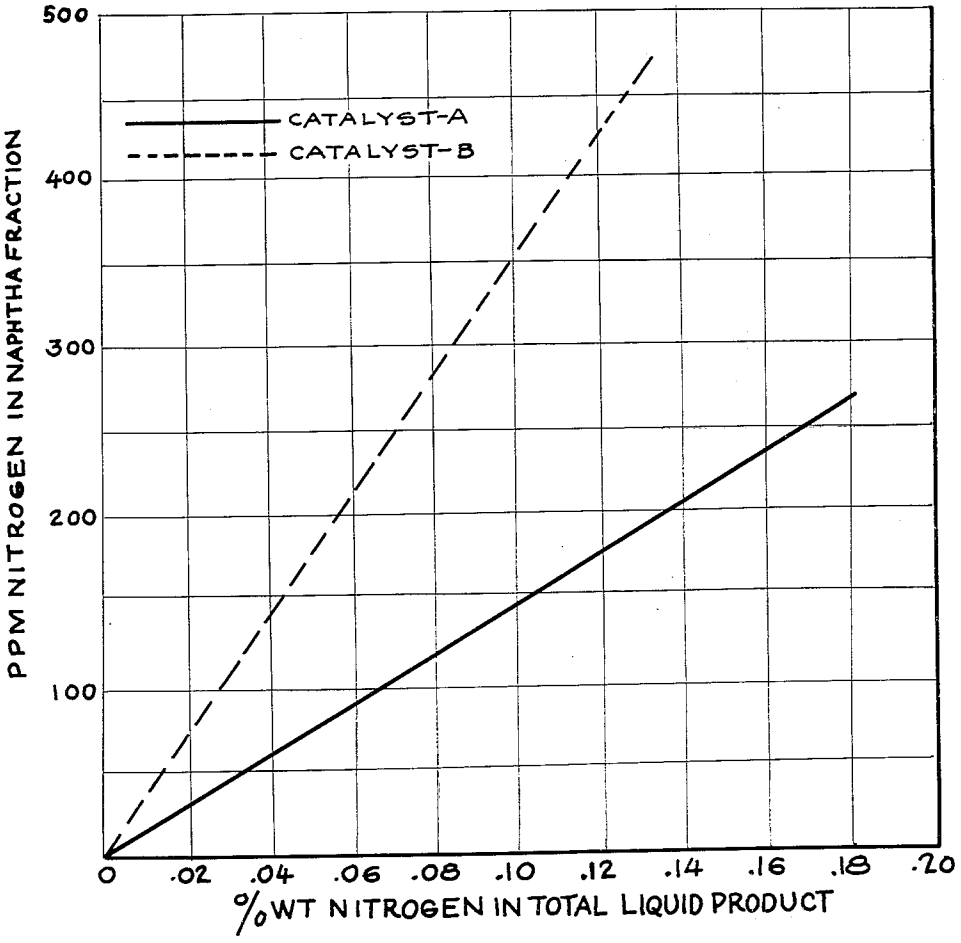
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PROCESS FOR REMOVING NITROGEN COMPOUNDS FROM HYDROCARBON OIL

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PROCESS FOR REMOVING NITROGEN COMPOUNDS FROM HYDROCARBON OIL

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This invention relates to a process for removing nitrogen compounds from hydrocarbon oils. More particularly, the invention is concerned with a process for treating nitrogen-containing petroleum oils and various liquid fractions obtainable therefrom in the presence of a catalytic composite which has been found to be usually effective in selectively removing nitrogen.

In the reforming of petroleum and fractions thereof, the presence of nitrogen compounds has heretofore been recognized as undesirable. Petroleum hydrocarbons generally contain varying amounts of nitrogen compounds as impurities, which are distributed in the various fractions and products obtained from the crude hydrocarbon stocks according to their boiling points or to their relative volatility in hydrocarbon mixtures. Also, the particular kind and amounts of nitrogen compounds present in a petroleum hydrocarbon vary with the previous manufacturing and processing operation to which said petroleum hydrocarbon has been subjected.

The presence of nitrogen compounds in hydrocarbon oils is objectionable for various reasons. For example, certain petroleum distillates may be marketed under specifications which recite a maximum nitrogen content. In other cases, nitrogen compounds in hydrocarbon oils tend to destroy the activity of hydrocarbon conversion catalysts with which the oil may be brought into contact during various processing operations. Thus, in catalytic cracking of a hydrocarbon oil containing an appreciable amount of nitrogen compounds, the catalyst prematurely loses activity due to the poisoning effects of the nitrogen compounds. Commercial cracking catalysts generally consist of natural or synthetic composites of silica and alumina. During the cracking reaction, nitrogen compounds undergo conversion to basic ammonia which combines with the active acid sites on the silica-alumina catalyst. This combination or poisoning inhibits the cracking reaction and reduces the conversion and gasoline yield.

The presence of nitrogen in naphtha feed to catalytic reformers has been shown to be similarly deleterious. The catalysts commercially employed in reforming generally contain a noble metal and particularly platinum deposited on silica-alumina or on alumina which may have halogen combined therewith. When effecting reforming in the presence of these catalysts, there results a certain degree of selective poisoning of the catalyst and a decrease in the activity thereof. The nitrogen compounds of the gasoline fractions become converted under the catalytic reforming conditions and it is believed that the resulting ammonia adversely poisons and deactivates the catalyst.

Numerous hydrogenation processes have heretofore been proposed to reduce the nitrogen content of hydrocarbon oils and various liquid fractions thereof, particularly those stocks intended for use as charge to cracking and reforming units. In these processes, the gas oil and naphtha charge stocks are sometimes hydrogen treated separately to effect removal of nitrogen. In other cases, the heavy gas oil is hydroprocessed in a single unit, the naphtha is distilled out and subsequently charged to a reformer pretreating unit to further reduce the nitrogen content of the naphtha charge before the same is brought into contact with the platinum or other noble metal-containing catalyst in the reforming unit.

The above hydrogenation processes for denitrifying nitrogen-containing hydrocarbon oils have been carried

out in the presence of various reagents and composites intended to catalytically promote the desired removal of nitrogen. Thus, various catalysts of metals and metal oxides have heretofore been proposed for such purposes including composites of chromia-alumina, chromia-molybdena-alumina, cobalt oxide-molybdenum oxide-alumina, nickel on alumina, cobalt on alumina and iron on alumina. While some of these catalysts have been found to be more effective for nitrogen removal than others, each of the aforementioned composites has certain operational disadvantages and none has proved to be exceptional when employed on a commercial basis.

It is accordingly a major object of the present invention to provide an improved, commercially attractive catalytic method for removing objectionable nitrogen compounds from hydrocarbon oils containing the same. A further object is the provision of a process for effecting selective denitrogenation of particular petroleum fractions wherein the nitrogen content thereof is effectively reduced without adversely influencing the yield and quality of the resulting denitrized product. A still further object is the provision of a catalytic hydrogenation process for removing nitrogen from hydrocarbon oils and fractions thereof carried out in the presence of a catalyst characterized by the ability to effect an unusual reduction in nitrogen content of the charge.

The above and other objects which will be apparent to those skilled in the art are achieved in accordance with the present invention. Broadly, the process described herein involves treating hydrocarbon oils containing nitrogen compounds with hydrogen under specified conditions of reaction in the presence of a catalyst consisting essentially of 15 to 40 percent by weight of silica, 1 to 8 percent by weight of cobalt oxide, 3 to 20 percent by weight molybdenum trioxide and remainder alumina.

It has been discovered, in accordance with the present invention, that catalysts of the above recited composition, under particularly defined hydrogenation reaction conditions hereinafter set forth, provide a highly efficient and selective means for effecting removal of nitrogen from hydrocarbon oils containing the same. It is contemplated that hydrocarbon oils which contain nitrogen compounds may generally be treated in accordance with the present process. Thus, petroleum crudes, shale oils, gas oils, gasoline, naphtha, aromatic solvent, kerosene, diesel fuel, transformer oil, lubricating oil, and other liquid petroleum fractions may be effectively treated with resulting denitrification thereof. While the process described herein is particularly applicable to the treatment of petroleum distillates, it is understood that it may be utilized with other organic compounds containing nitrogen impurities and may thus be utilized for the treatment of liquids comprising alcohols, aldehydes, ketones and acids.

In one embodiment, the present invention relates to an improvement in the removal of nitrogen from a nitrogen-containing gas oil by treating the same with hydrogen in a separte zone in the presence of a catalyst consisting essentially of 15 to 40 percent by weight silica, 1 to 8 percent by weight cobalt oxide, 3 to 20 percent by weight molybdenum trioxide and remainder alumina under conditions of hydrogen concentration, temperature and pressure such that nitrogen is substantially removed from the gas oil, and thereafter charging the substantially denitrized gas oil to a catalytic cracking unit utilizing a silica-alumina cracking catalyst and maintained under conventional conditions for effecting the cracking of gas oils to lighter materials boiling in the range of gasoline.

In another embodiment, the invention comprises a process for effecting removal of nitrogen from a high nitrogen content naphtha, particularly one having an initial boiling point within the approximate range of from 50° F. to 100° F. and an end boiling point within the range

of from about 325° F. to about 425° F. or a selected fraction thereof, for example, having an initial boiling point within the range of from 125° F. to 250° F. and an end boiling point within the range of from about 350° F. to 425° F. Such nitrogen-containing naphtha stocks are, in accordance with the present invention, treated in a separate zone with hydrogen in the presence of a catalyst consisting essentially of 15 to 40 percent by weight silica, 1 to 8 percent by weight cobalt oxide, 3 to 20 percent by weight molybdenum trioxide and remainder alumina under conditions of hydrogen concentration, temperature and pressure such that nitrogen is substantially removed from the naphtha and thereafter charging the substantially denitrized naphtha to a catalytic reforming unit utilizing a platinum or other noble metal-containing catalyst and maintained under conventional conditions for effecting reforming of naphtha charge stocks to improve the octane number thereof. In the reforming reaction, hydrogen is produced and the hydrogen thus produced may be utilized, at least in part, in the aforementioned zone for accomplishing denitrogenation.

The catalyst used in the present process for removing nitrogen from nitrogen-containing hydrocarbon oils contains predominant proportions of alumina and specified minor proportions of molybdenum trioxide, silica, and cobalt oxide combined in a particular manner such that the resulting composite is characterized by a silica content of about 15 to about 40 percent by weight, a molybdenum trioxide content of about 3 to about 20 percent by weight, a cobalt oxide content of about 1 to about 8 percent by weight and the remainder alumina. Preferably, the catalyst has a composition of about 15 to about 25 weight percent silica, about 7 to about 16 weight percent molybdenum trioxide, about 2 to about 4.5 cobalt oxide and the remainder alumina. Such catalyst employed in the process of the invention has been found to be highly effective in denitrifying the charge of nitrogen-containing hydrocarbon oil.

The catalyst components of silica, alumina, cobalt oxide and molybdenum trioxide may be combined in any suitable manner. It has been discovered, however, that it is preferable to produce the catalyst by mechanical admixture of the silica and alumina-containing components, rather than by chemical compositing of these oxides such as, for example, by cogelation. Either the silica or alumina-containing component may prior to admixture with the other have deposited thereon one or both of the other catalyst components, i.e. cobalt oxide and/or molybdenum trioxide. Thus, the catalyst utilized in the process of the invention may be produced by mechanically admixing silica with alumina which has previously been impregnated with the oxides of molybdenum and cobalt. Alternatively, the catalyst may result from mechanical admixture of alumina with silica which has previously been impregnated with the oxides of molybdenum and cobalt. Another method of combining the catalyst components involves admixture of silica impregnated with either molybdenum trioxide or cobalt oxide with alumina impregnated with the other of such metal oxides. It is also feasible, and in some aspects preferable, to initially intimately admix the silica and alumina components and thereafter to impregnate the resulting silica-alumina composite with the oxides of molybdenum and cobalt. The composite obtained, in accordance with any of the above techniques, is dried and calcined to obtain the finished catalyst.

While the alumina component is the predominating constituent of the present catalyst and has, of itself, no denitrogenation activity, its careful preparation is essential to the production of the catalyst affording the desired activity in the contemplated denitrogenation of the hydrocarbon charge. The alumina when properly prepared exerts of synergistic effect with the other catalyst components.

The alumina component of the catalyst utilized herein is a porous alumina, not adversely affected by the temperature conditions of the instant process, having a surface area greater than 100 square meters per gram and which may extend up to 500 square meters per gram or more. Catalyst prepared from alumina having a surface area of 100 square meters per gram or less have a considerably higher aging rate when employed in the instant denitrogenation process in comparison to catalysts in which the alumina component initially is characterized by a surface area in substantial excess of 100 square meters per gram. The term "surface area" as used herein designates the surface area as determined by the adsorption of nitrogen according to the method of Brunnauer et al., Journal American Chem. Soc., 60, 309 et seq. (1938). As noted above, the alumina itself is devoid of or exerts negligible catalytic activity under reaction conditions at which the present denitrogenation process is carried out. The density of the alumina employed i.e., the bulk density thereof, will usually be within the range of 0.2 to 2.0 g./cc. and more particularly between about 0.4 and about 1.2 g./cc.

The alumina component of the catalyst used in the present process for effecting removal of nitrogen from a hydrocarbon oil may be prepared by commingling a suitable basic compound including ammonium hydroxide, ammonium carbonate, etc. with an acidic compound of aluminum including chloride, bromide, iodide, fluoride, sulfate, phosphate, nitrate, acetate, etc. or by the addition of a suitable acidic compound including hydrogen chloride, sulfuric acid, phosphoric acid, etc. to an alkaline compound of the metal as for example, an alkali metal aluminate such as sodium aluminate. The resultant aluminum hydroxide is usually washed to remove soluble impurities and then is dried at a temperature of about 200 to 600° F. for a period of from 1 to 24 hours or more. In one method, the dried alumina is formed into particles of definite size and shape in any suitable manner such as casting, pelleting, extruding, etc. and then is subjected to calcination at a temperature of from about 600 to about 1600° F. In another method, the alumina may be formed into particles of spheroidal shape by dropping a suitable aluminasol into a suitable medium which may comprise air, an inert atmosphere as for example, nitrogen, carbon monoxide, etc. or into an oil or other suitable immiscible liquid. The resultant spheroids are then washed, dried and calcined in the manner hereinbefore set forth. Alternatively, the alumina may be prepared in the form of a precipitate by controlled reaction of aluminum metal with water in the presence of a mercury compound whereby the aluminum undergoes amalgamation and the resulting amalgamated aluminum reacts with the water to form alumina.

The silica component is initially prepared in the form of a hydrogel or gelatinous precipitate. Preferably, the silica component is prepared in the form of a hydrogel by reaction between sodium silicate and an acid such as sulfuric acid while maintaining the pH of the reaction mixture generally below about 6 and preferably in the approximate range of 3.5 to 5. The initially formed hydrosol of silica undergoes gelation after lapse of a suitable period of time to silica hydrogel. The time of gelation can be controlled within desired limits by well-known means such as adjustment in the temperature or solids concentration of the reaction mixture or hydrosol produced therefrom. The resulting hydrogel is thereafter water washed, base-exchanged to remove zeolitic sodium and dried. If it is desired to prepare silica initially free of alkali metal ions, such may be accomplished by effecting hydrolysis of alkyl silicates, i.e. ethyl silicate. The silica hydrogel may be produced in the form of granules or in the form of a mass which is thereafter broken up into pieces or particles of desired size. Alternatively, silica hydrogel may be produced in the form of spheroidal bead particles by methods such as those described by Marisic in U.S. 2,384,946 or in the form of uniformly shaped particles

prepared by casting or extrusion methods. It is also feasible to initially produce silica in the form of finely divided particles of requisite particle size by employing techniques used in the preparation of fluid catalyst particles for example by spraying or rapid agitation of a hydrosol to form minute particles of hydrosol that set to particles of hydrogel which upon drying yield discrete particles of silica gel. Generally, it is preferred that the silica component before admixture with the alumina-containing component be in a finely divided state generally of a particle size finer than 50 mesh (Tyler) and preferably of a particle size within the approximate range of 60 to 200 mesh (Tyler). The above-indicated finely divided state of silica can be obtained either during initial formation of the silica or by grinding larger size pieces of the requisite particle size.

The alumina and silica prepared as above may be composited by mechanically admixing and thereafter impregnated with cobalt oxide and molybdenum trioxide or either of these components prior to admixture with the other may be impregnated with suitable compounds of molybdenum and cobalt to effect deposition thereon of cobalt oxide and molybdenum trioxide. The base material, i.e. alumina, silica, or composite resulting from admixture of silica and alumina is contacted with an impregnating solution of a cobalt compound such as cobalt nitrate and of a molybdenum compound such as a ammonium molybdate. The particles of base material may initially be subjected to a vacuum to remove air from the pores thereof and while maintaining the vacuum, the above-described impregnating solution is brought into contact with the particles of base material. Alternatively, the base material for example, alumina in the form of an aqueous slurry may be impregnated with the solution of molybdenum compound and cobalt compound. It is understood that any other suitable method of commingling particles of the base material with the impregnating solution may be employed.

In another method for preparing a catalyst used in the present process, separate impregnating solutions of the molybdenum compound and of the cobalt compound are prepared and are composited successively with the base material with or without intervening heating of the support. In general, using this technique, it is preferred to composite the molybdenum component first and then the cobalt component although the reverse procedure may be employed. After the impregnation, the base material is dried and then calcined to convert the metal compounds to the oxides.

Other suitable cobalt compounds for effecting deposition of cobalt oxide on the base material may be employed including for example, cobalt ammonium nitrate, cobalt ammonium chloride, cobalt ammonium sulfate, cobalt bromide, cobalt bromate, cobalt chloride, cobalt chlorate, cobalt fluoride and cobalt fluorate. In similar manner, other suitable compounds of molybdenum may be employed. Suitable soluble molybdenum compounds include molybdenum tetrabromide, molybdenum oxydibromide, molybdenum tetrachloride, molybdenum dichloride, molybdenum oxypentachloride, and molybdenum oxytetrafluoride.

The silica-containing component, preferably in finely divided form, is intimately mixed with the alumina-containing component which likewise is in finely divided state, preferably having a particle size within the approximate range of 60 to 200 mesh (Tyler). After thorough mixing of the components, the resulting mixture is formed by pelleting, casting, molding or other suitable means into pieces of desired size and shape such as rods, spheres, pellets, etc. After forming into particles of desired size, the resulting particles are dried and thereafter calcined at an elevated temperature in the approximate range of 600 to 1200° F. It is understood that either of the silica and alumina-containing components may, prior to admixture, be impregnated with molybdenum trioxide and cobalt oxide or that the mixed composite of silica and alumina may subsequently be impregnated with the oxides of molybdenum and cobalt.

The impregnating solution used oridinarily contains the cobalt and molybdenum compounds in the portions desired in the final catalyst and the impregnation is controlled to produce a final catalyst containing these components in the desired concentrations. The concentrations of the cobalt and molybdenum oxides in the catalyst employed in the present process may respectively range from about 1 to about 8 percent by weight and from about 3 to about 20 percent by weight of the final catalyst. The preferred catalyst for use in the present denitrogenation process contain cobalt oxide (CoO) in a concentration of from about 2.0 to about 4.5 percent and molybdenum trioxide (MoO_3) in a concentration of from about 7 to 16 percent by weight of the final catalyst. After impregnation, the final composite generally is dried at a temperature of from about 200° to about 600° F. for a period of from about 2 to 24 hours or more and thereafter calcining at a temperature of from about 600° to about 1200° F. for a period of from about 1 to 12 hours or more.

It is an essential feature of the process described herein that the catalyst employed contain at least about 15 percent by weight of silica. Composites containing amounts of silica less than about 15 percent by weight do not possess the requisite denitrogenation activity observed in the case of the hereinabove described catalyst. The cobalt oxide content of the catalyst, as noted above, is preferably between about 2 and about 4.5 percent by weight. The molybdenum trioxide content of the catalyst used in the present process is preferably between about 7 and about 16 percent by weight. Catalysts having cobalt oxide and molybdenum trioxide contents outside the foregoing ranges resulted in substantially less effective removal of nitrogen compounds from the hydrocarbon stocks undergoing treatment.

The catalyst used in the process of the invention desirably has a surface area within the approximate range of 200 to 450 square meters per gram. Composites having surface area of less than about 200 square meters per gram were found to have considerably higher aging rates in the denitrogenation process and accordingly are less preferred than catalysts characterized by surface areas within the aforementioned range.

The process of this invention may be carried out in any suitable equipment for catalytic operations. The process may be operated batchwise. It is preferable, however, and generally more feasible to operate continuously. Accordingly, the process is adapted to operations using a fixed bed of catalyst through which the charge is passed at the desired temperature and pressure in either upward or downward flow. Also, the process can be operated using a moving bed of catalyst wherein the hydrocarbon flow may be concurrent or countercurrent to the catalyst flow. A fluid type of operation wherein the catalyst is carried in suspension in the hydrocarbon charge or a suspensoid type of operation in which the catalyst and charge are transported as a slurry into the reaction zone, may feasibly be employed in carrying out the present process.

As previously noted, hydrocarbon oils which contain nitrogen compounds may generally be treated with the hereinabove described catalyst. The particular conditions under which treatment is effected may vary depending on the charge stock employed. Broadly, the removal of nitrogen from hydrocarbon oils in accordance with the present process is carried out at a temperature between about 650° F. and about 950° F., utilizing a hydrogen partial pressure of between about 100 and about 5000 pounds per square inch gauge. The liquid hourly space velocity of fresh feed, i.e. the liquid volume of hydrocarbons per hour per volume of catalyst is between 0.1 and 10. The amount of fresh hydrogen charged is gen-

erally between about 200 and about 10,000 standard cubic feet per barrel (42 gallons at 60° F.) of hydrocarbon feed. When the charge stock is a nitrogen-containing gas oil, the conditions of treatment ordinarily involve a temperature between about 700° F. and about 900° F., a hydrogen partial pressure of between about 500 and 2000 pounds per square inch gauge, a liquid hourly space velocity of between 0.5 and 4, and a fresh hydrogen charge of between about 2500 to 3500 standard cubic feet per barrel of gas oil feed. When, the charge stock is a nitrogen-containing naphtha, the conditions of treatment ordinarily involve a temperature between about 650° F. and about 800° F., a hydrogen partial pressure of between about 100 and about 1000 pounds per square inch gauge, a liquid hourly space velocity of between 1 and 10 and the presence of between about 350 to 2500 standard cubic feet of hydrogen per barrel of feed.

Generally, the hydrocarbon oils undergoing treatment in accordance with the process described herein will have a nitrogen content in excess of 1 part per million which may extend, particularly for certain shale oils, up to 2 percent by weight or more. Naphtha charge stocks employed generally will contain between about 5 and about 1500 parts per million of nitrogen. It is generally desired to reduce such nitrogen content to less than 1 part per million, particularly in instances where the naphtha charge after treatment is to be subjected to reforming in the presence of a platinum or other noble metal-containing catalyst. Gas oil stocks employed generally will contain between about .02 and 1 percent by weight of nitrogen.

The following examples will serve to illustrate the process of this invention without limiting the same:

Example 1

A composite of cobalt and molybdenum oxides on alumina in the form of ⅛" x ⅛" pellets and prepared by impregnation of alumina gel with approximately 3 percent by weight CoO and approximately 9.5 percent by weight MoO_3 was crushed to a particle size of less than 100 mesh (Tyler). Approximately 85 parts by weight of the crushed material were mixed with approximately 43 parts by weight of silica hydrogel containing about 35 weight percent SiO_2 and 65 weight percent water and having a particle size of less than 60 mesh (Tyler). The resulting composite was intimately mixed by ball milling the components for about 24 hours at which time the particles were of 14 to 15 microns average size. The ball milled material was then pelleted to ⅛" diameter by 1/16" thick pellets. The pellets so obtained were then tempered for 3 hours at 1000° F. in dry air. The resulting product contained on a weight basis, about 2.5 percent CoO, about 8 percent MoO_3, about 15 percent SiO_2, and about 74.5 percent Al_2O_3 and possessed a surface area of approximately 220 square meters per gram.

Example 2

A hydrocarbon oil charge stock characterized by a gravity of 24.7° A.P.I., a boiling range of 375° F. to 744° F., an aniline number of 125.1° F. and a nitrogen content of 0.25 percent by weight was passed over a bed of the catalyst of Example 1 at a temperature of 750° F., a pressure of 1500 p.s.i.g. in the presence of hydrogen circulating at a rate of 3000 standard cubic feet per barrel of charge utilizing a liquid hourly space velocity of 2. The product obtained from such operation, upon analysis, was found to contain 0.07 weight percent nitrogen, corresponding to a removal of 72 weight percent of the nitrogen contained in the original charge.

For purposes of comparison, a silica-free catalyst of cobalt oxide and molybdenum oxide composited with alumina of the type heretofore employed for denitrogenation and containing 3.1 percent by weight cobalt oxide, 9.3 percent by weight molybdenum oxide and remainder substantially alumina was employed in treating the above stock under identical reaction conditions. The nitrogen content of the product obtained with use of this catalyst was 0.10 weight percent, corresponding to a removal of only 60 weight percent of the nitrogen contained in the original charge.

It will be evident from the comparative data of the above Example 2 that the addition of 15 weight percent silica to the cobalt oxide—molybdenum oxide—alumina catalyst resulted in a 12 weight percent more effective removal of nitrogen from the nitrogen-containing charge.

Example 3

A hydrocarbon oil charge stock such as used in Example 2 was passed over a bed of the catalyst of Example 1 at a temperature of 820° F., a pressure of 1500 p.s.i.g. in the presence of hydrogen circulating at a rate of about 3100 standard cubic feet per barrel of charge utilizing a liquid hourly space velocity of 2. The product obtained from such operation, upon analysis, was found to contain 0.018 weight percent nitrogen, corresponding to a removal of 92.8 weight percent of the nitrogen contained in the original charge.

For purposes of comparison, a silica-free catalyst of cobalt oxide and molybdenum oxide composited with alumina of the type heretofore employed for denitrogenation and containing 3.1 percent by weight cobalt oxide, 9.3 percent by weight molybdenum oxide and remainder substantially alumina was employed in treating the above stock under identical reaction conditions. The nitrogen content of the product obtained with the use of this catalyst was 0.047 weight percent, corresponding to a removal of 81.2 weight percent of the nitrogen contained in the original charge.

It will be evident from the comparative data of the above Example 3 that the addition of 15 weight percent silica to the cobalt oxide-molybdenum oxide-alumina catalyst resulted in an 11.6 weight percent more effective removal of nitrogen from the nitrogen-containing charge.

Example 4

A hydrocarbon oil charge characterized by a gravity of 23.8° A.P.I., a boiling range of 404° F. to 732° F., an aniline number of 131° F. and a nitrogen content of 0.25 percent by weight was passed over a bed of the catalyst of Example 1 at a temperature of 830–865° F., a pressure of 1640 p.s.i.g. in the presence of hydrogen circulating at a rate of 2500-3000 standard cubic feet of hydrogen per barrel of charge utilizing a liquid hourly space velocity of 2 and a liquid recycle to fresh feed ratio of 3/1. The product obtained was treated under the foregoing conditions until the nitrogen content thereof was reduced to 0.043 percent by weight. The product was then distilled to remove a naphtha fraction boiling in the approximate range of 180 to 390° F. This fraction, upon analysis, was found to contain 69 parts per million of nitrogen.

For purposes of comparison, a silica-free catalyst of cobalt oxide and molybdenum oxide composited with alumina of the type heretofore employed for denitrogenation and containing 3.1 percent by weight cobalt oxide, 9.3 percent by weight molybdenum oxide and remainder substantially alumina was employed in treating the above stock under identical reaction conditions until the nitrogen content thereof was likewise reduced to 0.043 percent by weight. The product was then distilled to remove a naphtha fraction boiling in the approximate range of 180 to 390° F. This fraction, upon analysis, was found to contain 160 parts per million of nitrogen.

It will be evident from the comparative data of the above Example 4 that the addition of 15 weight percent silica to the cobalt oxide-molybdenum oxide-alumina catalyst results in a marked selective denitrogenation of the naphtha contained in the total processed product treated to the same total denitrogenation level.

Example 5

A hydrocarbon oil charge such as used in Example 4 was passed over a bed of the catalyst of Example 1 at the same conditions of reaction as specified in Example 4

to reduce the nitrogen content to 0.06 percent by weight. The product was then distilled to remove a naphtha fraction boiling in the approximate range of 180 to 390° F. This fraction, upon analysis, was found to contain 83 parts per million of nitrogen.

For purposes of comparison, a silica-free catalyst of cobalt oxide, molybdenum oxide composited with alumina of the type described in Example 4 was employed in treating the same stock under identical reaction conditions until the nitrogen content thereof was likewise reduced to 0.06 percent by weight. The product was then distilled as above to remove a naphtha fraction boiling in the approximate range of 180 to 390° F. This fraction, upon analysis, was found to contain 200 parts per million of nitrogen.

The comparative data of the above Example 5 further establishes that the addition of silica to the cobalt oxide-molybdenum oxide-alumina catalyst resulted in a marked selective denitrogenation of the naphtha contained in the total processed product treated to the same total denitrogenation level.

The selective denitrogenation of naphtha utilizing a catalyst containing, on a weight basis, about 2.5 percent CoO, about 8 percent MoO_3, about 15 percent SiO_2 and about 74.5 percent Al_2O_3 designated as "catalyst A" as compared with a silica-free catalyst containing, on a weight basis, about 3.1 percent CoO, about 9.3 percent MoO_3 and remainder Al_2O_3 designated as "catalyst B" is shown in the attached figure. The data were obtained by treating a hydrocarbon oil charge of the type and under the conditions described in Example 4 with each of the above catalyst until the nitrogen content of said charge had been reduced to a predetermined extent corresponding to the abscissa of the figure. The product in each instance was then distilled to remove a naphtha fraction boiling in the 180–390° F. range. The fraction obtained in each case was analyzed for nitrogen. The nitrogen content of the naphtha fraction obtained in each instance expressed in parts per million was plotted, as will be seen from the attached figure, against the percent weight nitrogen in the corresponding total liquid product, i.e. the product obtained after treating but before removal therefrom of the above-indicated naphtha fraction. It will be evident from the data of the figure that in every instance a more selective denitrogenation of the naphtha fraction was achieved with catalyst A, i.e. cobalt oxide-molybdenum oxide-alumina composite containing silica than was obtainable with catalyst B, i.e. the silica-free cobalt oxide-molybdenum oxide-alumina composite.

It will be understood that the above description is merely illustrative of preferred embodiments of the invention of which many variations may be made within the scope of the following claims by those skilled in the art without departing from the spirit thereof.

I claim:

1. A process for removing nitrogen from a nitrogen-containing hydrocarbon oil which comprises contacting said oil in the presence of hydrogen with a catalyst consisting essentially of 15 to 40 percent by weight silica, 1 to 8 percent by weight cobalt oxide, 3 to 20 percent by weight molybdenum trioxide and remainder alumina, at a temperature between about 650° F. and about 950° F., a liquid hourly space velocity between about 0.1 and about 10 and a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge employing between about 200 and about 10,000 standard cubic feet of hydrogen per barrel of oil.

2. A process for removing nitrogen from a nitrogen-containing hydrocarbon oil which comprises contacting said oil in the presence of hydrogen with a catalyst consisting essentially of 15 to 25 percent by weight of silica, 2 to 4.5 percent by weight cobalt oxide, 7 to 16 percent by weight of molybdenum trioxide and remainder alumina, at a temperature between about 650° F. and about 950° F., at a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge employing between about 200 and about 10,000 standard cubic feet of hydrogen per barrel of oil.

3. A process for effecting selective denitrogenation of the naphtha fraction of a hydrocarbon oil made up of said fraction and components boiling outside the naphtha range which comprises contacting said oil with a catalyst consisting essentially of 15 to 40 percent by weight silica, 1 to 8 percent by weight cobalt oxide, 3 to 20 percent by weight molybdenum trioxide, and remainder alumina at a temperature between about 650° F. and about 950° F., at a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge employing between about 200 and about 10,000 standard cubic feet of hydrogen per barrel of oil, and thereafter separating from the treated hydrocarbon oil a naphtha fraction substantially free of nitrogen.

4. A process for effecting selective denitrogenation of the naphtha fraction of a hydrocarbon oil made up of said fraction and components boiling outside the naphtha range which comprises contacting said oil with a catalyst consisting essentially of 15 to 25 percent by weight silica, 2 to 4.5 percent by weight cobalt oxide, 7 to 16 percent by weight molybdenum trioxide and remainder alumina at a temperature between about 650° F. and about 950° F., at a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge employing between about 200 and a about 10,0000 standard cubic feet of hydrogen per barrel of oil, and thereafter separating from the treated hydrocarbon oil a naphtha fraction substantially free of nitrogen.

5. In a process for reforming a naphtha originally having a nitrogen content in excess of 1 part per million by contacting said naphtha under catalytic reforming conditions with a reforming catalyst adversely affected by the presence of nitrogen, the improvement which comprises treating said naphtha, prior to contact with said reforming catalyst, to reduce the nitrogen content thereof below 1 part per million by contacting with a catalyst consisting essentially of 15 to 40 percent by weight silica, 1 to 8 percent by weight cobalt oxide, and 3 to 20 percent by weight molybdenum trioxide and remainder alumina, in the presence of hydrogen at a temperature between about 650 and about 800° F. at a liquid hourly space velocity between about 1 and about 10, a hydrogen partial pressure between about 100 and about 1000 pounds per square inch gauge, employing between about 350 and about 2500 standard cubic feet of hydrogen per barrel of naphtha.

6. In a process for cracking a nitrogen-containing gas oil by contacting said gas oil under catalytic cracking conditions with a cracking catalyst adversely affected by the presence of nitrogen, the improvement which comprises treating said gas oil prior to contact with said cracking catalyst to reduce the nitrogen content thereof below the minimum which adversely affects said cracking catalyst by contacting with a catalyst consisting essentially of 15 to 40 percent by weight silica, 1 to 8 percent by weight cobalt oxide, and 3 to 20 percent by weight molybdenum trioxide and remainder alumina, in the presence of hydrogen at a temperature between about 700° F. and about 900° F. at a liquid hourly space velocity between about 0.5 and about 4, a hydrogen partial pressure between about 500 and about 2000 pounds per square inch gauge, employing between about 2500 and about 3500 standard cubic feet of hydrogen per barrel of gas oil.

7. A process for removing nitrogen from a nitrogen-containing hydrocarbon oil which comprises contacting said oil in the presence of hydrogen with a catalyst consisting essentially of 15 to 40 percent by weight silica, 1 to 8

percent by weight cobalt oxide, 3 to 20 percent by weight molybdenum trioxide and remainder alumina, prepared by impregnating the alumina component with the cobalt oxide and molybdenum trioxide components, mechanically mixing the resulting impregnated product with the silica component, drying and calcining the resulting composite at an elevated temperature, said contacting being affected at a temperature between about 650 and about 950° F., a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 500 pounds per square inch gauge, employing between about 200 and about 10,000 standard cubic feet of hydrogen per barrel of oil.

8. A process for removing nitrogen from a nitrogen-containing hydrocarbon oil which comprises contacting said oil in the presence of hydrogen with a catalyst consisting essentially of 15 to 40 percent by weight silica, 1 to 8 percent by weight cobalt oxide, 3 to 20 percent by weight molybdenum trioxide and remainder alumina prepared by mechanically mixing the alumina and silica components and impregnating the resulting composite with the cobalt oxide and molybdenum trioxide components, drying and calcining the resulting product at an elevated temperature, said contacting being effected at a temperature between about 650 and about 950° F., a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge, employing between about 200 and about 10,000 standard cubic feet of hydrogen per barrel of oil.

9. A process for removing nitrogen from a nitrogen-containing hydrocarbon oil which comprises contacting said oil with a catalyst characterized by a surface area in the approximate range of 200 to 450 square meters per gram and consisting essentially of 15 to 40 percent by weight of silica, 1 to 8 percent by weight cobalt oxide, 3 to 20 percent by weight molybdenum trioxide, and remainder alumina prepared by intimately mixing silica hydrogel with alumina having a surface area greater than 100 square meters per gram, impregnating the resulting composite with the colablt oxide and molybdenum oxide components, drying and calcining the resulting product at an elevated temperature, said contacting being effected at a temperature between about 650 and about 950° F., a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge, employing between about 200 and about 10,000 standard cubic feet of hydrogen per barrel of oil.

10. A process for removing nitrogen from a nitrogen-containing hydrocarbon oil which comprises contacting said oil with a catalyst characterized by a surface area within the approximate range of 200 to 450 square meters per gram consisting essentially of 15 to 40 percent by weight silica, 1 to 8 percent by weight cobalt oxide, and 3 to 20 percent by weight molybdenum trioxide, and remainder alumina prepared by impregnating alumina having a surface area greater than 100 square meters per gram with the cobalt oxide and molybdenum trioxide components, mechanically mixing the resulting impregnated product with silica hydrogel, drying and calcining the resulting composite at an elevated temperature, said contacting being effected at a temperature between about 650 and about 950° F., a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 500 pounds per square inch gauge, employing between about 200 and about 10,000 standard cubic feet of hydrogen per barrel of oil.

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UNITED STATES PATENT OFFICE

CERTIFICATION OF CORRECTION

Patent No. 3,004,913 October 17, 1961

Stanley Tucker

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 2, line 4, for "purposes" read -- purpose --; line 56, for "separte" read -- separate --; column 4, line 14, for "60" read -- 60 --; column 11, line 10, for "500" read -- 5000 --.

Signed and sealed this 3rd day of April 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents