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ISOTHERMAL ADSORPTION PROCESS FOR SEPARATION OF ORGANIC NITROGEN COMPOUNDS FROM HYDROCARBONS

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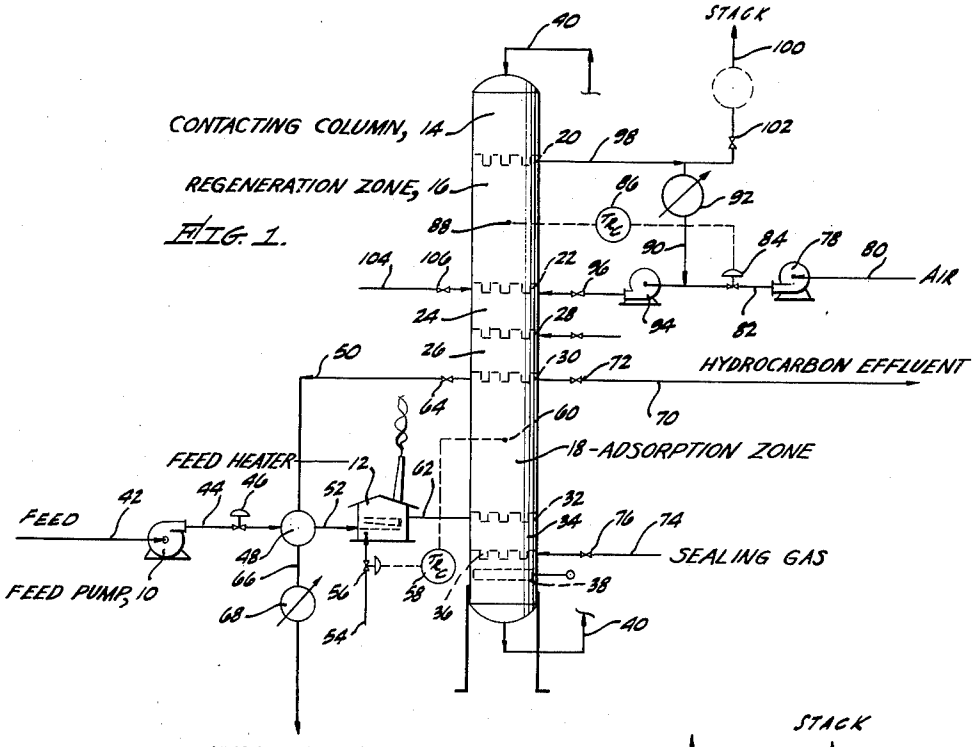


FIG. 1.

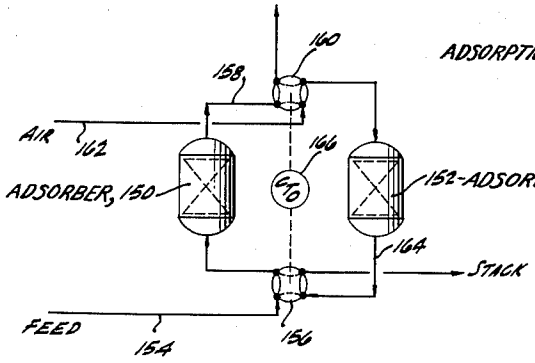


FIG. 3.

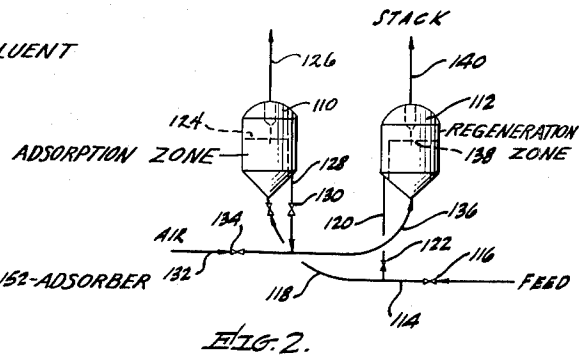


FIG. 2.

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ISOTHERMAL ADSORPTION PROCESS FOR SEPARATION OF ORGANIC NITROGEN COMPOUNDS FROM HYDROCARBONS

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7 Claims. (Cl. 208—254)

This invention relates to the refining of hydrocarbons, particularly those contaminated with organic nitrogen compounds and other polar materials. Such hydrocarbons include those which are produced as petroleum, as coal tar oil fractions, and shale oils among others.

Many crude petroleum streams are produced from the ground and are found to contain considerable quantities of organic compounds of nitrogen, sulfur, and oxygen in addition to the principal hydrocarbon constituents. In some cases the incidence of the nitrogen compounds is sufficient that the nitrogen analysis runs as high as 1.0% by weight. California crude oils in many cases average 0.5% by weight nitrogen analysis. Mexican and Venezuelan crudes have nitrogen analysis ranging from about 0.2% to about 0.35% by weight. Extensive analysis of these nitrogen-containing crudes indicate that much of the nitrogen occurs in the form of amines or the so-called nitrogen bases. These include pyridine, quinoline, and the mono, di, tri, and tetra alkylated derivatives of these materials. For example, in California kerosene distillate the di, tri, and tetra alkylated quinolines and alkylated pyridines are found. There is however considerable nonbasic nitrogen present in these materials. Coal tar oils produced in the coking of coal, contain extensive quantities of nitrogen bases and these are principally aromatic amines and heterocyclic nitrogen compounds. Shale oil produced by the heating and retorting of shale rock, such as that which is found in Colorado and elsewhere, resembles waxy crude but is characterized particularly in that it contains such extensive quantities of organic nitrogen compounds that the nitrogen analysis runs as high as about 2.5% by weight. Sulfur compounds are usually present also and the sulfur analysis may rise to 5.0% by weight. Oxygen compounds are present to a lesser degree, but all seriously affect the performance of the catalysts and adsorbents employed in many refining processes.

Crude petroleum, coal tar oils, and shale oils are principal or potential sources of liquid fuels and solvents. The presence of nitrogen compounds in the fuel or solvent product imparts a very bad odor to these materials. Their presence in the original oil very adversely affects hydrocarbon refining techniques by which the fuels and solvents or other materials are produced. They have, for example, well defined adverse effects on such processes as catalytic cracking, catalytic isomerization, catalytic reforming, and particularly platinum catalyzed halide promoted reforming. The nitrogen compounds appear to be adsorbed on a cracking catalyst and selectively deactivate its active cracking centers. The cracked gasoline yield may be reduced as much as 50% through the presence of sufficient organic nitrogen compounds to give the feed a nitrogen analysis of about 0.3% by weight, and it is reduced by 75% when the nitrogen analysis reaches about 0.45%. Platinum catalyzed reforming and other reforming processes in general are also adversely affected by presence of nitrogen compounds in the feed. In a platinum catalyzed gasoline reforming system using a halide promoted catalyst, the nitrogen compounds appear to react with the catalyst or the promoter to form ammonium halides which deposit in the apparatus. This deactivates the catalyst and lowers the yield unless the halide is continuously replenished.

Because of these adverse effects, repeated attempts have been made to remove the nitrogen compounds from hydrocarbon feedstocks in refining processes and from the products produced. For example, acid treating with dilute sulfuric acid forms water soluble salts with the basic nitrogen compounds, i.e., the nitrogen bases or amines. It is otherwise ineffective with respect to the nonbasic nitrogen compounds. Catalytic hydrogenation is effective to remove much of the nitrogen compounds, but in order to reduce their incidence in the hydrogenated product to a level which does not adversely affect a platinum catalyzed reforming process for gasoline, hydrogenation pressures of the order of 5,000 p.s.i. and higher are required.

The earlier suggested process for denitrogenation through contact with solid granular adsorbents suffer from a disadvantage involving high heat requirements in that the solids are generally cooled prior to the adsorbtion step, and then are heated to effect the displacement or desorption of the material from the adsorbent. Not only does this raise the quantity of heat necessary to maintain the process, but it also results unavoidably in thermal stresses in the equipment and also in the granular adsorbent particles.

The present invention comprises an improved process for the adsorptive denitrogenation of hydrocarbon fluid mixtures, and for the removal of other highly polar materials which deactivate catalysts and adsorbents. A particular inorganic solid adsorbent is used in this process, which is further characterized by conducting both the adsorption and regeneration steps at temperatures of the order of those used for catalyst regeneration. The operating temperature is sufficiently high to effect an efficient regeneration by oxidation and the adsorption step is effected at substanially the same temperature. Because this process allows adsorption at regeneration temperatures, the heat requirements of the process are only those necessary to supply heat losses from the system and to heat the feed stream to the operating temperature, and part of this heat however is recoverable. The heat requirement is thus substantially less than 10% of that required in the normal non-isothermal adsorption-regeneration processes. A treated product substantially free of nitrogen and other highly polar deactivating compounds is produced as a desirable product in itself or as a pretreated material for feeding to subsequent catalytic or adsorptive processes.

It is a primary object of this invention to provide an improved process for the removal of highly polar adsorbent or catalyst deactivating compounds from fluid mixtures, such as hydrocarbon streams contaminated with organic compounds of nitrogen, sulfur, and oxygen.

It is a more specific object of this invention to provide a substantially isothermal process for the pretreatment of feed hydrocarbons by contacting the material with a solid contact material having a specific affinity for hydrocarbon organic compounds of nitrogen, sulfur and oxygen, in preference to hydrocarbons of the same boiling range and which includes a regeneration step in which these compounds are burned from the solids by an oxygen-containing gas at substantially the adsorption temperature.

It is a more specific object of this invention to provide a pretreated hydrocarbon stream from which harmful organic compounds of nitrogen have been removed by means of an isothermal regenerative solid adsorption process employing a metallo alumino silicate absorbent

having substantially uniform sized pores of greater than about 7 A. in diameter and which operates at a temperature on the order of 700° F. to about 1050° F.

It is another object of this invention to effect the denitrogenation of hydrocarbon mixtures contaminated with organic compounds of nitrogen by means of an isothermal adsorption-regeneration process wherein the solid adsorbent is a static or moving bed, or may be fluidized.

Other objects and advantages of the present invention will become more apparent to those skilled in the art as the description and illustration thereof proceed.

Briefly, the present invention comprises an improved process for treating hydrocarbon streams contaminated with highly polar compounds which are known to deactivate adsorbents and catalysts, such as organic nitrogen, sulfur, and oxygen compounds derived from virtually any source, to remove such compounds and produce a non-contaminated hydrocarbon stream. The subsequent description will involve removal of nitrogen compounds for the sake of simplicity, and with the understanding that the oxygen and sulfur compounds are also removed.

In general, the process consists in contacting the hydrocarbon feed contaminated with organic nitrogen compounds with a granular solid natural or synthetic metallo alimino silicate zeolite of the type generally referred to as "molecular sieves" organic. The organic nitrogen compounds are actively separated from the hydrocarbons by sorption mechanisms and it is possible to produce in one or more contacting stages a virtually nitrogen-free hydrocarbon product, that is, one having a zero nitrogen analysis. The solid contact material saturated with the nitrogen compounds is then regenerated by air oxidation whereby the nitrogen compounds are burned off, leaving the metallo alumino silicate free of these materials and in condition to treat additional feed. The regenerated material is then reemployed to contact further quantities of the contaminated feedstock.

It has now been found that both of these adsorption and regeneration steps may be effected satisfactorily at temperatures which are equal to the regeneration temperature, so that the entire process becomes an isothermal operation. The oxygen-containing gas is fed into the regeneration zone in contact with the rich adsorbent and the nitrogen compounds are burned from the adsorbent at temperatures in the range of from about 700° F. to about 1050° F., depending upon the speed desired to effect the regeneration, the quantity and nature of the nitrogen compounds present on the adsorbent, the thermal stability of the adsorbent and the feedstock, and such considerations. Temperatures below about 700° F. are not satisfactory because the oxidative regeneration cannot be initiated or maintained, and temperatures above about 1050° F. are not satisfactory because the adsorbent is destroyed.

Surprisingly these specific adsorbents are able to absorb practically quantitatively the basic and non-basic nitrogen compounds from these hydrocarbon streams at substantially these same temperatures. The particular adsorbents involved are hereinafter more particularly described.

For example, a gasoline stream which is to be fed to a platinum catalyzed reforming process may contain organic nitrogen compounds to the extent that the feed analyzes about 0.1% by weight. Some organic compounds of sulfur and oxygen are also usually present. The process of this invention, operating essentially isothermally at temperatures of the order of from 700° F. to 1050° F., can effectively reduce the nitrogen analysis of the effluent to values on the order of one part per million as shown in the following examples. It is not necessary however that the effluent be subjected to further treatment since there are many cases in which hydrocarbon mixtures are desirable in and of themselves after the substantially complete denitrogenation has been effected. The effluent, from the process of this invention, under proper solids fluid ratio control, is free of organic nitrogen compounds and the other polar compounds in general and is thus in especially excellent condition for subsequent treatment in the noble metal catalyst refining processes such as reforming.

It has also been found that the nitrogen content of the effluent produced in the process of this invention is affected by the rate at which the feed stream is passed through contact with the adsorbent. This effect is critical insofar as it determines the maximum rate at which a given body of adsorbent can effectively reduce the nitrogen analysis of a particular type of hydrocarbon feed. In general however for the particular zeolitic silicate adsorbents referred to, the extent to which a given quantity of adsorbent may treat a given feed to produce an effluent analyzing less than about 10 p.p.m. of nitrogen is limited by the nitrogen compound concentration on the adsorbent, specifically about 0.2% by weight absorbent nitrogen analysis with a moving absorbent bed, and somewhat less with a static bed. At values above this the adsorbent is apparently saturated with nitrogen compounds and "break-through" of these materials occurs. However, even exceeding this value, the effluent has a substantially reduced nitrogen analysis compared with the feed stream but the extent of the denitrogenation is somewhat less and the product will have a somewhat higher nitrogen analysis than the 10 p.p.m. value mentioned above.

The solid contact material employed in the process of this invention is a solid granular material having a mesh size range between about 2 and 300 mesh or smaller, preferably between about 4 and about 30 mesh for static or moving solids bed contact, and preferably between about 30 and 200 mesh for fluidized contacts. It may be used in the form of a dense compact bed of material through which the nitrogen compound containing streams pass, either in the vapor phase or in the liquid phase. The process may employ a single static bed of material in which case the process is only semicontinuous. Preferably a plurality of two or more static beds of solids are employed with appropriate remotely operable valving so that the streams pass through one or more of the contacting vessels in a set while the regeneration stream passes through one or more of the other vessels in the set. In this case the feed and product flows are continuous, in either the vapor or liquid phase, and either up or down through the solids.

Another modification employs a continuously moving solids bed. In this case, the flow of feed is maintained continuously through one or more contacting zones. The flow of regeneration fluid is maintained continuously through a second contacting zone, and the granular solids are recirculated successively through these zones.

In another modification using the smaller sized mesh ranges or powdered solids, the material may be suspended or fluidized in and by the fluid streams contacting it, and a single or several stages are employed.

A number of theoretical and actual contact stages greater than one is readily obtained in moving bed systems using a single contacting zone, or with several static beds, or with several fluidized contacting zones. Plural stage contacting is highly desirable in the production of an effluent of very low nitrogen analysis, that is, of the order of about 1 p.p.m. (parts per million) and below. Reduced solids to oil ratios also result. A single contact stage is frequently sufficient, even with feed-stock of high nitrogen analysis, where the product nitrogen analysis need only be reduced to about 0.1% by weight.

The present invention may not be carried out with the commonly available solid granular adsorbents such as alumina, silica gel, charcoal, etc., primarily because at temperatures of the order of 700° F. to 1050° F. they lose their adsorption capacity for organic compounds of nitrogen, sulfur, and oxygen. It has been

found that particular materials which are highly efficient and preferred in the hydrocarbon denitrogenation process of the present invention are the natural or synthetic crystalline zeolitic metallo alumino silicates activated by partial dehydration and having pores in their crystal structure which are 7 A. or more in diameter. The composition of one typical synthetic zeolite having a pore size of about 13 A. is $5Na_2O.6Al_2O_3.15SiO_2$. It may be prepared by heating stoichiometric quantities of alumina and silica and excess caustic under pressure. The excess caustic is washed out. Other desired metal ions, such as calcium, for example, may then be introduced by ion exchange. Part of the sodium in this material can be ion exchanged with concentrated salt solutions at superatmospheric pressure and temperatures of 150–300° C. to introduce other metal ions. Another adsorbent having pore diameters of about 10 A. is $5CaO.12Al_2O_3.30SiO_2$. The particular added metal ion changes the pore diameter. Certain naturally occurring minerals, such as chabazite, analcite, gmelinite, and the like can be heated to dehydrate the molecule partially and obtain an activated zeolitic material similar in denitrogenation properties to the manufactured materials. These natural and synthetic materials are all zeolites and their sodium and calcium derivatives are very stable solids which apparently have "pores" active for high temperature adsorption and which are quite uniform in size. Other derivatives have different sized "pores." The metallo alumino silicates having pore diameters of 7 A. or more exert strong adsorptive effects on the polar hydrocarbon compounds of nitrogen, sulfur, and oxygen, whereas the hydrocarbons of the same boiling range are substantially unaffected.

The synthetic crystalline metallo alumino silicate zeolites having pore diameters of 7 A. or larger are presently available items of commerce marketed by Linde Air Products Company, 30 E. 42nd Street, New York 17, New York, under the name of "Molecular Sieves 10X, 13X, etc.," and these have pore diameters averaging 10 A. and 13 A. respectively.

The process of the present invention and several of its modifications will be more readily understood by reference to the accompanying drawings in which:

Figure 1 is a schematic flow diagram and an elevation view of part of the apparatus used to effect the process of this invention with a moving bed of the granular adsorbent,

Figure 2 is a simplified schematic flow diagram of the process of this invention using fluidized solids techniques well known to those skilled in the art, and

Figure 3 is a simplified schematic flow diagram illustrating the static solids bed modification of this process.

Referring now more particularly to Figure 1, the essential apparatus elements involved include feed pump **10**, feed heater **12**, and contact column **14** containing regeneration zone **16** and adsorption zone **18**. In contacting column **14** the metallo alumino silicate adsorbent is recirculated downwardly as a moving bed successively through regeneration gas disengaging zone **20**, regeneration zone **16**, regeneration gas engaging zone **22**, sealing zones **24** and **26** on opposite sides of seal gas engaging zone **28**, effluent disengaging zone **30**, adsorption zone **18**, feed engaging zone **32**, a sealing zone **34**, second seal gas engaging zone **36**, and solids feeder zone **38** within which the rate of flow of the moving bed of solid adsorbent and the uniformity of flow throughout the column cross section are determined. Any sort of a solids elevator **40** such as mechanical, pneumatic, or other, is provided to recirculate adsorbent removed from the bottom of column **14** to the top of that column.

Column **14** is of course provided with external insulation not shown to reduce heat losses of the system to an absolute minimum.

The feed stream, for present purposes of illustration, is considered to be a naphthenic gasoline suitable as a catalytic reformer feed and which analyzes about 0.1% by weight of nitrogen. These nitrogen compounds include the basic nitrogen bases such as pyridine, alkylated pyridines, quinoline, alkylated quinolines, and the like and other nonbasic nitrogen compounds such as pyrrole, alkylated pyrrole, nitriles, diphenylamine, etc. This feed stream is introduced through line **42** and is pumped by means of pump **10** through line **44** at a rate controlled by valve **46** through heat exchanger **48** in which, if the treated effluent is not sent to a subsequent treating step in which it should be at an elevated temperature, the feed is preheated by exchange with the effluent removed from disengaging zone **30** through line **50**. The feed, thus possibly partially preheated, is introduced through line **52** into a fired feed heater and vaporizer **12**. Fuel is introduced into this preheater through line **54** at a rate controlled by valve **56** in accordance with temperature recorder controller **58** at thermocouple point **60** disposed at some appropriate location within adsorption zone **18**. The feed vapor continues through transfer line **62** and is introduced into feed engaging zone **32**. The vapor passes upwardly countercurrent to the downwardly moving adsorbent at a temperature which may range from as low as about 700° F. to as high as about 1050° F. The feed rate is controlled at a value relative to the rate of flow of the adsorbent so as to produce an effluent having a nitrogen analysis which is suitable for the particular purposes at hand. If this is to be a catalytic reformer feed the nitrogen content is preferably as low as about one part per million. Under these circumstances the rate of hydrocarbon feed flow through adsorption zone **18** is preferably kept below a rate which is equivalent to adsorption of not more than about 0.2% by weight of nitrogen on the adsorbent. This of course can be readily controlled by adjustment of the adsorbent to feed ratios in zone **18**.

The nitrogen compounds, both basic and nonbasic, and any other polar compounds which may be present in the feed stream, are adsorbed by the adsorbent at the elevated temperature and are retained thereby while the hydrocarbon components remain substantially unadsorbed and collect in effluent disengaging zone **30**. If this material is to be used per se it is removed through line **50** at a rate controlled by valve **64** and passes through line **50** and exchanger **48** and continues through line **66** and product aftercooler **68**. This material is sent to storage facilities or other operations not indicated. Typically however, the thus treated hydrocarbon stream comprises the feedstock to a catalytic reforming operation in which case it is removed from effluent disengaging zone **30** through line **70** at a rate controlled by valve **72**. It is in the vapor phase under the circumstances and conditions selected for purposes of this example and may be heated additionally if necessary to reforming temperatures and then introduced into the catalytic reforming zone not shown. In some cases it may be necessary to cool the adsorption zone effluent slightly if the reforming temperature desired is somewhat less than the adsorption temperature maintained in adsorption zone **18**.

The spent adsorbent passes downwardly through sealing zone **34**, a sealing gas is introduced into second sealing zone **36** by means of line **74** at a rate controlled by valve **76**. This sealing gas may be steam, oxygen-free flue gas, carbon dioxide, methane, hydrogen, nitrogen, or any other inert fluid which is compatible with the adsorbent employed, with the hydrocarbon feed stream treated, and any subsequent operations on the effluent.

The adsorbent continues downwardly through solids feeder zone **38** at a temperature still ranging between 700° F. and 1050° F. and is conveyed through conveyor **40** to the top of column **14**. The hot rich adsorbent passes downwardly as a moving bed through regeneration zone **16** through which is maintained a recirculating stream of regeneration gas, which in this case is a stream of flue gas or combustion gas produced in this regenera-

tion and to which a small but effective amount of oxygen or air is introduced in quantities sufficient to maintain the combustion. An oxygen-containing gas such as air or any other such gas, is introduced by means of blower **78** and lines **80** and **82** at a rate controlled by valve **84** and temperature recorder controller **86** which in turn is actuated by temperature control point **88**. This air is mixed with spent flue gas flowing through line **90** from cooler **92** forming a gas mixture consisting essentially of nitrogen, carbon dioxide and water vapor, but which also contains a small controlled quantity of oxygen which may range between about 0.1% and about 5% by volume. This fresh regeneration gas is forced through regeneration zone **16** by means of blower **94** at a rate controlled by valve **96**. This gas passes upwardly through regeneration zone **16** and effects the combustion of the adsorbed nitrogen and any other adsorbed polar compounds on the adsorbent. This is an exothermic reaction and heat is liberated in this step to the extent that the combustible material is adsorbed on the adsorbent. Hot flue gas is disengaged from zone **20** and is passed through line **98** to stack **100** at a rate controlled by valve **102**. Part of the flue gas however is recirculated through cooler **92** in which part of the heat of regeneration is dissipated. This produces the recirculated fraction of regeneration gas to which the oxygen is added to produce the fresh regeneration fluid.

To effect startup of the process of this invention natural gas or other fuel may be introduced through line **104** at a rate controlled by valve **106** and burned with air introduced as previously described into regeneration zone **16**. After the entire circulating mass of adsorbent has been raised to the desired operating temperature within the limits set previously, the feed stream flow is started at approximately the same temperature in the manner also previously described. As the combustile nitrogen and other polar compounds accumulate on the adsorbent, combustion of these materials begins in regeneration zone **16** and is effective to supply at least part and sometimes all of the heat necessary to maintain the process. In this case the opening of valve **106** is gradually reduced until a setting is reached to maintain the regeneration temperature at approximately the desired value. This may result particularly when relative small amounts only of adsorbed materials are available for burning.

With feed streams containing rather extensive quantities of organic compounds of nitrogen, e.g., in some shale oil fractions in which the nitrogen analysis may rise as high as 2.0% by weight, there is a sufficient amount of adsorbed nitrogen compounds and the like which when burned will maintain the desired operating temperature of the solids in regeneration zone **16** and even generate an excess of heat which must be dissipated in cooler **92**. If the desired operating temperature is somewhat lower than the maximum allowable limit set by the adsorbent, then the temperature of the adsorbent during regeneration may be allowed to rise to a value of about 1050° F. for example and the heat dissipated by direct heat exchange in the adsorption zone with a feed stream which is introduced at a temperature somewhat below the desired operating temperature. For example the feed may be introduced at 600° F., be heated in adsorption zone **18** through adsorption of the sensible heat of the regenerated adsorbent to the desired operating temperature of 800° F. for example, and then removed at about this temperature. The spent adsorbent under these conditions is removed from adsorption zone **18** and introduced into regeneration zone **16** at a temperature of about 600° F. for example. The combustion of a large quantity of organic nitrogen compounds will raise this temperature to the maximum value before stated. In this way heat exchange required in the process is all or largely effected inside column **14**. The temperature change between 600° F. and 1050° F. causes some thermal stress in the system and in the solids, but it is very substantially less than the thermal stress characteristic of adsorption processes in which the feed stream is treated in an adsorption zone at a temperature of the order of 70° F. to 100° F., and then is regenerated under combustion conditions at temperatures on the order of 900–1000° F. or higher.

It should be understood that the description of Figure 1 is merely illustrative and that modifications may be made therein within the contemplation of this invention. For example, the position of the adsorption and the regeneration zones may be reversed from that shown if desired. The seal streams employed may be modified if desired by removing a mixture of the gases present in the contacting column instead of injecting a seal gas which turns up in the product streams as a contaminant. The use of other solids-fluid contacting process steps in conjunction with the process of this invention is contemplated, but since many of these are well known in the art they will not be extensively discussed here.

Although the previous example has dealt with gaseous fluids and since under the relatively high operating temperatures of 700° F. to 1050° F. most hydrocarbons are in the vapor phase, it is not intended to limit the present invention to vapor phase contacting only. It is well known for example that some hydrocarbon fractions remain in the liquid phase at temperatures above about 700° F. and do not begin to decompose thermally or otherwise until temperatures of the order of 900° F. are reached. With such materials the process of the present invention may be effected with the feed stream contacting the adsorbent in the adsorption zone in the liquid phase. Obviously there are conditions of feed streams of relatively wide boiling range in which the feed stream may be in a mixed condition, that is, partly vapor and partly liquid.

Referring now more particularly to Figure 2, a very simple schematic flow diagram of the process of the present invention, utilizing fluidized solid techniques well known to those skilled in the art, is shown. Here adsorption zone **110** and regeneration zone **112** are shown. The feed stream is introduced through line **114** controlled by valve **116** and passes upwardly through transfer line **118** into adsorption zone **110**. Hot regenerated solid adsorbent is dropped through standpipe **120** provided with valve **122** to form a fluidized suspension of solids. This suspension passes upwardly to adsorption zone **110** and forms fluidized solids level **124**. The unadsorbed hydrocarbons are discharged through line **126**, the spent adsorbent is discharged through standpipe **128** controlled by valve **130**.

The spent adsorbent is dropped into a stream of oxygen-containing regeneration gas flowing through line **132** at a rate controlled by valve **134** and it passes upwardly into regeneration zone **112** through transfer line **136**. Fluidized solids level **138** is maintained herein and adsorbed compounds combustion takes place. Hot stack gases are discharged through line **140** and the regenerated hot solids are dropped through standpipe **120** into transfer line **118** to contact further quantities of the feed.

It is contemplated that the various heat exchange and flow control steps shown in Figure 1 would also be used in the process of Figure 2, and that further techniques characteristic of fluidized solids processes would also be employed. These are well known to those skilled in the art.

In Figure 3 is shown a simplified schematic drawing of a continuous process employing static or stationary beds of solid adsorbent. A pair of vessels **150** and **152** are provided containing a static bed of the particular solid granular adsorbent disclosed previously. The flow of fluid through these vessels is staggered so that at any given time at least one bed of adsorbent is contacting the feed stream while the other is being regenerated according to the process of this invention. In Figure 3 the feed stream is introduced through line **154** and

four-way control valve **156** and passes upwardly through adsorber **150**, from which the unadsorbed fraction is removed through line **158** and four-way control valve **160**. Simultaneously an oxygen-containing regeneration gas flows through line **162** and valve **160** downwardly through adsorber **152** in which the adsorbed materials are burned from the adsorbent. The effluent stack gases are discharged through line **164** and flow through four-way control valve **156** to the stack. The intermittent actuation of control valve **156** and **160** is controlled by cycle timer operator instrument **166** in a suitable sequence. Again the various temperature and flow control steps equivalent to those described in Figure 1 are to be employed in this modification of the process to effect substantially isothermal adsorption and oxidative regeneration steps on the adsorbent.

In one application of the process of this invention a relatively heavy hydrocarbon mixture was processed with a moving bed of the adsorbent according to the present invention. The metallo alumino silicate adsorbent had pore diameters of about 13 A. and was maintained at a temperature of 900° F. The operating pressure was substantially atmospheric. The feed stream was a highly aromatic catalytic cycle oil from a catalytic cracking operation and had a boiling range of about 450–650° F. The oil was in the vapor phase during the process. It analyzed 0.096 weight percent nitrogen Kjeldahl. The regeneration temperature was held at 900° F. by variation of the quantity of oxygen contained in a flue gas introduced during the regeneration step. The feed to adsorbent ratio in the adsorption zone was controlled so that the spent adsorbent analyzed about 0.13% by weight nitrogen. This is sufficiently below the maximum nitrogen concentration discussed above and accordingly the nitrogen analysis of the effluent obtained was about 0.003% nitrogen by weight.

A repeat operation duplicating the conditions given immediately above was carried out with the single exception that the feed to adsorbent ratio was reduced to produce a spent adsorbent analyzing only about 0.08% by weight nitrogen. Under these circumstances the effluent analyzed 0.001 weight percent nitrogen Kjeldahl. This corresponds to an effluent analyzing 10 p.p.m. of nitrogen.

The same operation was repeated with the same feedstock except that the regeneration and the adsorption temperatures were reduced to a value as close to the minimum at which combustion could be initiated and maintained, that is, a temperature of about 700° F. The feed to adsorbent ratio was substantially reduced to produce a spent adsorbent analyzing about 0.08% nitrogen by weight. This is also substantially below the maximum figure previously discussed and the effluent analysis varied slightly near 0.0001 weight percent nitrogen Kjeldahl. This is 1 p.p.m. of nitrogen compound contamination and for most purposes the effluent is clean.

The 10 A. zeolitic silicate adsorbent referred to above gives substantially identical degrees of nitrogen compound adsorption.

The process of the present invention is readily applicable to the pretreatment of the hydrocarbons in the gasoline boiling range. The removal of organic compounds of nitrogen in such instances is extremely important for several reasons. First, such compounds impart to gasoline an extremely disagreeable odor. Second, the presence of even very small concentrations of such nitrogen compounds has an extremely adverse effect upon the performance of certain halide-promoted platinum catalyzed dehydroaromatization processes employed in the refining of gasoline to raise the antiknock rating thereof. The nitrogen compounds appear to react either with the halide promoter or the catalyst in some manner with the formation of extensive quantities of ammonium halide salts which precipitate in the system and cause plugging problems. Third, and in addition to the plugging problems, the ammonium halide formation, if allowed to continue, also simultaneously tends to deactivate the catalyst through removal of the promoter and ultimately results in decreased yields and octane improvement. The other polar sulfur and oxygen containing contaminants have well known undesirable effects.

In all of the preceding discussion, the nitrogen analyses given or referred to are Kjeldahl total nitrogen determinations and express the concentration of organic compounds of nitrogen, either in the fluid or on the adsorbent, as weight percent nitrogen.

It has been found that the process of this invention may be conducted in the liquid phase with heavy or high boiling feedstocks at contacting temperatures on the order of those noted above to effect a substantial degree of denitrogenation. It has been found also that at higher temperatures in this range the rate of denitrogenation is considerably higher as indicated by the lower nitrogen analyses of the products.

With lighter feedstocks it is preferred to treat them in the vapor phase because the holdup on the solids of feed hydrocarbon is considerably reduced and the denitrogenation rate is higher. With heavier feedstocks it is possible to treat them in the vapor phase by contacting them at reduced pressures with the silicate solids. It is also possible to so treat them by employing diluent gases such as hydrogen, nitrogen, carbon monoxide, carbon dioxide, methane, and other well known light and inert gases. With the very heavy feedstocks the contact must of necessity be conducted in the liquid phase as these materials are frequently non-vaporizable. Their contacting is facilitated under these circumstances with the use of diluent solvents.

A particular embodiment of the present invention has been hereinabove described in considerable detail by way of illustration. It should be understood that various other modifications and adaptations thereof may be made by those skilled in this particular art without departing from the spirit and scope of this invention as set forth in the appended claims.

We claim:

1. The process for the denitrogenation of a hydrocarbon mixture contaminated with organic nitrogen compounds, including heterocyclic nitrogen bases, having boiling points within the boiling range of the hydrocarbon components of said mixture, in minor amounts but not in such quantities that said mixture analyzes more than about 2.5 percent by weight of nitrogen, which process comprises: (1) contacting said mixture with a lean solid partially dehydrated zeolitic metallo alumino silicate adsorbent having substantially uniform pores of between about 7 A. and about 13 A. in diameter, whereby there is obtained a non-adsorbed hydrocarbon phase and a rich adsorbent containing said organic nitrogen compounds; (2) separating said non-adsorbed phase from said rich absorbent; and (3) contacting said rich adsorbent with an oxygen-containing gas for a period of time sufficient to burn off said organic nitrogen compounds and return the adsorbent to its lean state; said steps (1), (2) and (3) being carried out at substantially the same temperature between about 700° F. and about 1050° F.

2. A process according to claim 1 wherein said zeolitic adsorbent has a composition corresponding substantially to $5Na_2O.6Al_2O_3.15SiO_2$ and has pores of about 13 A. in diameter.

3. A process according to claim 1 wherein said zeolitic adsorbent has a composition corresponding substantially to $5CaO.12Al_2O_3.30SiO_2$ and has pores of about 10 A. in diameter.

4. A process as defined by claim 1 wherein said step (1) is terminated to be followed by said step (2) when the total nitrogen content of said rich adsorbent reaches a value not greater than about 0.2 percent by weight.

5. A process for the denitrogenation of a petroleum hydrocarbon mixture contaminated with normally inci-

dent organic nitrogen compounds, including heterocyclic nitrogen bases, having boiling points within the boil range of the hydrocarbon components of said mixture, in minor amounts but not in such quantities that said mixture analyzes more than about 2.5 percent by weight of nitrogen, which process comprises (1) passing said mixture at a temperature between about 700° F. and about 1050° F. through a bed of a lean solid partially dehydrated zeolitic metallo alumino silicate adsorbent having substantially uniform pores of between about 7 A. and about 13 A. in diameter, whereby there is obtained a non-adsorbed hydrocarbon phase of reduced nitrogen content and a rich adsorbent containing adsorbed organic nitrogen compounds; (2) separating said non-adsorbed hydrocarbon phase from said rich adsorbent at a temperature within said range; (3) passing an oxygen-containing gas through said rich adsorbent at a temperature within said range and for a period of time sufficient to burn off said adsorbed organic nitrogen compounds and return the said adsorbent to its lean state; and (4) returning the lean adsorbent so obtained to step (1).

6. A process according to claim 5 wherein, in step (1), said adsorbent is moved through an adsorption zone wherein it contacts said hydro-carbon mixture countercurrently, and, in step (3) said rich adsorbent is moved through a regeneration zone wherein it contacts said oxygen-containing gas.

7. A process according to claim 6 wherein the flow rates of said hydrocarbon mixture and said adsorbent through said adsorption zone are so controlled relative to each other that the rich adsorbent withdrawn from said adsorption zone contains not more than about 0.2 percent by weight of nitrogen.

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