930,760

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COMPLETE SPECIFICATION.

Improvements in and relating to the Manufacture and Use of Hydrocarbon Purification Catalysts.

We, UNIVERSAL OIL PRODUCTS COMPANY, a Corporation organized under the laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the purification, or treating, of hydrocarbons and hydrocarbon fractions, which process utilizes a hydrosulfurization catalyst in removing various metallic and non-metallic ~~contaminates~~ and more particularly contaminants of the group of olefinic hydrocarbons and sulfurous and nitrogenous compounds; the invention also relates to such catalysts and their manufacture. More specifically, the present invention involves catalytic composites which are prepared by a procedure wherein a composite containing alumina, silica, molybdenum oxide and nickel oxide is sulfided with a gaseous sulfiding mixture containing hydrogen sulfide and hydrogen at elevated temperature.

The purification process of the present invention may be utilized to great advantage in the preparation of saturated hydrocarbon charge stocks, substantially free from combined sulfur and nitrogen, for use in other processes within the petroleum industry. For example, it is especially applicable to the purification of straight-run gasolines, natural gasolines, cataytically-cracked naphtha fractions and thermally-cracked hydrocarbon distillates which are to be reformed for the purpose of improving the anti-knock characteristics thereof. Platinum-containing catalysts are highly effective in reforming and have an extended life when used in the processing of hydrocarbon fractions that are comparatively free from various contaminants. However, when processing charge stocks containing excessive concentrations of contaminants, there results a selective poisoning of the catalyst accompanied by a significant decline in the activity and stability thereof.

It is generally known that the most common contaminants ~~casing~~ catalyst causing poisoning in a catalytic reforming operation, in addition to oxygenated compounds, are combined sulfur and combined nitrogen. Further, most charge stocks to catalytic reforming processes contain minor, but significantly detrimental quantities of metals such as arsenic, copper, lead and manganese, which impair the activity and stability of platinum-containing catalysts. Elimination of the difficulties which arise as a result of the presence of various contaminants within the charge stock has been achieved in the past with fair success through the use of suitable hydrodesulfurization catalysts at particular conditions of operation, whereby metallic contaminants are removed, combined sulfur and nitrogen are converted to hydrogen sulfide and ammonia, and olefinic hydrocarbons are saturated to form paraffins and naphthenes. The present invention provides a hydrocarbon purification process and a catalyst for use therein which assure an appreciably greater success in the hydrocarbon purification treatment and meet the more stringent demands at present imposed on such catalysts.

In accordance with the present invention the catalyst for use in the purification of contaminated hydrocarbons is manufactured

[*Price 4s. 6d.*]

by a process which comprises treating a composite containing alumina, silica, molybdenum oxide and nickel oxide with a ~~gasees~~ gaseous sulfiding mixture containing hydrogen and hydrogen sulfide in a mol ratio of from 1:2 to 4:1 at a temperature between 204° and 427° C. prior to contact with any hydrocarbons to be purified and thereupon cooling the sulfided composite to a temperature below 204° C. under a superatmospheric pressure of hydrogen sulfide.

The catalyst composition provided by this invention is usually manufactured from an alumina-silica carrier material which has been prepared synthetically to contain the alumina and silica in a weight ratio between 3:1 and 20:1 and preferably in a weight ratio of from 7:1 to 8:1, and which has been impregnated with a molybdenum compound and a nickel compound and thereafter calcined in an oxidizing gas to form a composite containing alumina, silica, molybdenum oxide and nickel oxide. In a specific embodiment the alumina-silica carrier material may contain cobalt in a smaller amount than the nickel content of the catalyst composition and preferably in an amount of from 0.1 to 0.7% by weight of the total composition, the cobalt content being calculated as elemental cobalt. The alumina-silica carrier material is composited with molybdenum in an amount which is less than the silica content of the composite and generally not more than 10% and preferably from 5 to 10% by weight of the total composite, the molybdenum content being calculated as elemental molybdenum. Moreover, the silica-alumina carrier material is composited with nickel in an amount substantially less than that of the molybdenum and preferably within the range of from 1% to 5% by weight of the total composite, the nickel content being calculated as elemental nickel. Prior to the treatment of this composite with the gaseous sulfiding mixture the molybdenum and nickel, and also the cobalt if present, are present as oxides, whereas they are present as the sulfides after the treatment of the composite with the gaseous sulfiding mixture. In a preferred embodiment the reductive sulfiding of the composite is effected over a range of temperatures increasing from an initially low temperature of 204° C. to a temperature in the range of 399—427° C. and thereupon the sulfided composite is cooled from the final high temperature to below 204° C. under a superatmospheric pressure of hydrogen sulfide preferably in the range of from 0.34 to 1.02 atmospheres. The gaseous sulfiding mixture utilized in the sulfiding step may contain inert gas such as nitrogen and preferably contains the hydrogen and hydrogen sulfide in a mole ratio of from 1.5:1 to 4:1.

Also in accordance with the present invention contaminated hydrocarbons are purified at elevated temperature and under imposed hydrogen pressure with a hydrodesulfurization catalyst which has been prepared by treating a composite containing alumina, silica, molybdenum oxide and nickel oxide with a gaseous sulfiding mixture containing hydrogen and hydrogen sulfide in a mol ratio of from 1:2 to 4:1 in the absence of said hydrocarbons at a temperature between 204° and 427° C. and thereupon cooling the sulfided composite to below 204° C. under a superatmospheric pressure of hydrogen sulfide.

In a more specific embodiment of the present process for the purification of hydrocarbons, normally liquid hydrocarbons contaminated by sulfurous and nitrogenous compounds are passed into a hydrogenation reaction zone maintained under an imposed hydrogen pressure in excess of 6.8 atmospheres and containing a hydrodesulfurization catalyst which consists of a composite of an alumina-silica carrier material with the sulfides of molybdenum, nickel, and cobalt and which has been prepared by subjecting a composite containing the silica and alumina in a weight proportion of from 7:1 to 8:1 and containing the oxides of cobalt, molybdenum and nickel in amounts equivalent to from 0.1 to 0.7% by weight of cobalt, from 5.0 to 10.0% by weight of molybdenum and from 1.0 to 5.0% by weight of nickel to treatment with a gaseous sulfiding mixture containing hydrogen sulfide and hydrogen in the manner set forth above and cooling the sulfided composite to below 204° C. under a superatmospheric pressure of hydrogen sulfide prior to any contact of the composite with said contaminated hydrocarbons, removing from said hydrogenation reaction zone a mixture of normally liquid hydrocarbons and normally gaseous material containing hydrogen sulfide and ammonia, thereafter subjecting said mixture to separation for the purpose of removing the normally gaseous material and recovering said liquid hydrocarbons substantially free from sulfurous and nitrogeneous compounds.

Processes for effecting the purification, by catalytic hydrogenation, of hydrocarbons and hydrocarbon fractions contaminated by unsaturated hydrocarbons and/or other contaminants of the kind referred to above are well known in the prior art and have been successful to an appreciable extent in the pretreatment, or purification, of such hydrocarbons. Most processes make use of a hydrogenation catalyst consisting of an alumina carrier material which has been combined with catalytically active metallic components of cobalt and molybdenum. The prior art indicates a variety of methods for the preparation of such catalytic composites, as well as a wide range in the com-

position thereof. The various methods employed for the preparation of the cobalt and molybdenum-containing catalyst include single and double impregnations of the active metallic components, calcination at various elevated temperatures, reduction treatments, and the use of various reagents in the impregnating procedure to yield a final composite in which the metallic components exist in some chosen, combined form. Although the hydrogenation processes employing these cobalt- and molybdenum-containing desulfurization catalysts may be advantageously utilized in treating various hydrocarbons, they fall short of fulfilling the present-day requirements which have been imposed on these processes as a result of the great demand for high quality distillate fuels and catalytically reformed products in large liquid volumetric yield. This demand has brought about a certain degree of criticality, and especially with respect to the condition of the particular hydrocarbon charge stock employed in the catalytic reforming process. The pretreating processes and purification catalyst of the prior art are insufficiently capable of treating the charge stocks to the extent that the same become sufficiently satisfactory for use in the catalytic reforming processes employed at present. The tolerable degree of concentration of the various contaminants previously described, has been lessened significantly due to the operating demands which have been placed on the catalyst employed in the reforming process. In short, the processes and hydrogenation catalysts of the prior art no longer suffice to prepare the charge stock to the extent which is now considered suitable for further processing in a catalytic reforming unit.

The purification process of the present invention utilizes at least a four-component catalyst comprising an alumina-silica carrier material which has been impregnated with molybdenum and nickel, and further prepared to yield a final catalyst in which the nickel and molybdenum exist as the sulfides thereof. It has further been found that a five-component catalyst, the fifth component being a minor quantity of cobalt, may be utilized to greater advantage in the purification of hydrocarbon charge stocks for the catalytic reforming process, as well as in the purification of various heavy naphthas and cycle stocks which are to be used as fuel and lubricating oils. Whether the four-component or five-component catalyst is employed within the present process, the essential feature of this invention involves the preparation of such catalyst through the utilization of a precise combination of manufacturing procedures, more particularly the reductive sulfiding at elevated temperature above 204° C. followed by the cooling to below 204° C. under a superatmospheric hydrogen sulfide pressure.

In regard to the most common contaminants found in the various hydrocarbons, and hydrocarbon distillates, namely olefinic hydrocarbons and nitrogenous and sulfurous compounds, the hydrogenation of the olefinic hydrocarbons to yield paraffins and cyclic paraffins is most readily effected; the conversion of the sulfurous compounds into the hydrocarbon counterpart and hydrogen sulfide is slightly more difficult, whereas the removal of nitrogenous compounds through the conversion of the same into the hydrocarbon counterpart and ammonia, is the most difficult to obtain. The degree of success, in regard to the elimination of nitrogenous compounds is dependent upon many considerations including the quantity thereof within the hydrocarbon being processed, the various physical and chemical characteristics of the hydrocarbon and the concentrations therein of the olefinic hydrocarbons and the sulfurous hydrocarbons. It has been found that the hydrogenation catalyst suffers a loss of activity for removing nitrogenous compounds as the removal of the olefinic and sulfurous hydrocarbons progresses. The activity of the four and five-component catalysts of the present invention, in regard to the removal of nitrogenous compounds, is virtually twice that exhibited by the widely utilized alumina-cobalt-molybdenum catalyst. The increased removal of nitrogen results in a definite improvement in subsequent catalytic reforming operations, and also permits the inclusion of greater quantities of cracked gasolines within the charge stocks to such reforming processes. In the case of intermediate napthas, and light and heavy gas oils, the greater removal of nitrogen compounds affords improved color and storage stability since these nitrogen compounds exhibit the tendency to form gums and varnishes. The activity of the catalyst of the present invention, in regard to removal of sulfurous compounds, as well as for the hydrogenation of olefinic hydrocarbons, is also significantly greater than that of the presently utilized hydrogenation catalyst.

The particularly preferred catalyst of the present invention consists of a composite of an alumina-silica carrier material with molybdenum, nickel and cobalt in the form of the sulfides thereof prior to contact with the particular hydrocarbon mixture to be treated. This five-component catalyst is advantageously prepared by first co-precipitating the alumina-silica carrier material to contain the desired quantity of cobalt, within the range of 0.1% to 0.5% by weight, and impregnating the formed carrier material with a single impregnating solution containing suitable water-soluble molybdenum and

nickel compounds. Following this single impregnating procedure, the resulting alumina - silica - cobalt- molybdenum - nickel composite is calcined in an atmosphere of air at a high temperature, such as for example about 593° C., to convert the catalytically active metallic components to the oxides thereof. Before the oxidized composite is subjected to the reductive sulfiding treatment it is first freed from oxidizing gas and is cooled to a temperature below 260° C. but not below 204° C.; it is then contacted at this temperature with the gaseous sulfiding medium which contains hydrogen and hydrogen sulfide, the hydrogen being present preferably in the greater concentration but not exceeding 4 mols of hydrogen per mol hydrogen sulfide. The temperature of the composite during the initial sulfiding procedure is increased to a level of about 400° C., and the sulfiding is continued at this temperature for a period of about one hour or until sulfidation is substantially complete. Following the complete sulfidation of the catalytically active metallic components, hydrogen sulfide is introduced into contact with the composite intermittently so that a superatmospheric pressure of hydrogen sulfide is maintained on the sulfided catalyst, while the latter is being cooled to a temperature below 204° C. At this stage of the manufacturing procedure, a stream of suitably inert gaseous material such as nitrogen may be employed to cool the sulfided catalyst further in order to facilitate handling and storage.

Various modifications of this procedure may be employed to yield a catalytic composite possessing a high degree of activity in regard to the removal of sulfurous and nitrogenous compounds, in addition to the saturation of olefinic hydrocarbons. Such modifications include the preparation of a four-component catalyst, differing from the five-component catalyst in the omission of the cobalt component therefrom. Both single and double impregnating techniques may be employed; that is, the active metallic components may be individually and separately composited with the carrier material while applying a calcination after each individual impregnation. The order in which the metallic components are combined may be altered without departing from the present invention. In addition, the sulfiding technique may be varied in detail, most advantageously the catalysts are produced by the method of first contacting the catalyst with a mixture of hydrogen sulfide and hydrogen at a comparatively low temperature of the range of from 204° to 427° C. and then maintaining such contact while the catalyst is being heated to a more elevated temperature which is within this same range and at which the greater portion of sulfidation takes place. As hereinbefore set forth, and as will be hereinafter illustrated, beneficial results are obtained when a superatmospheric pressure of hydrogen sulfide is maintained on the catalyst while the latter is being cooled from the elevated sulfiding temperature to a temperature below 204° C. Although the particularly preferred embodiment of the present invention employs a sulfiding medium, in which the hydrogen predominates over the hydrogen sulfide within a mol ratio range of 1.5:1 to 4:1, excellent results, in regard to an increase of activity of the catalyst, have been achieved through the use of a sulfiding medium in which hydrogen sulfide predominates. Thus, the mol ratio of hydrogen to hydrogen sulfide may range from 1:2 to 4:1, with the more advantageous results being obtained with gaseous media in which the mol ratio of hydrogen to hydrogen sulfide is within the range of 2:1 to 3:1. While beneficial results are obtainable through the use of an alumina-silica carrier material having an alumina to silica weight ratio in the range of from 3:1 to 20:1, it is preferred to assure obtaining the beneficial aspects of the combination with avoidance of excessive hydrocracking by using a carrier material in which the alumina to silica weight ratio is within the range of from 7:1 to 8:1. It is understood that these slight modifications of the particularly preferred procedure of catalyst preparation are within the scope of the present invention.

The purification treatment of hydrocarbons containing contaminants such as unsaturated hydrocarbons and sulfurous and nitrogenous compounds is usually effected in a reaction zone which contains the composite catalyst and to which the hydrocarbons are supplied under a gauge pressure of from 6.8 to 68 atmospheres in admixture with hydrogen at an inlet temperature generally in the range of from 93° to 400° C. and more commonly of at least 204° C. and at a liquid hourly space velocity (defined as volumes of the hydrocarbon charge, measured in liquid state, per volume of catalyst per hour) in the range of from 1 to 20. The hydrogen is supplied to the reaction zone at a rate which assures an excess of hydrogen being dicharged with the reaction products from the reaction zone and which ordinarily corresponds to from 178 to 890 normal liters of hydrogen per liter of liquid hydrocarbon charge, although in some cases, as hereinafter illustrated, a smaller proportion of hydrogen to hydrocarbon charge may be sufficient for obtaining the desired purification.

The following examples are given for the purpose of illustrating the present invention, and particularly for indicating the method by which the catalyst to be employed in

the hydrocarbon purification process is prepared.

EXAMPLE I:

This example illustrates one of the specific embodiments for the manufacture of the five-component catalyst, and the use thereof in a unit which simulates a commercial-size hydrodesulfurization process. The manufacture of 90.72 kg. of the sulfided catalytic composite is illustrated by description in three major divisions in the interest of clarity and simplicity.

ALUMINA-SILICA PREPARATION.

Water glass, containing 28% by weight of silica and having a specific gravity of 1.38, in an amount of 39.01 kg. was diluted with water to a total weight of 78.02 kg. Similarly, 16.33 kg. of hydrochloric acid (32% by weight hydrogen chloride and having a specific gravity of 1.16) was diluted with water to a total weight of 36.29 kg. In order to prevent formation of flocculent material, the hydrochloric acid and water glass solutions were intimately commingled with vigorous stirring. Cobalt nitrate was added to the resulting clear solution in an amount to yield a final catalytic composite containing 0.25% by weight of cobalt. 1043 kg. of an aqueous solution of aluminum sulfate were then added to the previously prepared water glass-hydrochloric acid mixture containing cobalt nitrate; the aqueous solution of aluminum sulfate contained 7.65% by weight of aluminum oxide and 26% by weight of aluminum sulfate, and had a specific gravity of 1.31. A stream of the resulting mixture was commingled with a stream of an aqueous solution of 28% by weight ammonium hydroxide until approximately 578.8 kg. of said mixture had been mixed with 117.93 kg. of the solution of ammonium hydroxide. The individual rates of the two streams, at which the commingling was effected, were such that the *p*H of the resulting mixture was maintained at a constantly acidic *p*H of about 6.0, the *p*H not being permitted to vary beyond the limits of 5.5 to 6.5.

272.15 kg. of the 28% by weight aqueous solution of ammonium hydroxide were added to the constantly acidic, *p*H-6 precipitation mixture, and the second half (approximately 578.8 kg.) of the aluminum sulfate-water glass-hydrochloric acid solution was added thereto at a rate sufficient to control the *p*H of the resulting precipitating mixture at a *p*H level within the range of 8.0 to 8.5. The resulting finally divided slurry of basic aluminum sulfate, in admixture with aluminum hydroxide and silica, and containing co-precipitated cobalt, was subjected to filtration. Hot water was employed to wash the filter cake, the *p*H of each resulting slurry being adjusted with ammonium hydroxide to a level of about 8.0. The final filter cake was dried to contain volatile matter in an amount from 17% to 20% by weight, and the thus dried material was ground into a talc-like powder. A lubricating and binding agent was added thereto, and the powder formed into 3.2 mm. × 3.2 mm. cylindrical pills possessing a crushing strength of about 5.45 kg. The formed pills were then calcined, in an atmosphere of air, for a period of about 2 hours and at a temperature of 670° C. The calcined pills contained less than 1.0% by weight of sulfate ions, and had a highly desirable apparent bulk density within the range of 0.48 to 0.52.

CATALYST IMPREGNATING PROCEDURE.

Approximately 236 grams each of molydbic acid (85% by weight molydbic oxide) and hydrated nickel nitrate, (containing nickel in an amount to yield a final catalytic composite containing about 2% by weight thereof) were individually and separately commingled with 236 ml. of a 28% by weight solution of ammonium hydroxide. The individual solutions were then commingled to form the nickel-molybdenum impregnating solution which was then intimately commingled with the previously prepared, cobalt-containing alumina-silica carrier material. The impregnated alumina-silica pills were then dried for a period of three hours at a temperature of about 150° C.; the temperature was increased to 593° C., and the composite calcined at this temperature in an atmosphere of air for a period of about one hour.

PRE-SULFIDING PROCEDURE.

The calcined impregnated alumina-silica pills, while still at the calcination temperature of 593° C., were swept with a stream of nitrogen for the purpose of purging the composite of any free oxygen remaining from the calcination procedure, and to cool the oxidized composite to a temperature below 260° C., and preferably as low as 204° C. Hydrogen was then added to the stream of nitrogen, and the catalyst was swept with this gas mixture for a period of about fifteen minutes to ensure the absence of free oxygen within and about the catalytic composite prior to its contact with hydrogen sulfide. A gaseous mixture of hydrogen sulfide, hydrogen and nitrogen, obtained from a gas reservoir hereinafter described, was passed on a once-through basis through the catalytic composite initially at the lowered temperature between 204° and 260° C., and the effluent gases therefrom were vented to a gas scrubber. This initial sulfiding step employed a gaseous mixture containing six parts of hydrogen, two parts of hydrogen sulfide, and two parts of nitrogen, or a mol

ratio of hydrogen to nitrogen of 3:1, and a mol ratio of hydrogen to hydrogen sulfide of 3:1. The temperature of the catalyst was then increased to 371° C., and the component concentration of the gaseous sulfiding mixture was changed to the extent that the mol ratio of hydrogen to hydrogen sulfide was decreased to about 2:1, the mol ratio of hydrogen to nitrogen remaining at a level of about 3:1. This gaseous sulfiding mixture was externally recycled through a condenser and water separator, and returned to the inlet of the sulfiding zone. While the gaseous sulfiding mixture was recycled through the sulfiding zone, the temperature of the catalyst therein was increased to a level of about 399° C., and maintained at this level for a period of about two hours. The sulfiding stream was discontinued, and the catalyst cooled to a temperature of about 150° C.; during the period of cooling, from the final sulfiding temperature of 399° C. down to 150° C., a superatmospheric pressure of 0.68 atmospheres was maintained upon the sulfiding zone through the intermittent introduction of 100% hydrogen sulfide. After the catalyst temperature reached a level of 150° C., a stream of nitrogen was introduced for the purpose of purging the same of residual hydrogen sulfide and hydrogen, the vent gases being transmitted to a gas reservoir for utilization in the initial portion of the next succeeding sulfiding procedure effected upon the next batch of catalyst.

The final catalytic composite thus prepared was a five-component catalyst consisting of about 6.0% by weight of molybdenum, 2.0% by weight of nickel and 0.25% by weight of cobalt, all of which existed within the composite as the sulfides thereof. These % concentrations are those of the elemental metals, and not those of the combined form thereof; the amounts of the carrier material components in the final catalytic composite were approximately 76.0% by weight of alumina (as Al_2O_3) and 11.0% by weight of silica (as SiO_2). With any of the concentrations of molybdenum, nickel and cobalt within the ranges hereinbefore set forth, the alumina to silica weight ratio is preferably at a level of 7:1 to 8:1.

Results obtained with this sulfided, five-component catalyst are shown on Figures 1, 2 and 3 of the accompanying drawings.

Figure 1 is a graphical representation which compares the results, with respect to the residual sulfur content (shown in parts per million along the ordinate) of the liquefied hydrogenated product, obtained through the use of the well-known alumina-cobalt-molybdenum catalyst (A) and the sulfided, five-component catalyst of the present invention (B).

Figure 2 is an illustration of the comparison of the results obtained with these two catalysts A and B in regard to the bromine number (shown along the ordinate) as determined on the saturated hydrocarbon product. The bromine number is an indication of the quantity of olefinic hydrocarbons within the given liquid hydrocarbon mixture; the higher the bromine number, the greater the weight per cent concentration of unsaturated molecules.

Figure 3 indicates the significant difference in the quantity of residual basic nitrogen compounds (shown in parts per million along the ordinate) within the individual liquid products resulting from the processes employing the two catalysts A and B. The results are plotted on each of the Figures 1, 2 and 3, in relation to liquid hourly space velocity which is shown along the abscissae.

The cobalt-molybdenum catalyst A, employed as the standard hydrogenation catalyst, with which the catalyst B of the process of the present invention is compared, was a three-component catalyst consisting of an alumina carrier material composited with about 6% by weight molybdenum and 2.2% by weight of cobalt. The catalyst A was prepared by impregnating 3.2 mm. × 3.2 mm. alumina pills with a single impregnating solution of ~~molydbic~~ acid containing 85% by weight of molybdenum oxide and sufficient cobalt nitrate to provide the 6% by weight of molybdenum and the 2.2% by weight of cobalt in the final catalyst. Following the impregnation, this standard catalyst was subjected to calcination in an atmosphere of air, followed by sulfiding with a stream of pure hydrogen sulfide diluted by nitrogen. This sulfiding was effected at an elevated temperature of about 400° C.

Each catalyst was individually and separately tested by processing a thermally-cracked California naphtha therethrough; this charge stock had a specific gravity of 0.8095 at 15.6° C., an initial boiling point at 143° C., a 50% volumetric distillation point of 160° C. and an end boiling point of 200° C. (ASTM distillation method D86—56). The thermally-cracked naphtha contained 1.46% by weight of sulfur, 240 ppm. (= parts per million) of basic nitrogen and had a bromine number of 61, the latter indicating that the naphtha contained a significant quantity of unsaturated hydrocarbons. The charge stock was passed into a reactor fabricated from 25.4 mm. stainless steel (67.9 Fe, 0.1 C, 17 Cr, 3.0 Mo, 12 Ni). The reactor was equipped with a thermocouple well to which perforated baffle plates were fastened to serve as the vaporization, pre-heating and mixing zone for the hydrogen and the liquid hydrocarbon charge. The reactor contained a single catalyst bed of 50 cubic centimeters, and was maintained under an imposed hydrogen pressure of 54.4

atmospheres, the hydrogen being circulated at a rate of 534 normal liters per liter of liquid charge; the inlet temperature to the catalyst in each instance was 371° C.

The two operations were each individually effected at several varying liquid hourly space velocities (liquid hourly space velocity is defined as the volume of liquid hydrocarbon charged to the reaction zone per volume of catalyst contained within the reaction zone per hour). The liquid hourly space velocity was varied for the purpose of obtaining several points from which the curves indicated in the Figures could be defined. Referring now to Figure 1, it is immediately noted that the curve representing the results obtained through the use of the five-component catalyst of the present invention (labeled B) is, at all points along its length, below the curve representing the results obtained through the use of the standard cobalt-molybdenum catalyst (labeled A). This factor is significant in that it indicates that a liquid product substantially lower in sulfur content may be obtained through the use of the catalyst of the present invention at the same liquid hourly space velocity, or conversely, a greater liquid hourly space velocity is possible when utilizing the catalyst of the present invention to obtain a liquid product containing the same sulfur concentrations as that obtained when the standard cobalt-molybdenum catalyst is used. For example, at the sulfur concentration of about 5 ppm. (0.0005% by weight), the maximum allowable liquid space velocity, employing the cobalt-molybdenum catalyst A is about 2.3, whereas, when employing the catalyst B of the present invention, a liquid hourly space velocity of about 5.0 is possible. When operating at identical liquid hourly space velocities, for example 6.0, the catalyst B of the present invention lowers the sulfur concentration to about 6.3 ppm. (0.00063% by weight) while the cobalt-molybdenum catalyst A results in a product containing abot 37.5 ppm. sulfur (0.00375% by weight). The latter value is considerably in excess of that sulfur concentration which can be tolerated by the platinum-containing catalysts of the present-day catalytic reforming processes.

Figure 2 represents the comparison of the results in regard to the bromine number of the saturated liquid product. As indicated in Figure 2, the catalyst B of the present invention lowered the bromine number of the original thermally-cracked naphtha to a level at all times lower than that achieved through the use of the standard cobalt-molybdenum catalyst A at liquid hourly space velocities of 3 to 6.3 (approximately). Similarly, as was shown in regard to the sulfur concentration, the catalyst of the present invention in general permits a greater quantity of liquid throughput per volume of catalyst, while lowering the bromine number to an identical level.

Perhaps the most significant results are those illustrated in Figure 3, in which Figure a comparison is made with respect to the residual basic nitrogen content of the liquid hydrogenated products. As hereinbefore set forth, the most difficult function of hydrodesulfurization catalysts is the removal of nitrogenous compounds. It is readily seen from Figure 3 that the catalyst of the present invention presents little difficulty in providing a liquid hydrogenated product virtually free from basic nitrogen. At a liquid hourly space velocity of 5.0, the catalyst B of the present invention resulted in a basic nitrogen of about 0.25 ppm., whereas the standard cobalt-molybdenum catalyst A produced a liquefied product contaminated by 25 ppm. of basic nitrogen at this liquid hourly space velocity.

This example clearly indicates the detailed method by which the five-component catalyst of the present invention is manufactured, and the unusually excellent results obtained through the utilization thereof in the purification of a typical hydrocarbon charge stock.

The purification process of the present invention is illustrated in the accompanying Figure 4; in the interest of simplicity and clarity, many details including heaters, condensers, valves, controls, and instruments, are omitted from the drawing: only the vessels and connecting lines necessary for complete understanding of the process are indicated. The hydrocarbon, or hydrocarbon mixture containing sulfurous and nitrogenous compounds and undesired olefinic hydrocarbons is introduced into the process through line 1. These hydrocarbons are commingled with a hydrogen-rich gas stream in line 2 and the resulting mixture is heated to the operating temperature in heater 3 and introduced through line 4 into reactor 5. Reactor 5 is illustrated as a single reaction zone in which the material to be processed flows downwardly through catalyst bed 6. Catalyst bed 6 consists of an alumina-silica carrier material composited with molybdenum, nickel and less than 0.7% by weight of cobalt, these three metals existing as the sulfides thereof prior to, and during, contact with the hydrocarbons entering through line 4. The reaction products are passed through line 7 into cooler 8 and through line 9 into separator 10. Separator 10 is operated at substantially room temperature to facilitate removal of the normally gaseous components through line 14 into compressor 15. Compressor 15 discharges through line 16 into line 2, and, as hereinbefore stated, is commingled with the hydrocarbon charge in line 1. An

outside source may be employed to supply the hydrogen necessary to effect complete saturation and removal of the various contaminants, and to maintain the quantity of hydrogen recycle. Such outside source of hydrogen is indicated as entering the process through line 17, and may be directed either to the suction side of the compressor through line 18, or directly into heater 3 through line 2.

The normally liquid reaction products are removed from separator 10 through line 11, and introduced into stripper column 12. A hydrogenated liquid product, substantially free from nitrogenous and sulfurous compounds is removed from stripper 12 through line 13. The liquid product in line 13 may either be utilized as such or may be subjected to further processing and/or fractionation as the particular case may be. A mixture of normally gaseous material and light hydrocarbons is removed from the top of stripper 12 through line 19, and is passed through cooler 20 and line 21 into separator 22. A gaseous stream is removed from separator 22 via line 23 and contains a greater portion of hydrogen sulfide, ammonia, and those light paraffinic hydrocarbons which may have resulted from the slight degree of hydrocracking inherent in processes employing elevated temperatures. The liquid light hydrocarbon product is removed through line 24 and utilized as reflux through stripper column 12. Where desired, a portion of this liquid light hydrocarbon product may be removed through line 25 and either subjected to further processing, or utilized as fuel.

Minor modifications of the process above described are not considered to be outside the scope of the invention. For example, provision may be made for the introduction of water upstream of separator 10 for the purpose of adsorbing the ammonia formed during the conversion of nitrogenous compounds. Separator 10 is then modified to permit a separator water draw-off by which means the ammonia is removed from the process. Similarly, the separation of the total reactor effluent into the gaseous and liquid phase may be effected in two or more stages. The flow through the bed, or beds, of catalyst may be crossflow or upflow instead of downflow as illustrated. Other modifications will be readily recognized by those skilled in the art.

EXAMPLE II.

A comparison of the catalysts, A and B as prepared in the foregoing Example 1, was made while processing a blend of straight-run and coker distillates. The charge stock characteristics, including the concentrations of the various contaminates, the catalyst evaluation conditions, and a brief summary of the product inspection date are given in the following Table I.

TABLE I:

CATALYST COMPARISON—BLEND OF STRAIGHT RUN AND COKER DISTILLATES.

Charge Stock Characteristics		
Specific gravity at 15.6° C.		0.7511
Initial Boiling Point, °C.		90
50% Boiling Point, °C.		138
End Boiling Point, °C.		209
Nitrogen Content, ppm.		9.4
Bromine Number		7.2
Sulfur Concentration, Weight %		~~0.025 (250 ppm.)~~
Catalyst Evaluation Conditions		
Catalyst Designation	A	B
Operating Pressure, atm.	54.4	54.4
Catalyst Temperature, °C.	371	371
Hydrogen Circulation, 1/1	142.4	142.4
Liquid Hourly Space Velocity	6	14
Product Inspection		
Specific gravity at 15.6 °C.	0.7539	0.7539
Initial Boiling Point, °C.	97	88
50% Boiling Point, °C.	137	135
End Boiling Point, °C.	211	210
Nitrogen Content, ppm.	0.24	0.20
Bromine Number	0.4	0.3
Sulfur Concentration, Weight %	0.0012 (12 ppm.)	0.00006 (0.6 ppm.)

As indicated in the table, although the concentration of the various contaminants was orginally relatively low, both catalysts effected a considerable degree of purification of the distillate blend. Perhaps the two most significant factors to be derived from the tabulated data are concerned with the liquid hourly space velocity at which the catalysts were compared, and the concentration of sulfur remaining in the liquid product derived therefrom. Catalyst A lowered the sulfur concentration from 0.052 weight per cent (520 ppm.) to a level of 0.0012 weight per cent (12 ppm.): the sulfur concentration of the liquid product resulting through the use of catalyst B was lowered to 0.00006 weight per cent, or 0.6 ppm. It is seen that the catalyst of the present invention effected a considerably greater degree of purification than the standard catalyst employed in the purification process, even though the catalyst of the present invention was tested at a liquid hourly space velocity of 14, as compared to a liquid hourly space velocity of 6 during the testing of the standard hydrogenation catalyst. In short, the utilization of the process of the present invention, when employing the five-component catalyst therein, permits a much greater throughput while effecting a more subtantial degree of purification of the charge stock.

The same type of catalyst comparison, as hereinabove described, was made with respect to a hydrocarbon mixture which is more difficult to convert to a hydrocarbon which is suitable as a charge stock to a catalytic reforming unit, or which is more suitable for use as a lubricating or fuel oil. This charge stock was a light cycle oil having a specific gravity of 0.8990 at 15.6° C., and containing considerably greater concentrations of contaminants than the blend of straight-run and coker distillates described in Table I. Other charge stock characteristics, the catalyst evaluation conditions and various product inspection data are given in Table II. As indicated in the table, although the catalyst testing procedures were effected at identical conditions including the hourly space velocity, catalyst B, the five-component catalyst of the present invention, was distinctly more successful in purifying the cycle stock.

TABLE II:

CATALYST COMPARISON—LIGHT CYCLE OIL.

Charge Stock Characteristics

Specific gravity at 15.6° C.	0.8990
Initial Boiling Point, °C.	162
50% Boiling Point, °C.	285
End Boiling Point, °C.	354
Nitrogen Content, ppm.	322
Bromine Number	15.6
Sulfur Concentration, Weight %	0.35 (3400 ppm.)

Catalyst Evaluation Conditions

Catalyst Designation	A	B
Operating Pressure, atm.	54.4	54.4
Catalyst Temperature, °C.	382	382
Hydrogen Circulation, 1/1	356	356
Liquid Hourly Space Velocity	3	3

Product Inspection

Specific gravity at 15.6° C.	—	0.8811
Initial Boiling Point, °C.	—	163
50% Boiling Point, °C.	—	245
End Boiling Point, °C.	—	289
Nitrogen Content, ppm.	55.0	12.5
Bromine Number	6.4	2.3
Sulfur Concentration, Weight %	0.02 (200 ppm.)	0.02 (200 ppm.)

EXAMPLE III.

In this example reference is made to a "Standard Relative Activity" test method. The relative activity of a particular catalyst is defined as the ratio of the space velocity required to result in a given product improvement, while employing the test catalyst, to the space velocity required to yield the same degree of product improvement while employing a primary, standard

catalyst, which relative activity is expressed as a percentage. The catalyst employed as the standard catalyst was an alumina-cobalt-molybdenum composite consisting of about 2.2% by weight of cobalt and about 5.9% by weight of molybdenum. The product quality improvement was measured in terms of the residual basic nitrogen content of the liquid product: as hereinbefore stated, the removal of nitrogenous compounds is the function of a hydrodesulfurization catalyst most difficult to effect, and, therefore, the relative activity of a given catalyst is more logically based thereon, rather than on an improvement in either the sulfur concentration or the quantity of olefinic hydrocarbons as indicated by the bromine number.

The relative activity test method consists essentially of processing a particular middle fraction of a California thermally-cracked naphtha boiling within the range of 143° C. to 199° C. The catalyst is placed in a reaction zone in an amount of 50 cubic centimeters and a hydrogen pressure of 54.4 atmospheres is imposed thereon. The catalyst bed inlet temperature is maintained at a level of 371° C. and hydrogen is passed therethrough (on a once-through basis) in an amount of 534 normal liters per liter of liquid charge. Three distinct test procedures are effected at various liquid hourly space velocities within the range of 2 to 10. The liquid effluent, upon which the product inspection is made, is collected over a period of operation of 4 to 7 hours. The thermally-cracked naphtha fraction, employed as the test charge stock, is further characterized in that the concentration of the contaminants is 1.33% by weight of sulfur, 300 ppm. of basic nitrogen, and a quantity of unsaturated hydrocarbons which gives a bromine number of 61. The basic nitrogen concentration in each of the three liquid products are plotted on a logarithmic scale against the reciprocals of the three space velocities employed. From the resulting curve, drawn through the three points, a determination is made of the reciprocal of the space velocity required to yield a liquid product having a residual basic nitrogen content of 2 ppm. The relative activity of the test catalyst is derived from the ratio of the reciprocal space velocity, to yield 2 ppm. basic nitrogen, in regard to the primary standard catalyst and compared to that of the catalyst being tested. The ratio is multiplied by the factor of 100, and a relative activity factor not greater than 100% indicates a test catalyst having a greater activity than the primary standard catalyst; obviously, a catalyst having relative activity less than 100%, is less active than the primary standard catalyst.

A variety of catalytic composites were prepared in accordance with the procedure set forth in Example I, with slight modifications thereof, and subjected to the activity test as hereinabove described. The modifications of the procedure as set forth in Example I were concerned with the composition of the catalyst, the impregnating procedure and the sulfiding technique, the latter involving a change in the composition of the gaseous medium therein employed.

The first catalyst, designated in Table III as catalyst "C," was prepared by impregnating an alumina-silica carrier material with an aqueous solution containing nickel nitrate and molybdic acid to yield a catalyst having the composition indicated in Table III. The impregnating procedure was a single impregnation; that is, all the catalytically active metallic components to be composited with the carrier material were added thereto in a single step. The impregnated alumina-silica pills were calcined, in an atmosphere of air, at a temperature of 593° C. for a period of one hour. The calcined pills were cooled to a temperature of 260° C. with a mixture of hydrogen and nitrogen in a 3:1 mol ratio, hydrogen sulfide was added at this temperature, and the mixture of hydrogen, nitrogen and hydrogen sulfide was circulated through the catalyst while the temperature thereof was increased to 399° C. The sulfiding was continued for a period of one hour at this elevated temperature while the composition of the sulfiding medium was a 3:1 mol ratio of hydrogen to nitrogen and a 1:2 mol ratio of hydrogen to hydrogen sulfide. As hereinbefore set forth, it is preferred that the sulfiding medium have a mol ratio of hydrogen to hydrogen sulfide within the range of 1.5:1 to 4:1. It has been found that the chemical equilibrium existing between the metallic components to be sulfided and the gaseous medium employed for the sulfiding, affects the activity and stability of the final catalytic composite through the deposition of elemental sulfur. Although an active hydrodesulfurization catalyst may be produced when hydrogen sulfide is present in greater concentration than the hydrogen, a still more active catalyst is prepared when the hydrogen is of the greater concentration, and within the aforesaid range of a mol ratio of 1.5:1 to 4:1 and more preferably from 2:1 to 3:1. Further, there are no detrimental effects as a result of the deposition of elemental sulfur. After one hour at the elevated temperature of 399° C., the sulfided catalytic composite was cooled to a temperature of 149° C., and during this cooling, a superatmospheric pressure was maintained through the intermittent introduction of hydrogen sulfide, the hydrogen and nitrogen having been shut off. The catalyst was then further cooled to a temperature of 38° C. with a stream of nitrogen.

TABLE III:

ACTIVITY OF NICKEL-MOLYBDENUM CATALYSTS.

Catalyst Composition, Weight %							
Catalyst Designation	C	D	E	F	G	H	I
Nickel	2.23	2.22	2.33	2.24	2.46	2.07	1.87
Molybdenum ...	5.51	6.43	5.82	5.88	5.44	5.88	5.84
Cobalt	—	—	0.25	0.24	0.19	0.31	0.25
Impregnating Procedure							
Type	Single	Single	Single	Double	Double	Single	Double
First Solution ...	—	—	—	Co	Ni-Mo	—	Ni-Mo
Sulfiding Technique (Components Present)							
Nitrogen ...	X	X	X				X
Hydrogen ...	X		X				X
Hydrogen Sulfide	X	X	X	X	X	X	X
Activity Test Data							
Relative Activity	216	142	194	181	191	158	203
*Carbon Weight, %	0.60	0.90	0.65	0.65	0.66	0.79	0.66

*Carbon deposition as a result of the activity test.

The second catalyst, designated in Table III as catalyst "D," was prepared utilizing a single impregnating procedure and a sulfiding medium consisting of hydrogen sulfide diluted with an inert gas, nitrogen. A comparison of the activities of the two catalysts, "C" and "D", indicates a substantial difference in the relative activities of these catalysts when the composition of the sulfiding medium is considered. The principal difference in the preparation of the two catalysts was the change in the sulfiding medium from a mixture of hydrogen and hydrogen sulfide to pure hydrogen sulfide, the nitrogen effectively disregarded as being an inert material. In addition, a significantly smaller quantity of carbon was deposited upon catalyst "C" in the activity test procedure.

Five additional catalysts were prepared, varying the method of preparation, but all of which contained minor quantities of cobalt in addition to the nickel and molybdenum. The compositions of these catalysts, as well as the impregnating and sulfiding procedures, are given in Table III. The double impregnating procedures indicated for catalysts "F," "G" and "I," were effected through the use of two separate solutions, one containing both nickel and molybdenum compounds and the other containing only cobalt. The catalysts were subjected to high temperature calcination at a temperature of 593° C. between the two impregnating steps. Catalyst "F," was prepared by first depositing the cobalt and subsequently impregnating with the solution containing the nickel and molybdenum. Catalysts "G" and "I" were prepared by impregnating the carrier with the nickel and molybdenum compounds prior to the addition of the cobalt. The preparation of catalyst "H" employed a single impregnating procedure and a sulfiding medium consisting solely of hydrogen sulfide.

It is readily seen that catalysts "D" and "H" are significantly less active, and effect a greater carbon deposition, than the catalysts prepared by other means. Catalysts "D" and "H" employed a single impregnation, and pure hydrogen sulfide in the sulfiding procedure. Catalysts "C," "E" and "I" were prepared by various methods of the present invention. As hereinafter indicated, the particularly preferred method of the present invention utilizes a catalyst prepared via a single impregnation procedure and a sulfiding technique utilizing a mixture of hydrogen and hydrogen sulfide. In this particular preferred catalyst, the cobalt component is co-precipitated with the alumina-silica prior to the formation of the latter into the desired size and shape.

EXAMPLE IV.

This example is given to illustrate the desirability of pre-sulfidation of the catalyst, in regard to the overall stability thereof, and

also to indicate the unexpected benefits derived from utilizing nickel and molybdenum as compared to a catalyst consisting essentially of cobalt and molybdenum. The catalysts were tested over a period of more than 24 days, the space velocity being continually adjusted to yield a liquid product having about 2 ppm. residual basic nitrogen. This is in accordance with the "Standard Relative Activity" test procedure hereinbefore set forth in detail. The California thermally-cracked naphtha fraction was processed at a temperature of 371° C., a pressure of 54.4 atmospheres and in the presence of 534 normal liters of hydrogen per liter of liquid hydrocarbon charge. As hereinbefore stated, the relative activities are based upon the results obtained using the standard alumina - cobalt - molybdenum catalyst.

The first catalyst subjected to the 24-day stability test was the standard hydrogenation catalyst, consisting of cobalt and molybdenum on an alumina carrier material, but this catalyst was subjected to a pre-sulfiding technique at 371° C. with a mixture of hydrogen and hydrogen sulfide in a mil ratio of about 2:1. After 5 days, the relative activity of this catalyst was 138; after 18 days the relative activity had decreased to 135, and at the end of 25 days, the activity was found to be 131. The pre-sulfiding procedure increased the relative activity of the standard catalyst to a substantial extent.

The second catalyst subjected to the extended stability test was a cobalt-molybdenum catalyst composited with a silica-alumina carrier material in which the ratio of alumina to silica was 7.3:1. After 5 days of operation, the relative activity of this catalyst was 186; after 12 and 19 days of operation, the relative activity was 169 and 163 respectively; at the end of 25 days, the relative activity was 142, which activity is greater than the initial activity of the catalyst in which the carrier material consited solely of alumina.

A nickel-molybdenum catalyst, composited with the alumina-silica carrier material, and prepared in accordance with the method of the present invention, including a pre-sulfiding with a mixture of hydrogen and hydrogen sulfide indicated a relative activity of 234 after the first 6 days of the stability test. This catalyst, after a total of 14 days indicated an activity of 234; after 24 days, the relative activity was 225.

Example V.

This example is given for the purpose of illustrating the effect of various pre-sulfiding techniques on the activity of the catalyst. The data in Table IV indicate advantageous results from the use of all the catalysts so prepared, however, it is apparent that the catalyst prepared in accordance with the particularly preferred embodiment of the present invention is the more highly active catalyst. The catalysts were tested in accordance with the relative activity test procedure described above, utilizing the California thermally-cracked naphtha fraction. The first catalyst, designated as catalyst "J" was prepared to contain 6% molybdenum and 2.0% nickel, composited with the alumina-silica carrier. The molybdenum and nickel were deposited via a single impregnating procedure and the catalyst immediately subjected thereafter to calcination and sulfidation utilizing a sulfiding medium of hydrogen and hydrogen sulfide in a 2:1 mol ratio. The catalyst was contacted with the sulfiding mixture initially at a temperature of about 260° C. and was maintained in contact therewith while the temperature was increased to 399° C. A positive pressure of hydrogen sulfide was maintained while cooling the sulfided catalyst to a temperature of 149° C. This catalyst indicated a relative activity of 193. The same catalyst, with the addition of 0.25% by weight of cobalt to the alumina-silica, designated as catalyst "L," indicated a relative activity of 195. A decrease in activity was observed on the catalyst which was exposed to air while being cooled from the sulfide temperature of 399° C. This catalyst is designated as catalyst "M."

Catalyst "K" was prepared by a double impregnating technique in which the alumina-silica carrier material is formed and calcined prior to being impregnated with the cobalt component. Following the cobalt impregnation, the catalyst was again calcined at an elevated temperature, after which a single impregnating solution was utilized to composite therewith the molybdenum and nickel. In addition, catalyst "K" was subjected to a hydrogen pretreatment, rather than to a treatment with a 3:1 mixture of hydrogen and nitrogen, prior to being contacted with the sulfiding gaseous mixture at 399° C. It is immediately noted that this catalyst exhibited the lowest relative activity.

The catalyst prepared by the particularly preferred embodiment of the present invention, catalyst "N," in which embodiment the cobalt, alumina and silica are commingled prior to the formation of the carrier material, and the molybdenum and nickel are composited in a single impregnating procedure, and which includes the hydrogen sulfide contact initially at the lower temperature and while the catalyst is being heated to the sulfiding temperature of 399° C., indicated the highest relative activity, that of 242.

TABLE IV:

EFFECT OF PRE-SULFIDING TECHNIQUE.

Catalyst Designation	J	K	L	M*	N
Catalyst Composition, Weight %					
Molybdenum	6.0	6.0	6.0	6.0	6.0
Nickel	2.0	2.0	2.0	2.0	2.0
Cobalt	—	0.25	0.25	0.25	0.25
Hydrogen Pretreatment	No	Yes	No	No	No
Impregnating Technique	Single	Double	← Single** →		
Relative Activity	193	183	195	190	242

* Sulfided catalyst exposed to air without cooling in hydrogen sulfide.
** 0.25 weight % cobalt incorporated with the alumina-silica carrier material.

The foregoing examples clearly illustrate the several embodiments of the process of the present invention and the manufacture of the catalytic composites to be utilized therein. The benefits afforded to processes for the purification, or treating, of various hydrocarbons and hydrocarbon mixtures are indicated. The purification process of the present invention, employing a particular catalyst, results in a hydrocarbon product which is substantially completely free from the various contaminants which otherwise prohibit the use or further processing of such hydrocarbons.

WHAT WE CLAIM IS:—

1. Process for manufacturing a catalyst for use in the purification of hydrocarbons which comprises treating a composite containing alumina, silica, molybdenum oxide and nickel oxide with a gaseous sulfiding mixture containing hydrogen and hydrogen sulfide in a mol ratio of from 1:2 to 4:1 at a temperature between 204° and 427° C. prior to contact with any hydrocarbons to be purified and thereupon cooling the sulfided composite to a temperature below 204° C. under a superatmospheric pressure of hydrogen sulfide.

2. Process as claimed in Claim 1, characterized in that the sulfiding of the composite with the gaseous sulfiding mixture is effected over a range of temperatures increasing from an initially low temperature of 204° C. to a temperature in the range of 399—427° C.

3. Process as claimed in Claim 1 or 2, characterized in that the sulfiding treatment is effected with a gaseous sulfiding mixture containing the hydrogen and hydrogen sulfide in a mol ratio in the range of from 1.5:1 to 4:1.

4. Process as claimed in any of the Claims 1 to 3, characterized in that the said superatmospheric hydrogen sulfide pressure is in the range of from 0.34 to 1.02 atmospheres.

5. Process as claimed in any of the Claims 1 to 4, characterized in that the reductive sulfiding treatment is applied to a composite which contains the alumina and silica in a weight proportion of from 7:1 to 8:1 together with from 5 to 10 per cent molybdenum and from 1 to 5 per cent nickel, said molybdenum and nickel being calculated as per cent metal relative to the weight of the total composite.

6. Process as claimed in Claim 5, characterized in that the reductive sulfiding treatment is applied to a composite which also contains from 0.1 to 0.7 per cent cobalt, calculated as metal, relative to the weight of the total composite.

7. Process as claimed in 6, characterized in that the reductive sulfiding treatment is applied to a composite which has been prepared by coprecipitating alumina, silica and cobalt oxide, drying and calcining the precipitate, impregnating the calcined precipitate with a solution containing a water-soluble molybdenum compound and a water-soluble nickel compound, drying the impregnated precipitate and calcining it in air.

8. The process for manufacturing a catalyst as claimed in Claim 1 and substantially as hereinbefore described.

9. Catalyst for use in the purification of hydrocarbons whenever produced by the process of any of the Claims 1 to 8.

10. Process for purifying hydrocarbons at elevated temperature and under an imposed hydrogen pressure with a hydrodesulfurization catalyst which has been prepared by the process of any of the Claims 1 to 8

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4. Process as claimed in any of the Claims 1 to 3, characterized in that the said superatmospheric hydrogen sulfide pressure is in the range of from 0.34 to 1.02 atmospheres.

5. Process as claimed in any of the Claims 1 to 4, characterized in that the reductive sulfiding treatment is applied to a composite which contains the alumina and silica in a weight proportion of from 7:1 to 8:1 together with from 5 to 10 per cent molybdenum and from 1 to 5 per cent nickel, said molybdenum and nickel being calculated as per cent metal relative to the weight of the total composite.

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