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3,340,180

HYDROFINING - HYDROCRACKING PROCESS EMPLOYING SPECIAL ALUMINA BASE CATALYSTS

Harold Beuther, Gibsonia, and Stephen L. Peake and Bruce K. Schmid, Pittsburgh, Pa., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

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Our invention relates to the hydrogen treatment of heavy petroleum hydrocarbons and derivatives or fractions thereof and in particular relates to the removal of sulfur and nitrogen compounds therefrom and to the hydrocracking thereof.

These heavy petroleum hydrocarbons are available commercially in considerable abundance but they are of relatively low value. In many instances such heavy petroleum hydrocarbons are employed as low-grade fuels without further treatment. This, at best, results in a poor return to the producer and the return is being further reduced since many jurisdictions have adopted regulations restricting the amount of sulfur containing material that can be present in fuels burned within their boundaries, thereby requiring removal of substantial quantities of sulfur from these hydrocarbons, such as residuals, prior to sale. It has previously been suggested that sulfur be removed from residual fractions and other heavy petroleum hydrocarbons by subjecting the heavy hydrocarbon to treatment with hydrogen in the presence of hydrogenation catalysts. These suggested procedures, however, entail the employment of expensive operating conditions such as, for example, unusually high pressures, i.e., at least 2000 p.s.i. Previous attempts to remove sulfur from residual stocks by hydrogenation at moderate pressures have resulted in extremely rapid deactivation of the catalysts by metal and coke deposition on the catalysts due to the metalliferous and asphaltic contaminants contained in such stocks. Further, the previous attempts have resulted in an unsatisfactorily low degree of desulfurization. Similarly, attempts to enhance the value of these heavy petroleum hydrocarbons by removal of nitrogen through hydrogenation have been confronted with the same problems.

An alternative course which has been proposed as a means of enhancing the value of these heavy petroleum hydrocarbons is to hydrocrack such stocks in order to produce more valuable, lower-boiling fractions. To effect hydrocracking of heavy hydrocarbons, it is necessary to employ a catalyst which is extremely active in the presence of asphaltic and metalliferous contaminants and which has extremely good aging characteristics, i.e., maintains its cracking activity for long periods of time while exposed to large quantities of asphaltic materials. Such characteristics are not necessarily required when hydrocracking lighter stocks such as, for example, a middle distillate fraction. As mentioned above, however, metal impurities in the stocks to be treated cause rapid deterioration of the activity of the catalysts, and the coking of the catalysts due to the presence of asphaltics in the stocks also has a strong deactivating effect. Thus, a commercially acceptable hydrocracking process for heavy petroleum hydrocarbons requires not only the employment of an extremely active catalyst in the presence of asphaltic and metalliferous contaminants but also the employment of a catalyst and operating conditions which provide good catalyst aging.

It is an object of our invention to provide improved procedure for the hydrogen treatment of heavy petroleum hydrocarbons.

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Another object of our invention is to provide improved procedure for the removal or reduction of sulfur and/or nitrogen compounds from heavy petroleum hydrocarbons by catalytic hydrogen treatment.

A further object of our invention is to provide improved procedure for hydrodesulfurization of heavy petroleum hydrocarbons employing moderate pressures, e.g., below about 2000 p.s.i.

Another object is to provide improved procedure for hydrocracking heavy petroleum hydrocarbons, particularly a procedure which enables high conversion into lower boiling materials.

These and other objects are accomplished by our invention which includes treating a heavy petroleum hydrocarbon with hydrogen in the presence of a catalyst comprising essentially a minor amount of a hydrogenation catalyst composited with a major amount of an activated alumina having less than 5 percent of its pore volume that is in the form of pores having a radius of 0 to 300 A. in pores larger than 100 A. radius and having less than 10 percent of said pore volume in pores larger than 80 A. radius. This activated alumina is prepared by treating a substance which is predominantly composed of a crystalline alumina hydrate containing from 1.2 to 2.6 mols of water of hydration and which is substantially free of alumina monohydrate and alumina trihydrate; the alumina hydrate being prepared by precipitation from a solution of an aluminum compound at a pH between 7 and 12, and drying to the above-mentioned water of hydration content prior to substantial transformation to an alumina hydrate having a higher or lower water of hydration content. The dried alumina hydrate is then hydrothermally treated by heating it in the presence of water in an autoclave at a temperature sufficient to vaporize the water and under the pressure generated in the autoclave at the temperature. This is followed by drying and calcining the hydrothermally treated alumina hydrate to provide the activated alumina.

The heavy petroleum hydrocarbons treated in accordance with our invention contain sulfur, asphaltic and metalliferous compounds as contaminants, contain substantial amounts of hydrocarbon components boiling above 300° F., and contain residual materials. As employed herein the term "residual materials" means the undistilled petroleum fraction containing the highest boiling components of the crude. There are many natural petroleum hydrocarbons of a heavy nature containing residual materials and containing the contaminants mentioned. All such stocks can be treated in accordance with our invention. Also many petroleum hydrocarbons yield residual fractions on distillation under reduced or atmospheric pressures, which fractions contain the contaminants mentioned. Examples of such stocks are reduced and topped crudes. Our invention is applicable to the treatment of all such residual fractions. Further, our invention is particularly useful in the treatment of petroleum fractions boiling in the range above about 700° F. and even above 1000° F.

Broadly, the operating conditions employed in the practice of our invention include a hydrogen pressure from about 300 to about 3000 p.s.i., a space velocity from about 0.1 to about 10.0 volumes of heavy hydrocarbon per volume of catalyst per hour, a hydrogen feed rate from about 2000 to about 30,000 standard cubic feet per barrel of charge stock (s.c.f./b.), a hydrogen consumption rate from about 1 to about 30 or 40 mols of hydrogen per atom of sulfur removed from the charge stock and a temperature from about 700° to about 900° F. The pressures mentioned throughout the specification and in the claims are to be construed as hydrogen partial pressures whether specifically so stated in each instance or not. The temperatures mentioned herein and in the claims are average reac-

tor temperatures since the difference between inlet and outlet temperatures can differ as much as 30° F. and even more depending upon the charge stock and the severity of other operating conditions.

As indicated, the activated alumina carrier or support employed in the process of our invention is obtained by drying and calcining an alumina hydrate derived from the hydrothermal treatment of a material predominantly composed of a crystalline alumina hydrate containing from 1.2 to 2.6 mols of water of hydration and which is substantially free of alumina monohydrate and alumina trihydrate. Any aluminum salt may be employed in preparing this alumina hydrate containing 1.2 to 2.6 mols of water of hydration. For instance aluminum nitrate, chloride, acetate, formate, fluoride, sulfate, and other salts of aluminum may be used. Also a variety of bases such as sodium hydroxide, ammonium hydroxide, potassium hydroxide, etc. may be employed to precipitate the alumina hydrate. However, it is preferred to employ salts of aluminum and bases which do not give reaction byproducts or salts which are difficult to separate from the desired alumina hydrate. For instance, if aluminum sulfate and/or sodium hydroxide are employed or even if aluminum sulfate and ammonium hydroxide are employed, sulfate salts are formed which are difficult to remove by water washing and usually require prolonged water washing for complete removal. On the other hand, if aluminum nitrate, aluminum chloride or an aluminum salt of an organic acid is used and a base such as ammonium hydroxide is employed, the salts which are formed are readily soluble in water and can be easily removed by water washing of the alumina hydrate. For the above reasons potassium and sodium hydroxide are considered to be of little value as compared with aqueous ammonia. Regardless of the specific aluminum salt and base that are used, the final product should be substantially free of such salts. Because of ease in removing salts it is preferred to use aluminum nitrate or chloride and neutralize with ammonium hydroxide.

The utilization of a pH between 7 and 12 is essential in order to obtain the particular alumina hydrate utilized to obtain the catalyst support employed in the process of our invention. In other words, the use of a pH above or below this range results in formation of large amounts of undesirable alumina hydrates containing higher and/or lower quantities of water of hydration than 1.2 to 2.6 mols per mol of Al_2O_3 . Also, care must be employed at all times during the neutralization to avoid a localized higher or lower pH. If a local pH above or below this value exists at any time, a less satisfactory form of alumina hydrate having a different water of hydration content will be formed in this local region. This less satisfactory form will dilute the desired form and will reduce its value to a degree greater than to be expected from the amount which is present. For this reason, it is desirable to utilize a basic solution having the desired pH between 7 and 12 and to add the aluminum salt in small amounts, preferably an aqueous solution thereof, to the basic solution with rapid agitation. If this expedient is used, the resultant alumina hydrate is unlikely to be precipitated even in local regions at a pH below 7 or greater than 12. A pH of 7-8.5 is advantageous since in many cases it gives a higher yield and a more active product. Stoichiometric amounts of the aluminum salt and base are advantageously used. It is also preferred to use solutions of both base and aluminum salt which are either dilute or of moderate concentration, such as between about one and 20 percent aluminum salt and between about one and 20 percent of basic solution. However, higher or lower concentrations can be used. The alumina hydrate thus formed is separated from the aqueous mixture by filtration, centrifuging, decanting, or any other suitable method. Washing to remove salts as described above is advantageous and is necessary if the salt is not readily volatilized during the subsequent treatment.

This separated alumina hydrate still contains entrained, adherent or mechanically held water, and it must be dried to remove this water before a stable product is obtained. Even though the desired form of alumina hydrate is initially prepared, it is unstable and may undergo transformation during the process of precipitation, separation and/or drying and it is necessary to observe certain precautions to avoid this harmful transformation. Therefore, before giving details on the drying procedure, it would be best to consider procedures which may be employed to avoid this harmful transformation, particularly during the process of neutralization and precipitation.

One method for avoiding this harmful transformation is to use elevated temperatures such as above about 170° F. These elevated temperatures reduce or prevent the undesirable transformation of the alumina hydrate into one having a lower or higher water of hydration content. However, for these temperatures to have these beneficial effects, they should be maintained throughout the above mentioned precipitation and washing steps and until the drying is completed. Generally, the temperature should be kept as close to 170° F. as is convenient but if a temperature in the range of 200° F. or slightly above is employed, the residence time should be reduced accordingly. This specific mode of preparing alumina hydrate of 1.2 to 2.6 mols of water of hydration content is the subject of U.S. application Serial No. 118,240, filed June 20, 1961, in the names of W. L. Kehl and M. M. Stewart, now U.S. Patent No. 3,188,174.

According to another method of avoiding the transformation into less desirable forms the precipitation and drying are carried out with promptness. Thus the time required for the transformation to take place is such that the entire precipitating and drying operations can be carried out even with relatively large or commercial quantities if care is taken to do so expeditiously. Ordinarily formation and drying should take place within a period of at most 24 hours and preferably within about 4 to 8 hours or less when this expedient is used. It is especially advantageous to use a pH of 7-8.5 in connection with this particular method.

The undesirable transformation can be avoided by other methods of preparation. For instance, the presence of acetate ion greatly delays the transformation even at ordinary temperatures. Also buffered precipitating solutions may be used. These expedients are the subject matter of applications S.N. 118,279, filed June 20, 1961 and S.N. 118,241, filed June 20, 1961, in the names of W. L. Kehl and M. M. Stewart, now U.S. Patents Nos. 3,151,940 and 3,151,939, respectively.

The drying of the alumina hydrate may be carried out in any desired manner so long as it is completed prior to the harmful transformation. As may be gathered from the above described procedures for avoiding the transformation, a temperature of above 170° F. will prevent the transformation from taking place. Therefore it is advantageous to employ temperatures at least as high as this for drying. The drying may be carried out in vacuum if desired. It, of course, follows that considerably higher temperatures than 170° F. may be employed. For instance, it is entirely satisfactory to utilize temperatures such as 212° F. or even 250° F. This drying removes the mechanically held water and yields a stable product. It is predominantly composed of the desired crystalline alumina hydrate containing 1.2 to 2.6 mols of water of hydration and is substantially free of alumina monohydrate and alumina trihydrate.

After drying, this alumina hydrate is subjected to hydrothermal treatment by placing the alumina hydrate together with water in a sealed vessel, such as an autoclave, and heating at an elevated temperature for a period of time. Generally, the quantity of water employed is sufficient to immerse completely the dried alumina hydrate. The sealed vessel is then heated so as to raise the temperature gradually over a period of time, such as,

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for example, about 2 to 8 hours, and the temperature is then maintained at an elevated level from about 225° or 250° F. up to about 500° F. or 700° F., in any event a temperature adequate to provide sufficient water vapor pressure to prevent dehydration of the alumina hydrate, for a period from a few minutes up to several hours, for example, from 2 or 3 minutes up to 8 or 16 hours. It has been found that the roles of time and temperature in the hydrothermal treatment are to a considerable extent interchangeable. Thus, one might by suitably extending the duration of treatment produce the desired conversion at a low temperature which would be essentially the same as that obtained in a shorter period of time employing a higher temperature. For example, employing a temperature of 250–300° F. for a period of 4 hours is usually sufficient to bring about substantially complete conversion, while treatment at a lower temperature for the same period of time effects a partial conversion and yet treatment at a lower temperature for a longer period can usually effect substantially complete conversion. Accordingly, by gradually raising the temperature of the autoclave from room temperature up to about 325° F. over a period of 4 hours and then maintaining the temperature at that level for an additional four hours, resulting in a total processing time of 8 hours, substantially complete conversion can be effected. A certain degree of caution, however, must be exercised, since the employment of too high a temperature for a particular length of time of treatment will destroy the desired unique pore structure of the product. For example, the employment of a temperature from about 250° F. up to about 325° or 350° F. for a period of four hours will produce an alumina hydrate which upon calcination provides an alumina having the necessary pore size distribution of less than 5 percent of the pore volume in pores larger than 100 A. and less than 10 percent of the pore volume in pores larger than 80 A., while the employment of a temperature much above about 350° F. results in a final alumina having a pore size distribution somewhat outside this range. The employment of a temperature of 400° F. for a treatment period of four hours so completely destroys the structure that an alumina is obtained having about 30 percent of the pores larger than 100 A. and about 50 percent of the pores larger than 80 A. It is believed that the heating permits the metastable dried alumina hydrate which is hydrothermally treated to rearrange to a stable form of alumina hydrate while the water pressure prevents dehydration of the alumina hydrate to alumina. Accordingly, we believe that any water vapor pressure above the dehydration pressure of the dried alumina hydrate at the particular temperature selected is adequate for the hydrothermal treatment. It is preferred, however, to employ an excess of pressure obtained by employing a quantity of water in excess of the minimum required as a safety precaution, thereby insuring that the minimum required water vapor pressure is present. Generally, the pressure will be in the range from about 30 to about 700 p.s.i.g., although it can vary from a low of 10 p.s.i.g. at 200° F. to a high of 3100 p.s.i.g. at 700° F. The employment of a slight excess of water vapor pressure in the hydrothermal processing of our invention has no deleterious effects upon the conversion or the product hydrothermally treated alumina hydrate.

The hydrothermally treated alumina hydrate is substantially a monohydrate which can be described as a less well crystallized boehmite having crystallites of an extremely small diameter. Thus, commercially available boehmites and boehmites obtained, for instance, by hydrothermal treatment of a trihydrate have an average crystallite diameter in the range from about 1200 or 1300 A. up to about 2000 A. or above, while the average crystallite diameter of the hydrothermally treated alumina hydrate described herein is about 100 A.

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At the completion of this treatment the hydrothermally treated alumina hydrate is then dried and calcined to obtain the activated alumina which constitutes the carrier for the catalyst employed in our invention. Any conventional method heretofore used for calcining a dried alumina can be employed. However, a temperature above about 1600° F. should not be used since such elevated temperatures cause deactivation of the activated alumina. A temperature of between about 800° F. and 1200° F. ordinarily is satisfactory. A calcining time of between about 2 and 24 hours ordinarily will be satisfactory. In most cases the shorter time periods will be used with the higher temperatures and the longer periods with the lower temperatures. The final product is opaque, hard and glassy. It has a unique pore structure and is Al_2O_3 which still contains a small amount of water—usually less than about 3 percent.

This unique pore structure of the alumina used in our process can be characterized as including a substantial, usually a predominant, portion of the total pores and consisting of pores less than 300 A. radius having the particular pore size distribution described previously. For example, a similar alumina has been found to be composed almost entirely of pores less than 300 A. radius, which pores comprise more than 90 percent of the total pore volume.

In the practice of our invention we employ the activated alumina described above as the catalyst support rather than a commercial alumina-containing silica support inasmuch as it provides the desired activity but does not possess the extremely high initial activity of commercial silica-alumina supports and, therefore, does not cause extremely high initial cracking which in turn causes rapid coking of the catalyst.

Surprisingly, we have found that when this activated alumina is composited with suitable metals having catalytic activity, a catalyst composition is obtained which yields unexpectedly superior results in the hydrocracking and hydrodesulfurization of heavy petroleum hydrocarbons. Such activity is particularly unexpected in light of the fact that, when the alumina described above is substituted for commercially available aluminas of a different type in certain other hydrocarbon treatment processes, e.g., hydroreforming, the results achieved are no better than and, in some instances, even inferior to the results obtained employing the commercial supports.

The activated alumina carrier described above is composited with a metalliferous hydrogenating component. Any of the conventional procedures for preparation of such a two-component catalyst may be used. Ordinarily we prefer to impregnate the activated alumina carrier with an aqueous solution of a salt of the metalliferous hydrogenating catalyst and then dry and calcine to obtain the finished hydrogenation catalyst. Any hydrogenating component such as Group VIII or Group VI metal oxides or sulfides, such as molybdenum or tungsten oxides and sulfides or nickel or cobalt metals, oxides or sulfides may be used. It is frequently desirable to employ mixtures of these catalysts such as cobalt-molybdenum, nickel-cobalt-molybdenum, nickel-tungsten, etc., their oxides or sulfides. A particularly desirable catalyst is a mixture of oxides of nickel, cobalt and molybdenum such as described in U.S. Patent 2,880,171, March 31, 1959, Flinn et al.

In one aspect our invention relates to the desulfurization of heavy petroleum hydrocarbons. When operating in accordance with this aspect of our invention, the contacting of the charge stock with hydrogen is carried out under conditions of temperature and space velocity which avoid substantial or extensive cracking of carbon-to-carbon bonds. We have found that by operating in accordance with this procedure moderate hydrogen partial pressures of between about 300 and 2000 p.s.i. can be employed yet nevertheless long onstream periods or high throughputs may be used to give extensive desulfuriza-

tion. This procedure not only results in improved removal of sulfur compounds but also in an improved removal of nitrogen-containing impurities. Other advantages such as lower coke deposits and lower carbon residue are also obtained.

Generally, temperatures within the range from about 700° to about 875° F. and preferably between about 750° and 850° F. are employed. By employing temperatures within these ranges is meant to commence operation at the lower end of the temperature range and gradually increase the temperature during the course of operation in order to maintain the rate of desulfurization or the sulfur content of the product constant until a terminal temperature is reached, at which time the reactor is shut down and the catalyst regenerated. Thus, for example, the hydrodesulfurization process can be commenced at a temperature within the range from about 700° to 800° F. and the temperature increased incrementally until a temperature in the range of about 775° to 875° F. is attained, preferably the process can be commenced at a temperature of about 750° to 775° F. and the temperature increased gradually until a temperature of about 800° to 850° F. is attained at the end of the run.

Also when practicing this aspect of our invention a pressure between about 300 and 2000 p.s.i. and preferably between 1000 and 1500 p.s.i. is used, a space velocity between about 0.10 and 10.0 and preferably between 0.2 and 3.0 can be used, a hydrogen feed rate from about 5000 to about 30,000 s.c.f./b. and preferably from about 4000 to about 10,000 s.c.f./b. is employed, and a hydrogen consumption of about 1 to about 5 mols of hydrogen per atom of sulfur removed from the charge stock and preferably from about 2 to about 5 mols of hydrogen per atom of sulfur is employed. While hydrodesulfurization causes the formation of lower boiling materials due to the rupture of the sulfur bonds in the hydrocarbon molecule, this type of rupturing does not cause deposition of coke on the catalyst and is desirable. Since the process of this aspect of our invention results in extensive rupturing of sulfur bonds, there will be lower boiling hydrocarbons formed as a byproduct and these hydrocarbons have desirable properties as compared with the residual material being treated. Since the objective is the utilization of as long an onstream period as possible, it is best to use conditions which avoid carbon-to-carbon cracking inasmuch as this results in deposition of coke on the catalyst and this in turn increases the rate of deactivation of the catalyst. Therefore, this cracking should be maintained below about 20 percent formation of volatile material over and above that formed by rupturing of sulfur bonds. The space velocity and temperature can be regulated to give the desired mild conditions which avoid extensive carbon-to-carbon cracking. Thus, with a given catalyst the higher the temperature and the lower the space velocity the higher will be the amount of carbon-to-carbon cracking whereas the reverse conditions utilizing a lower temperature in the range given and a higher space velocity will reduce the carbon-to-carbon cracking. If this carbon-to-carbon cracking is kept below the above mentioned maximum value, the reaction may be continued for relatively long periods of time on the order of 3 to 75 barrels of residual feed stock per pound of catalyst. Eventually the catalyst will require regeneration and this is accomplished in the usual fashion by terminating the onstream reaction and burning the carbonaceous material from the catalyst by combustion regeneration. The regenerated catalyst then may be reused in the process.

Of the catalysts mentioned above it is preferred to utilize a catalyst of the cobalt molybdate type in practicing this aspect of our invention since such catalyst has a high deculfurization activity and a low activity for carbon-to-carbon splitting. As mentioned above, a particularly desirable catalyst of this type is a mixture of the

oxides of nickel, cobalt and molybdenum as described in U.S. Patent 2,880,171. Other nickel-cobalt-molybdenum catalysts in which the total metal content is less than about 20 to 25 percent by weight of the catalyst and in which the atomic ratio of Group VIII to Group VI metals is greater than 1.0 can also be employed with equally satisfactory results.

Another aspect of our invention relates to the hydrocracking of heavy petroleum hydrocarbons. When operating in accordance with this aspect of our invention the heavy hydrocarbon is contacted with hydrogen under hydrocracking conditions of temperature and pressure in the presence of a two-component catalyst. The hydrogenating component of this catalyst comprises a Group VI metal together with a Group VIII metal or their oxides or sulfides. Thus, for example, mixtures of these components such as nickel-cobalt-molybdenum, cobalt-molybdenum, nickel-molybdenum, nickel-tungsten, etc. and their oxides and sulfides can be employed. The support for the hydrogenating component is the activated alumina described above. The activated alumina is composited with the hydrogenating component in accordance with any of the conventional procedures for impregnation of porous carriers with multi-component catalysts. Ordinarily we prefer to impregnate the activated alumina carrier with an aqueous solution of a salt of a Group VI metal such as molybdenum followed by drying and calcining and then to impregnate with an aqueous salt of a Group VIII metal such as nickel or cobalt followed by a second drying and calcining. If desired the oxides of the metal components can be reduced or partially reduced by treatment with hydrogen prior to employment in our process. In the event a sulfide is to be present, the catalyst can be treated with hydrogen sulfide to form the metal sulfides. This is advantageously carried out by treating with a mixture of hydrogen and hydrogen sulfide at a temperature between about 450° and 950° F. Also the metal components can be reduced and/or sulfided by contacting with the feed stock. Alternatively, the catalyst may be formed by precipitating the sulfides of the metals in aqueous impregnating solutions as by treatment with hydrogen sulfide.

In accordance with this aspect of our invention the heavy hydrocarbon to be hydrocracked is contacted with the above described catalyst at a temperature between about 750° and 900° F. and preferably between 780° and 875° F. By employing temperatures within these ranges is meant to commence operation at the lower end of the temperature range and gradually increase the temperature during the course of operation until a terminal temperature is reached, at which time the reactor is shut down and the catalyst regenerated. Thus, for example, the hydrocracking process can be commenced at a temperature within the range from about 750° to about 850° F. and the temperature increased incrementally until the temperature range of about 810° to about 900° F. is attained, at which point the run is terminated. Preferably the process can be commenced at a temperature within the range from about 780° to about 810° F. and then increased incrementally until a temperature in the range from about 840° to about 875° F. is attained. The temperature is increased during the course of the process from the lower starting range at a rate sufficient to maintain the volume of distillate yield at a predetermined satisfactory level and this gradual increase of temperature is continued until such time as the upper limit of the temperature range has been achieved.

When operating in accordance with this aspect of our invention a hydrogen partial pressure between about 1500 and 3000 p.s.i., preferably between about 2000 and 2500 p.s.i., a space velocity from about 0.1 to 5.0, preferably from about 0.2 to 2.0, a hydrogen feed rate from about 5000 to about 30,000 s.c.f./b. and preferably from about 7,000 to about 20,000 s.c.f./b. and a hydrogen consump-

tion rate from about 6 to about 40 mols of hydrogen per atom of sulfur removed from the charge stock, preferably from 6 to 20 mols of hydrogen per atom of sulfur, can be employed.

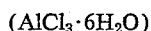
The characteristics of the products obtained from the practice of this aspect of our invention will depend upon the feed stock, particularly the boiling point of the feed stock, and the reaction conditions employed. Thus, it is possible to produce a furnace oil product which is usable directly from the processing unit. Furthermore, this aspect of our invention can also be employed to produce a low octane gasoline directly from residual stocks. In the practice of this aspect of our invention, it is also possible to recycle to the reactor all portions of the product boiling above a particular range, such as, for example, the gas oil range (1050° F.), thereby increasing the net yield of usable products per volume of heavy hydrocarbons charged.

As mentioned previously, the pore size distribution of the activated alumina employed in our invention in the areas of both hydrocracking and hydrodesulfurization of heavy petroleum hydrocarbons yields unexpectedly superior results. It is theorized that these unexpectedly superior results are due principally to the extremely small pore size of the support. As is well known in the art, heavy petroleum hydrocarbons, such as residual stocks, for example, contain large quantities of asphaltic and metalliferous materials and that the presence of such contaminants adversely affects catalyst life; the asphaltics by depositing coke on the catalyst and the metalliferous materials by depositing metals on the catalyst surface thereby poisoning the catalyst. As is also well known, the asphaltic compounds are polyaromatic molecules of comparatively large size and the metals present in petroleum stocks are normally contained in the form of extremely large molecules. We believe that the mechanics of the hydrocracking and hydrodesulfurization aspects of our invention are such that, since a substantial portion of the surface area of the catalyst is within the extremely small pores of the catalyst, a great number of the extremely large molecules present in the stock are prevented from entering the small pores where they might be adsorbed on the catalyst surface and react. Thus, the particular type of activated alumina described above when employed in our invention permits only a limited amount of the large molecular asphaltic and metalliferous materials to react while providing an active catalyst of high surface area suitable for adsorbing the comparatively smaller hydrocarbon molecules and permitting them to react. It is believed, therefore, that minimizing the reaction of the asphaltic and metalliferous materials in this manner also minimizes the coke and metal deposition on the surface of the catalyst without any reduction in the desired reactions. A comparison of the products obtained in accordance with our invention with those obtained by known processes tends to substantiate this theory, inasmuch as the products of our process have a higher metals content and contain more higher boiling asphaltics. We believe, therefore, that this theory accounts for the unique coaction of the particular activated alumina described above with heavy petroleum hydrocarbons in accordance with our invention.

In order to illustrate our invention in greater detail, reference is made to the following examples:

Example I

A 4730 gram quantity of aluminum chloride



was dissolved in 20 liters of water and 500 grams of glacial acetic acid was then added to the solution. In another vessel 2000 milliliters of ammonium hydroxide (28% NH_3) was mixed with 5000 milliliters of water, and

this solution was then added to the aluminum chloride solution until a pH of 8 was obtained. The slurry formed from mixing the two solutions was filtered and washed on the cake until the conductivity of the wash water lined out indicating that the washing was complete. The wet filter cake was then dried at 250° F. for 16 hours to provide an alumina hydrate containing from 1.2 to 2.6 mols of water of hydration. A 500 gram sample of the alumina hydrate was charged to an autoclave with 500 milliliters of distilled water and heated to 350° F. in four hours and maintained at that temperature for an additional four hours under the pressure generated by the water. The material from the autoclave was filtered and the hydrothermally treated alumina hydrate was dried at 250° F., sized to 10–20 mesh and calcined at 1000° F. for 16 hours to provide the alumina support.

An ammonium molybdate solution was prepared by dissolving 33.6 grams of ammonium paramolybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ in distilled water and 15 milliliters of ammonia (28% NH_3) and diluting to 130.5 milliliters with distilled water. The final solution weighed 156.8 grams and contained 11.5 percent molybdenum. This solution was added with stirring to an evaporating dish which contained 196.4 grams of the alumina support described above. The solution completely wet the alumina support (incipient wetness—0.665 milliliters of solution per gram) and left no excess solution in the dish. The wet material was dried at about 250° F. for 24 hours.

A nickel nitrate-cobalt nitrate solution was prepared by dissolving 4.4 grams of nickel nitrate $(\text{NiNO}_3 \cdot 6\text{H}_2\text{O})$ and 11.6 grams of cobalt nitrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ in distilled water and diluting to 108 milliliters. The final solution weighed 121.0 grams and contained 0.94 percent nickel and 1.88 percent cobalt. This solution was then added with stirring to an evaporating dish containing 228.8 grams of the dried material from the molybdenum impregnation above. The solution completely wet the molybdenum impregnated material (incipient wetness—0.473 milliliters of solution per gram) and left no excess solution in the dish. The resulting wet mixture was dried at about 250° F. for 24 hours and then calcined in air in an electric muffle furnace at 900° F. for about 10 hours. The final metal content of the catalyst was about 0.5 percent nickel, 1.0 percent cobalt and 8.0 percent molybdenum.

To illustrate the process of our invention, a Kuwait vacuum residue (18 percent by volume crude) containing sulfur, asphaltic and metalliferous contaminants was subjected to hydrogen treatment in accordance with the process of our invention employing the nominal conditions of 1000 p.s.i.g., 750° F., 0.5 liquid hourly space velocity and 10,000 standard cubic feet of hydrogen per barrel of feed. In order to afford a basis of comparison for our invention with previously suggested procedures, two separate runs were carried out; one employing the catalyst required in our invention produced as described above and the other using a catalyst comprising the same metals composition stated above but employing a commercial alumina which is widely used in this country as a carrier for hydrogenation catalysts. The physical characteristics of the two different aluminas, including pore size distribution, are shown in Table I below. The pore size distributions shown in Table I were determined by the technique of nitrogen adsorption and desorption isotherms described in the article by Ballou and Doolen in Analytical Chemistry, volume 32, page 532, April 1960. It will be noted that in the alumina employed in our invention less than 5 percent of the pore volume is in pores larger than 100 A. radius and less than ten percent of the pore volume is in pores larger than 80 A. radius, while the pore size distribution of the commercial alumina is outside this range.

TABLE I

	Hydrothermal Al ₂ O ₃	Commercial Al ₂ O ₃
Surface area, M. ² /g.-----	170	171.5
Pore volume, cc./g.-----	0.37	0.47
Avg. pore radius (2V/A), Å-----	43.8	55
Tap density, g./cc.-----	0.89	0.71
Pore size distribution, percent of pore vol. in range:		
200-300 Å. radius.-----	0.6	0.9
100-200 Å. radius.-----	2.2	8.9
80-100 Å. radius.-----	6.8	17.2
60-80 Å. radius.-----	28.6	21.1
50-60 Å. radius.-----	11.5	17.0
40-50 Å. radius.-----	20.0	8.2
30-40 Å. radius.-----	16.1	13.8
20-30 Å. radius.-----	12.9	12.8
15-20 Å. radius.-----	1.2	0.0
10-15 Å. radius.-----	0.0	0.0
0-10 Å. radius.-----	0.0	0.0
>100 Å. radius.-----	2.8	9.8
>80 Å. radius.-----	9.6	27.0

The inspection data of the Kuwait vacuum residue employed as a charge stock is shown in column 1 of Table II below. Columns 2 and 3 of Table II show the exact operating conditions and the results obtained during two different operating periods of the run embodying the process of our invention and employing the catalyst required in our invention, while columns 4 and 5 show the operating conditions and the results obtained during two different periods of operation in the run employing the commercial alumina.

TABLE II

	1 (Charge)	2	3	4	5
		Run Interval, hours			
		8-24	24-104	8-24	24-96
Operating conditions:					
Pressure, p.s.i.g.-----		1,000	1,000	1,000	1,000
Average temp., ° F.-----		749	750	749	751
Hydrogen rate, s.c.f./b.-----		8,700	9,600	10,000	10,400
Space velocity, vol./hr./vol.-----		0.55	0.49	0.50	0.48
Inspections:					
Gravity, ° API-----	5.5	17.7	16.7	16.3	14.7
Viscosity, SUV, sec.:					
100° F.-----		2,237	3,349	4,255	7,411
130° F.-----		768	1,019	1,296	2,061
Sulfur, percent-----	5.45	0.80	0.87	1.40	1.84
Nitrogen, percent-----	0.43	0.26	0.31	0.34	0.37
Carbon residue, percent-----	23.11	8.80	9.72	10.54	12.83
Insol. in n-pentane-----	15.14	4.54	5.59	3.65	5.34
Nickel, p.p.m.-----	32	11.6	10.9	7.7	12.2
Vanadium, p.p.m.-----	102	14.5	20.0	7.9	16.7
Desulfurization, percent-----		85.3	84.0	74.3	66.2
Yield, percent by wt. of charge: Gases, C ₁ -C ₃ -----		1.2	1.4	0.9	0.8
Yield, percent by vol. of charge:					
Gasoline (C ₄ -400° F.)-----			6.9		4.8
Light gas oil (400-670° F.)-----			10.5		8.8
Heavy gas oil (670-1,000° F.)-----			39.6		20.7
670° F. residue-----			86.2		90.6
1,000° F. residue-----			46.6		69.9
Catalyst deposits: Carbon, percent by wt.-----			14.1		17.9
Hydrogen consumption:					
S.c.f./b.-----			880		520
Mols H ₂ /atom S removed-----			4.5		3.3
Percent desulfurization, at:					
30 hours-----			84.4		73.8
60 hours-----			82.9		67.5
90 hours-----			81.3		61.4
Deactivation rate:					
Percent sulfur in product/100 hours-----			0.28		1.2
Percent desulfurization/100 hours-----			5.1		22.0

A comparison of the data set forth in Table II clearly demonstrates the superiority of the process of our invention over a process operating under similar conditions but employing a commercial alumina support. For example, it can be seen that the process of our invention provides a remarkable improvement in initial sulfur removal during the period of 8 to 24 hours (column 2), as opposed to the amount of sulfur removed during the comparable period but employing a commercial alumina support (column 4). Furthermore, such improved sulfur removal is maintained during continued operation as

shown in the 24-104 hour period (column 3). Thus, the percent desulfurization obtained during the period of 24 to 104 hours in accordance with our invention is 84.0 percent, while the run employing the commercial alumina support during the period of 24-96 hours (column 5) only provides a 66.2 percent desulfurization. The true advantageous results unexpectedly provided by the process of our invention are more clearly evidenced by a comparison of the percent desulfurization obtained at 30, 60 and 90 hours. It will be noticed that the percent desulfurization obtained with the process of our invention (columns 2 and 3) decreased only 3.1 percent during the period of 30-90 hours, while the percent desulfurization obtained when employing the commercial catalyst decreased 13.4 percent during a similar period. A more dramatic illustration of this point is that the percent desulfurization obtained after 90 hours' operation in accordance with our invention is substantially superior to the percent desulfurization obtained after only 30 hours' operation employing the commercial catalyst. This is further emphasized by the deactivation rates shown for catalyst in the process of our invention as opposed to the commercial catalyst as shown at the bottom of Table II. From these data it can be seen that the life of the catalyst employed in our invention is about four times the life achieved with the commercial catalyst.

It will also be noted that the process of our invention provides a greater increase of product gravity in degrees API than is provided by the process employing the com-

mercial alumina for comparable periods—17.7 versus 16.3 and 16.7 versus 14.7. A comparison of the n-pentane insolubles along with the metals content, particularly vanadium, of the products tends to substantiate the theory of operation of the particular alumina catalyst support employed in our invention when in contact with a charge stock containing asphaltic and metalliferous contaminants. It is thereby shown that a far greater quantity of metalliferous contaminants, particularly vanadium, are passed through the catalyst bed during comparable periods of operation as well as greater quantities of asphaltic mate-

rial. As state previously, we believe that the particular alumina employed in accordance with our invention permits a greater portion of the asphaltic and metalliferous contaminants to pass through the reactor bed unconverted inasmuch as these large molecular contaminants are precluded from entering the smaller sized pores of the contaminants, thereby lowering coke deposit. This is even further substantiated by the lower coke deposition on the catalyst in the process of our invention as opposed to the quantity of coke deposited on the commercial alumina catalyst.

Example II

In this example the same residual stock used in Example I is employed as the charge stock to a hydrodesulfurization process. The catalyst employed in this example is also the same nickel-cobalt-molybdenum catalyst supported on alumina derived from a hydrothermally treated alumina hydrate that was employed in Example I. After completion of normal start-up procedures which include introducing the charge stock to the reactor at a low temperature, usually well below operating temperatures, and then gradually increasing the temperature over a period of time, usually about 6 to 8 hours, until a normal operating temperature is reached, the run of this example is commenced at an initial operating temperature of 750° F. Throughout the duration of the run the other operating conditions are maintained constant at a hydrogen partial pressure of 1000 p.s.i.g., a LHSV of 0.8 and a hydrogen recycle rate of 5000 s.c.f./b. The sulfur content of the total liquid product obtained initially is 1.0 percent by weight. During the course of this run the temperature is increased at an average rate of approximately 0.75° F./day in order to maintain the level of sulfur content in the total product at 1.0 percent or below. This operation is continued until an operating temperature of 840° F. is achieved (about 120 days of operation), at which time the operation is discontinued. During the course of this run the hydrogen consumption is about 4 mols of hydrogen per atom of sulfur removed from the charge stock.

Thus, when operating in accordance with the particular embodiment of our invention described immediately above, it will be seen that a process for desulfurizing a heavy petroleum hydrocarbon while operating at a low pressure is provided. Further, the gradual increase in the operating temperature, in this example 0.75° F./day, provides a product with a constant low sulfur content, i.e., 1.0 percent or less, while also providing an unexpectedly long catalyst life.

Example III

In this example the same residual stock used in Example I is employed as the charge stock to a hydrocracking process. The catalyst employed in this example is also the same nickel-cobalt-molybdenum catalyst supported on alumina derived from a hydrothermally treated alumina hydrate that was used in Example I. After completion of normal start-up procedures, which include introducing the charge stock to the reactor at a low temperature, usually well below operating temperatures, and then gradually increasing the temperature over a period of time, usually about 6 to 8 hours, until a normal operating temperature is reached, the run of this example is commenced at an initial operating temperature of 790° F. Throughout the duration of the run the other operating conditions are maintained constant at a pressure of 2000 p.s.i.g., a space velocity of 0.5 LHSV and a hydrogen recycle ratio of 10,000 s.c.f./b. The initial conversion of the charge stock to distillate boiling at less than 1000° F. when employing the initial conditions is 65 percent by volume. During the course of this run the temperature is increased at an average rate of approximately 0.75° F./day in order to maintain the level of conversion at 65 percent by volume of the feed to distillate boiling at less than 1000° F. This operation is con-

tinued until an operating temperature of 880° F. is achieved, at which time the operation is discontinued. During the course of this run the hydrogen consumption is about 7 mols of hydrogen per atom of sulfur removed from the charge stock. Further, the product of this run has a substantially higher API gravity (about 20) than the charge stock. The product also has a comparatively high metals content.

Thus, when operating in accordance with the particular embodiment of our invention described immediately above, it will be seen that a process for hydrocracking a heavy petroleum hydrocarbon while operating at a low pressure is provided. Further, the gradual increase in the operating temperature, in this example 0.75° F./day, provides a constant level of conversion, while also providing an unexpectedly long catalyst life.

We claim:

1. A process for hydrogen treatment of heavy petroleum hydrocarbons containing sulfur, asphaltic and metalliferous compounds as contaminants, containing substantial amounts of hydrocarbon components boiling above 300° F. and containing residual materials, which process comprises contacting the hydrocarbons with hydrogen at a pressure from about 300 to about 3000 p.s.i., a space velocity from about 0.1 to about 10.0 volumes of heavy hydrocarbon per volume of catalyst per hour, a hydrogen consumption rate from about 1 to about 40 mols of hydrogen per atom of sulfur removed from the heavy hydrocarbons and at a temperature from about 700 to about 900° F. in the presence of a catalyst comprising essentially a minor amount of a hydrogenating catalyst composited with a major amount of an activated alumina having less than 5 percent of its pore volume that is in the form of pores having a radius of 0 to 300 Å. in pores larger than 100 Å. radius and having less than 10 percent of said pore volume in pores larger than 80 Å. radius which alumina is prepared by treating a substance which is predominantly composed of a crystalline alumina hydrate containing from 1.2 to 2.6 mols of water of hydration and which is substantially free of alumina monohydrate and alumina trihydrate, said alumina hydrate being prepared by precipitation from a solution of an aluminum compound at a pH between 7 and 12, and drying to the above specified water of hydration content prior to substantial transformation to an alumina hydrate having a higher or lower water of hydration content, said treating comprising hydrothermally treating the dried alumina hydrate by heating it in the presence of water at a temperature sufficient to vaporize the water under autogenous pressure, whereby the alumina hydrate is converted substantially to a monohydrate and drying and calcining the hydrothermally treated alumina hydrate.

2. The process of claim 1 wherein the hydrogenating catalyst is selected from the group consisting of Group VI metals, Group VIII metals, their oxides and sulfides.

3. The process of claim 1 wherein the hydrogenation catalyst consists essentially of the oxides of nickel, cobalt and molybdenum.

4. The process of claim 1 wherein the contacting temperature is from about 750° to about 875° F., the pressure is from about 1000 to about 2500 p.s.i., the space velocity is from about 0.2 to about 3.0 volumes of heavy hydrocarbon per volume of catalyst per hour and the hydrogen consumption rate is from about 2 to about 20 mols of hydrogen per atom of sulfur removed from the heavy hydrocarbons.

5. A process for hydrodesulfurizing heavy petroleum hydrocarbons containing asphaltic and metalliferous compounds as contaminants, containing substantial amounts of hydrocarbon components boiling above 300° F., containing residual materials, and containing harmful amounts of sulfur compounds, which process comprises contacting the hydrocarbons with hydrogen at a temperature from about 700 to about 875° F., a pressure from about 300 to about 2000 p.s.i., a space velocity from about

0.1 to about 10.0 volumes of heavy hydrocarbon per volume of catalyst per hour and a hydrogen consumption rate from 1 to about 5 mols of hydrogen per atom of sulfur removed from the heavy hydrocarbons in the presence of a catalyst comprising essentially a minor amount of a hydrogenating catalyst composited with a major amount of an activated alumina having less than 5 percent of its pore volume that is in the form of pores having a radius of 0 to 300 A. in pores larger than 100 A. radius and having less than 10 percent of said pore volume in pores larger than 80 A. radius prepared by treating a substance which is predominantly composed of a crystalline alumina hydrate containing from 1.2 to 2.6 mols of water of hydration and which is substantially free of alumina monohydrate and alumina trihydrate, said alumina hydrate being prepared by precipitation from a solution of an aluminum compound at a pH between about 7 and 12, and drying to the above specified water of hydration content prior to substantial transformation to an alumina hydrate having a higher or lower water of hydration content, said treating comprising hydrothermally treating the dried alumina hydrate by heating it in the presence of water at a temperature sufficient to vaporize the water under autogenous pressure, whereby the alumina hydrate is converted substantially to a monohydrate and drying and calcining the hydrothermally treated alumina hydrate.

6. The process of claim 5 wherein the contacting temperature is from about 750° to about 850° F., the pressure is from about 1000 to about 1500 p.s.i., the space velocity is from about 0.2 to about 3.0 volumes of heavy hydrocarbon per volume of catalyst per hour and the hydrogen consumption rate is from about 2 to about 5 mols of hydrogen per atom of sulfur removed from the heavy hydrocarbons.

7. The process of claim 5 wherein the hydrogenating catalyst is selected from the group consisting of Group VI metals, Group VIII metals, their oxides and sulfides.

8. The process of claim 5 wherein the hydrogenating catalyst consists essentially of the oxides of nickel, cobalt and molybdenum.

9. A process for hydrocracking heavy petroleum hydrocarbons containing sulfur asphaltic and metalliferous compounds as contaminants, containing substantial amounts of hydrocarbon components boiling above 300° F., and containing residual materials, which process comprises contacting the hydrocarbons with hydrogen at a temperature from about 750° to about 900° F., a pressure from about 1500 to about 3000 p.s.i., a space velocity from about 0.1 to about 5.0 volumes of heavy hydrocarbon per volume of catalyst per hour and a hydrogen consumption rate from about 6 to about 40 mols of hydrogen per atom of sulfur removed from the heavy hydrocarbons in the presence of a catalyst comprising essentially a minor amount of a hydrogenating catalyst composited with a major amount of an activated alumina having less than 5 percent of its pore volume that is in the form of pores having a radius of 0 to 300 A. in pores larger than 100 A. radius and having less than 10 percent of said pore volume larger than 80 A. radius prepared by treating a substance which is predominantly composed of a crystalline alumina hydrate containing from 1.2 to 2.6 mols of water of hydration and which is substantially free of alumina monohydrate and alumina trihydrate, said alumina hydrate being prepared by precipitation from a solution of an aluminum compound at a pH between about 7 and 12, and drying to the above specified water of hydration content prior to substantial transformation to an alumina hydrate having a higher or lower water of hydration content, said treating comprising hydrothermally treating the dried alumina hydrate by heating it in the presence of water at a temperature sufficient to vaporize the water under autogenous pressure, whereby the alumina hydrate is converted substantially to a monohydrate, and drying and calcining the hydrothermally treated alumina hydrate.

10. The process of claim 9 wherein the contacting

temperature is from about 780° to about 875° F., the pressure is from about 2000 to about 2500 p.s.i., the space velocity is from about 0.2 to about 2.0 volumes of heavy hydrocarbon per volume of catalyst per hour and the hydrogen consumption rate is from about 6 to about 20 mols of hydrogen per atom of sulfur removed from the heavy hydrocarbons.

11. The process of claim 9 wherein the hydrogenating catalyst is selected from the group consisting of Group VI metals, Group VIII metals, their oxides and sulfides.

12. The process of claim 9 wherein the hydrogenating catalyst consists essentially of the oxides of nickel, cobalt and molybdenum.

13. A process for hydrodesulfurizing heavy petroleum hydrocarbons containing asphaltic and metalliferous compounds as contaminants, containing substantial amounts of hydrocarbon components boiling above 300° F., containing residual materials, and containing harmful amounts of sulfur compounds, which process comprises contacting the hydrocarbons with hydrogen at an initial temperature from about 700° to about 800° F., gradually increasing the temperature at a rate sufficient to maintain the sulfur content of the product below a predetermined level and terminating the contacting when a temperature in the range from about 775° to about 875° F. has been reached, while maintaining a pressure from about 300 to about 2000 p.s.i., a space velocity from about 0.1 to about 10.0 volumes of heavy hydrocarbon per volume of catalyst per hour and a hydrogen consumption rate from about 1 to about 5 mols of hydrogen per atom of sulfur removed from the heavy hydrocarbons, the contacting being conducted in the presence of a catalyst comprising essentially a minor amount of a hydrogenating catalyst composited with a major amount of an activated alumina having less than 5 percent of its pore volume that is in the form of pores having a radius of 0 to 300 A. in pores larger than 100 A. radius and having less than 10 percent of said pore volume in pores larger than 80 A. radius prepared by treating a substance which is predominantly composed of a crystalline alumina hydrate containing from 1.2 to 2.6 mols of water of hydration and which is substantially free of alumina monohydrate and alumina trihydrate, said alumina hydrate being prepared by precipitation from a solution of an aluminum compound at a pH between about 7 and 12, and drying to the above specified water of hydration content prior to substantial transformation to an alumina hydrate having a higher or lower water of hydration content, said treating comprising hydrothermally treating the dried alumina hydrate by heating it in the presence of water at a temperature sufficient to vaporize the water under autogenous pressure, whereby the alumina hydrate is converted substantially to a monohydrate, and drying and calcining the hydrothermally treated alumina hydrate.

14. The process of claim 13 wherein the initial temperature is from about 750° to about 775° F., the contacting is terminated when a temperature in the range from about 800° to about 850° F. is reached, the pressure is from about 1000 to about 1500 p.s.i., the space velocity is from about 0.2 to about 3.0 volumes of heavy hydrocarbon per volume of catalyst per hour and the hydrogen consumption rate is from about 2 to about 5 mols of hydrogen per atom of sulfur removed from the heavy hydrocarbons.

15. The process of claim 13 wherein the hydrogenating catalyst is selected from the group consisting of Group VI metals, Group VIII metals, their oxides and sulfides.

16. The process of claim 13 wherein the hydrogenating catalyst consists essentially of the oxides of nickel, cobalt and molybdenum.

17. A process for hydrocracking heavy petroleum hydrocarbons containing sulfur, asphaltic and metalliferous compounds as contaminants, containing substantial amounts of hydrocarbon components boiling above 300°

F., and containing residual materials, which process comprises contacting the hydrocarbons with hydrogen at an initial temperature from about 750° to about 850° F., gradually increasing the temperature at a rate sufficient to maintain a predetermined rate of conversion and terminating the contacting when a temperature in the range from about 810° to about 900° F. has been reached, while maintaining a pressure from about 1500 to about 3000 p.s.i., a space velocity from about 0.1 to about 5.0 volumes of heavy hydrocarbon per volume of catalyst per hour and a hydrogen consumption rate from about 6 to about 40 mols of hydrogen per atom of sulfur removed from the heavy hydrocarbons, the contacting being conducted in the presence of a catalyst comprising essentially a minor amount of a hydrogenating catalyst composited with a major amount of an activated alumina having less than 5 percent of its pore volume that is in the form of pores having a radius of 0 to 300 A. in pores larger than 100 A. radius and having less than 10 percent of said pore volume in pores larger than 80 A. radius prepared by treating a substance which is predominantly composed of a crystalline alumina hydrate containing from 1.2 to 2.6 mols of water of hydration and which is substantially free of alumina monohydrate and alumina trihydrate, said alumina hydrate being prepared by precipitation from a solution of an aluminum compound at a pH between about 7 and 12, and drying to the above specified water of hydration content prior to substantial transformation to an alumina hydrate having a higher or lower water of hydration content, said treating comprising hydrother-

mally treating the dried alumina hydrate by heating it in the presence of water at a temperature sufficient to vaporize the water under autogenous pressure, whereby the alumina hydrate is converted substantially to a monohydrate, and drying and calcining the hydrothermally treated alumina hydrate.

18. The process of claim 17 wherein the initial temperature is from about 780° to about 810° F., the contacting is terminated when a temperature in the range from about 840° to about 875° F. is reached, the pressure is from about 2000 to about 2500 p.s.i., the space velocity is from about 0.2 to about 2.0 volumes of heavy hydrocarbon per volume of catalyst per hour and the hydrogen consumption rate is from about 6 to about 20 mols of hydrogen per atom of sulfur removed from the heavy hydrocarbons.

19. The process of claim 17 wherein the hydrogenating catalyst is selected from the group consisting of Group VI metals, Group VIII metals, their oxides and sulfides.

20. The process of claim 17 wherein the hydrogenating catalyst consists essentially of the oxides of nickel, cobalt and molybdenum.

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DELBERT E. GANTZ, *Primary Examiner*.

30 SAMUEL P. JONES, *Examiner*.

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,340,180

September 5, 1967

Harold Beuther et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 12, for "derviatives" read -- derivatives --; line 66, for "metalliferrous" read -- metalliferous --; column 2, line 19, for "radium" read -- radius --; column 5, lines 9 and 10, for "exten" read -- extent --; line 40, for "temployment" read -- employment --; column 7, line 73, for "deculfurization" read -- desulfurization --; column 10, line 32, for "11.6" read -- 11.26 --.

Signed and sealed this 20th day of August 1968.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents