbons being initially heated to a temperature of about 725°F. to about 750°F. prior to contacting the catalytic composite. The operating pres-
sure should be in excess of about 500 p.s.i.g., having an upper economic limit of about 5,000 p.s.i.g., the preferred pressure range being from about 1,000 to about 3,000 p.s.i.g.

In carrying out this process, it is important to minimize cracking, and particularly the thermal cracking of the colloidosly dispersed asphaltenes in a petroleum crude oil, and the partially agglomerated asphaltenes in a reduced or topped crude oil. From the standpoint of maintaining the process equipment and various appurtenances in an operable condition, it is highly desirable to minimize cracking prior to introducing the heavy hydrocarbon charge stock into the hydrodefining zone, to contact the catalytic adsorptive hydrogenation catalyst particles, the heavier liquid phase portion of the charge is at least partially adsorbed into the catalyst particles, and partly entrained as a very fine mist, in the fast-flowing hydrogen stream; the hydrogen-rich gaseous phase is returned to the hydrodefining zone ad mixutre 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. charge, the precise amount being dependent upon the physical and chemical characteristics of the charge stock.

The fluidized-fixed bed catalyst system is especially advantageous in processing those charge stocks containing excessive quantities of oil-insoluble asphaltenes and organo-metallic compounds, these impurities being effectively converted by the auto-solvent hydrodefining mechanism of this process. As hereinbefore set forth, asphaltic material hydrodefined under mild hydrodefining conditions which preclude the thermal cracking thereof, to yield oil-soluble, high-boiling hydrocarbons, comprises an excellent solvent for untreated asphaltenic material, and if of itself, is present as insoluble and collooidally dispersed in the crude oil charge. This results in a superior correlation of weight hourly space velocity and recycle hydrogen rate, not all of the hydrodefined oil is removed from the catalyst particles by hydrogen stripping, but a portion of the hydrodefined asphaltenic material is left absorbed within the catalyst particles to function as the solvent for incoming asphaltenes, and reaches an equilibrium level in a steady, lined-out operation.
Eventually, however, the catalyst particles will have absorbed therein, or accumulated, unreacted asphaltic material in an amount above about 35.0% by weight. As has already been mentioned, the high surface area of the catalyst makes it an effective adsorbent for asphaltic material. The catalyst particle is then dried in an oven at a temperature of not less than 60°C for 24 hours. By this method, the absorbed asphaltic material is subjected to thermal cracking, and to a certain extent hydrocracking, the products of the cracking reaction being stripped from the catalyst particles and concentrated in the high-pressure separator.

The preferred technique at this stage of the process is to cease the flow of fresh hydrocarbon charge stock, continuing, however, the flow of hydrogen through the catalyst bed. By this procedure, the absorbed asphaltic material is subjected to thermal cracking, and to a certain extent hydrocracking, the products of the cracking reaction being stripped from the catalyst particles and concentrated in the high-pressure separator.

The reaction zone is then isolated from the rest of the process by means of valves, and pressure is applied to the catalyst particle to generate the necessary pressure drop across the catalyst bed. The catalyst particle is then subjected to a pressure of not less than 200 atm, and the liquid flows through the catalyst particle at a rate of not less than 1 m/s.

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The reaction zone is then isolated from the rest of the process by means of valves, and pressure is applied to the catalyst particle to generate the necessary pressure drop across the catalyst bed. The catalyst particle is then subjected to a pressure of not less than 200 atm, and the liquid flows through the catalyst particle at a rate of not less than 1 m/s.
etters ranging from about 5 to about 1000 microns; in the case of non-spherical particles, the maximum dimension of such a particle should fall within the aforesaid range. Particle sizes of this magnitude may be readily achieved by spray-drying the carrier or by grinding the catalyst in a colloid mill. By way of specific example, a satisfactory hydrogenation catalyst, having the requisite surface area and pore characteristics, comprised about 2.0% by weight of nickel and about 16.0% by weight of molybdenum calculated as the elemental metals, on an equimolar alumina-silica carrier comprising 63.0% by weight of alumina, 1.0% by weight of nickel and 8.0% by weight of molybdenum on a carrier material comprising 68.0% by weight of silica and 22.0% by weight of boron phosphate.

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

Example 1

The charge stock employed to illustrate the process of the present invention was a topped Wyoming sour crude oil. As received, this sour crude oil, having a gravity of 23.2° API at 60°F, was contaminated by the presence of 2.8% by weight of sulfur, 2700 p.p.m. of total nitrogen, 100 p.p.m. of metallic porphyrins (computed as elemental nickel and vanadium), and contained a high boiling pentane-insoluble asphaltene fraction of about 8.3% by weight of the total crude oil. This sour Wyoming crude oil was "topped" having 5.0% of light-end removal, and indicated a gravity, degrees API at 60°F, of 19.5, and contained 3.0% by weight of sulfur, 2900 p.p.m. of total nitrogen, 105 p.p.m. of nickel and vanadium, the pentane-insoluble asphaltene fraction being about 8.5% by weight.

The catalytic composite utilized a spray-dried, alumina-silica carrier material comprising 63.0% by weight of alumina. This carrier material was prepared by initially precipitating, at a pH above 8.0, a blend of acidified water glass and an aluminum chloride hydrate with ammonium hydroxide. The hydroxide was washed free from sodium ions, chloride ions and ammonium ions, and spray-dried. An impregnating solution was prepared from molybdc acid (85.0% by weight of molybdenum trioxide) and nickel nitrate hexahydrate, the spray-dried carrier material being impregnated with an ammoniacal solution thereof. The impregnated composite was dried at a temperature of about 210°F, and finally oxidized in an atmosphere of air at a temperature of about 1100°F for about one hour. The finished catalyst contained 2.0% by weight of nickel and 16.0% by weight of molybdenum existing as oxides, calculated, however, as if existing as the elemental metal, and indicated a particle size ranging from 20 to about 150 microns (approximately 99.0% by weight of the catalyst particles were of a size less than 150 microns).

A total of 220 grams of the nickel-molybdenum catalytic composite was supported in the reaction zone on a sintered metal disk. The reaction zone was fabricated from one and one-half inch, schedule 40, type 316 stainless steel pipe, equipped at the bottom portion thereof with a spiral preheater around which the oil entered from the top. By means of a short piece of tubing, the top of the preheater extended through the sintered plate, the end of the tubing being covered by an inverted cup which served to prevent the catalytic composite from falling into the preheater zone. After passing through the tube and under the cup, the partially vaporized charge stock entered the catalyst and the hydrogen, the latter entering the reactor from the side, traveling upwardly around the oil-preheater section; the hydrogen passes through the sintered metal plate and ebulliates the catalyst bed. The reaction products and excess hydrogen con-tinue upward to a disengaging zone fabricated from two and one-half inch, schedule 40, type 136 stainless steel pipe. In this zone, the gas velocity is reduced to approximately one-half the velocity in the reaction zone itself in order that entrained catalyst particles will tend to fall back into the reaction zone. After leaving the reaction zone, the reaction products were passed through sintered metal tubes, to remove any coarse fines that may have been entrained. The reaction products were cooled and passed into a high pressure separator from which the liquid hydrocarbon product was removed to a receiver, the hydrogen-rich gas being removed from the separator through a water scrubber and recycled back to the reactor. In order to compensate for the quantity of hydrogen consumed within the process and absorbed by the normally liquid product effluent, fresh hydrogen was added to the recycle gas as determined by the operating pressure within the reaction zone.

The above-described, fixed fluidized system was operated for a period of 204 hours, the first four of which constituted the start-up of the unit, the remaining 200 being divided into twenty-five, 8-hour individual test periods. The weight hourly space velocity throughout the entire test period was 0.86, based upon an average liquid charge to the reaction zone of 190 grams per hour (a low rate of 184 and a high rate of 194). The reaction zone pressure was maintained at about 2000 p.s.i.g., through compressive hydrogen recycle ranging from 52,300 to 56,000 s.c.f./bbl. of liquid charge; the hydrogen purity was, at all times, in excess of about 90.0% ranging from about 91.7% to 96.1% throughout the entire 204 hours.

In the following abbreviated table, data from seven of the 8-hour test periods are given as being representative of the overall operation:

<table>
<thead>
<tr>
<th>Tabulated Data</th>
<th>3</th>
<th>40</th>
<th>84</th>
<th>116</th>
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<td>Hours on Stream</td>
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<td>Sulfur, wt. percent</td>
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<td>Metals, p.p.m.</td>
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</table>

The operation was intentionally stopped at the termination of the twenty-fifth test period, or after 204 consecutive hours of operation. It will be noted that although the concentration of pentane-insoluble asphaltenic material is considerably below a level of 0.5% by weight, averaging approximately 0.15% throughout the entire operating period, and the concentration of organo-metallic compounds is well below the limit of 0.5 p.p.m., the operating temperature has been increased a total of about 25°F, and further that the gravity °API at 60°F of the normally liquid product effluent indicates a decline. In addition, the sulfurous and nitrogenous compounds remaining in the normally liquid product effluent have increased considerably from 0.22% by weight of sulfur and 881 p.p.m. of nitrogen. These four factors combine to indicate that the catalytic composite is accumulating unreacted asphaltenic material at an increased rate, and that the catalytic composite is slowly suffering a loss of its hydrogenation/hydrocracking activity. That is, as the pentane-insoluble, the capability to remove sulfur and nitrogen is initially affected, followed by an increasing inability to remove metals and convert the pentane-insolubles. Thus, it was decided to cease the operation, notwithstanding that the catalytic composite continued to
We claim as our invention:

1. A process for regenerating an adsorptive hydrogenation catalyst containing asphaltenes in an amount of from about 35% to about 50% by weight, which comprises heating said catalyst to a temperature level above that at which thermal cracking of asphaltenes is effected and cracking said asphaltenes to produce normally liquid hydrocarbons therefrom and to regenerate the catalyst, maintaining the catalyst at said temperature level until the asphaltenes on the catalyst are converted and removed from the catalyst, and recovering the resultant regenerated asphaltene-free catalyst.

2. The process of claim 1 further characterized in that said catalyst comprises at least one metallic component selected from the metals of Groups V-B, VI-B and VIII of the Periodic Table.

3. The process of claim 2 further characterized in that said catalyst comprises a vanadium component.

4. The process of claim 1 further characterized in that said catalyst comprises a molybdenum component.

5. The process of claim 1 further characterized in that said catalyst comprises a nickel component.

6. The process of claim 1 further characterized in that said catalyst comprises a molybdenum component and a nickel component.

7. The process of claim 1 further characterized in that said temperature level is above about 785° F.

8. The process of claim 1 further characterized in that the products of cracking are stripped from the catalyst by the passage of hydrogen through the catalyst during the heating thereof.

9. A process for regenerating an adsorptive hydrogenation catalyst containing asphaltenes in an amount of from about 35% to about 50% by weight, which comprises heating said catalyst to a temperature level above that at which thermal cracking of asphaltenes is effected and cracking said asphaltenes to produce normally liquid hydrocarbons therefrom and to regenerate the catalyst, maintaining the catalyst at said temperature level until the asphaltenes on the catalyst are converted and removed from the catalyst while passing hydrogen upwardly through the catalyst to maintain the catalyst in a fluidized state, and recovering the resultant regenerated asphaltene-free catalyst.

10. The process of claim 9 further characterized in that said temperature level is above about 785° F.

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