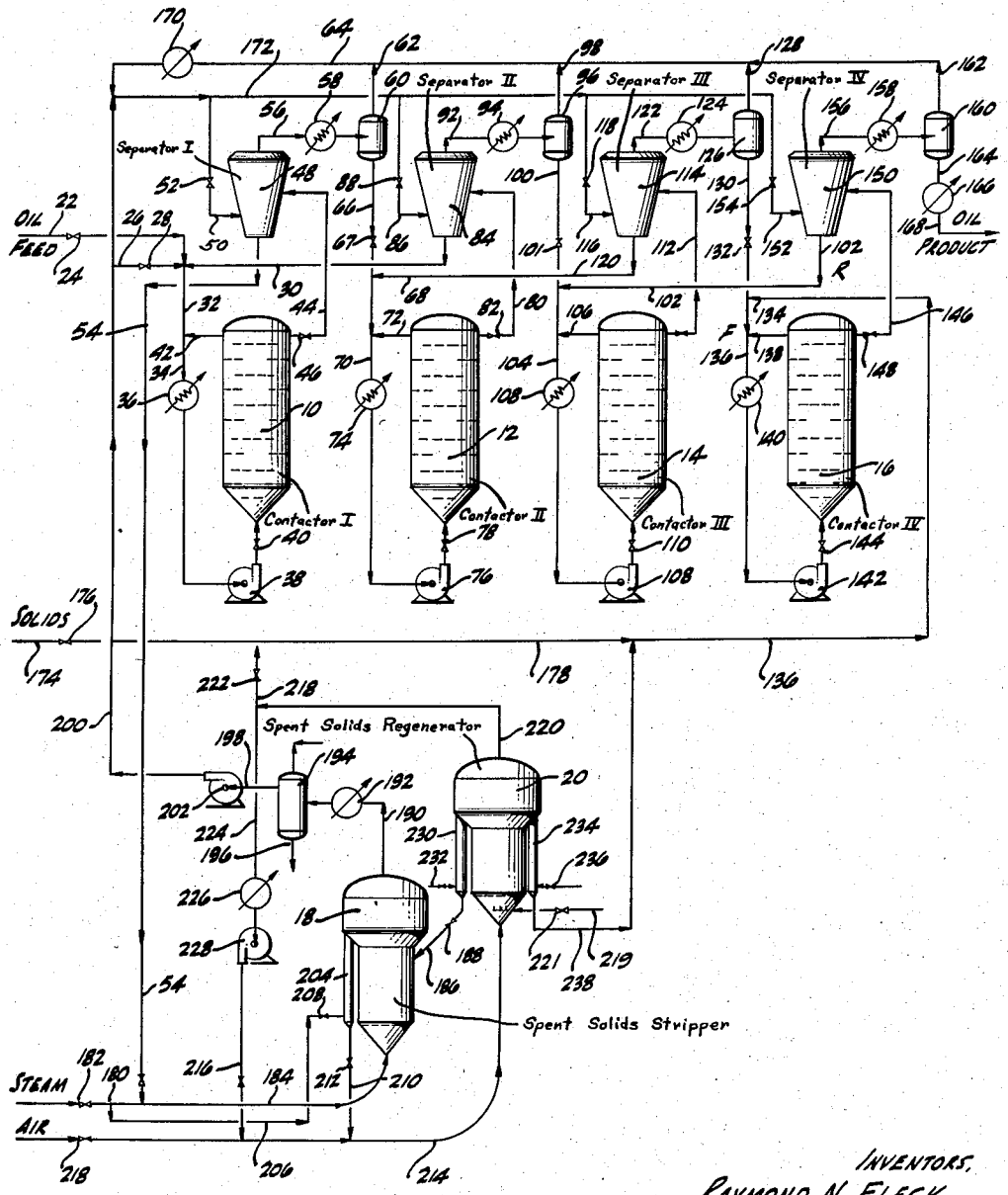
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REMOVAL OF ORGANIC NITROGEN COMPOUNDS FROM HYDROCARBONS WITH A ZEOLITE

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REMOVAL OF ORGANIC NITROGEN COMPOUNDS FROM HYDROCARBONS WITH A ZEOLITE

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

Many crude petroleum streams contain considerable quantities of organic nitrogen compounds in addition to the principal hydrocarbon constituents. In some cases the incidence of these 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. Mexican and Venezuelan crudes have nitrogen contents ranging from about 0.2% to about 0.35% by weight. Extensive analyses 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 content runs as high as about 2.5% by weight.

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 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 reforming gasoline reforming system using a halide promoted catalyst, the nitrogen compounds appear to react with the catalyst or the promotor forming 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. Treatment of such materials with Fuller's earth tends to reduce the quantity of nitrogen compounds, but this involves a relatively high liquid yield loss through retention of hydrocarbons on the adsorbent. The nitrogen compounds are lost through disposal of the spent adsorbent, and seldom if ever is the nitrogen organic reduced sufficiently to avoid the above-mentioned problems in platinum catalyzed reforming.

The present invention is directed to a highly efficient and improved process for removing the basic organic and non-basic nitrogen compounds from petroleum, coal tar, and shale oil crudes, distillates, and other fractions.

It is a primary object of this invention to provide an improved process for the denitrogenation of hydrocarbons contaminated with organic nitrogen compounds.

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

It is another object of this invention to denitrogenate hydrocarbon streams contaminated with organic nitrogen compounds by contacting such streams with a solid metallo alumino silicate having substantially uniform pores of at least 7 A. in diameter, separating the hydrocarbons from the solids as a process product, washing the spent solids with a solvent to recover residual quantities of hydrocarbons, regenerating the silicate solids by means of an oxygen-containing gas, and recirculating the regenerated solids in the process.

It is a further object of this invention to provide a plurality of contact stages in the process as defined in the foregoing objects.

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 organic nitrogen compounds, and derived from virtually any source to remove such compounds and produce a hydrocarbon stream having a substantially reduced nitrogen analysis. In general the process consists in contacting the hydrocarbon feed mixed with organic nitrogen compounds with a granular solid natural or synthetic metallo alumino silicate zeolite. 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 first treated to separate occluded hydrocarbons. This may be done by heating with or without stripping, by solvent extraction, by light solvent washing, and the like. This material is then regenerated by air oxidation whereby the adsorbed organic nitrogen com-

pounds are burned, leaving the metallo alumino silicate free of these materials and in condition to treat additional feed. The regenerated material is then re-employed to contact further quantities of the contaminated feedstock.

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 slurry or fluidized contacts in the liquid or vapor phases, respectively. 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. In the liquid phase, a slurry is formed and agitated in each contact zone.

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 slurry or 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 feedstock 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. It has been found that the 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 $5Na_2O \cdot 6Al_2O_3 \cdot 15SiO_2$. 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 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. These materials are all zeolites and their sodium and calcium derivatives are very stable solids which apparently have "pores" active for denitrogenation 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 denitrogenation effects on the organic nitrogen compounds 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 will be more readily understood by reference to the accompanying drawing which shows a process flow diagram of this invention using a series of four contact stages. It should be understood however that more or fewer contact stages may in certain instances be required depending upon the composition of the feedstock and the desired extent to which the nitrogen content is to be reduced. The drawing description is conducted in terms of a specific example of the process of this invention applied in the denitrogenation of a full range hydrogenated shale oil coker distillate. The properties of the feedstock are given in Table 1.

TABLE 1

Feedstock properties

Boiling range, ° F.: Temperature—	Volume percent
120	2.2
120–400	36.1
400–500	21.4
500–600	18.8
600+	21.5
	100.0
Gravity, ° API	41.2
Nitrogen, wt. percent (Kjeldahl)	0.160

Referring now to the drawing, the essential equipment items required in the process are first, second, third, and fourth contactors **10**, **12**, **14**, and **16**. These contactors are of the internally baffled mixing vessel type through which a slurry of the oil to be treated and the silicate solids are recirculated in suspension. Other major equipment items include spent solids stripper **18** and stripped solids regenerator **20**.

The feedstock is introduced at a rate of 5,000 barrels per day through line **22** controlled by valve **24**. If desired, a diluent solvent may be introduced through line **26** controlled by valve **28**. Such diluent is not necessary with the present feedstock, but is highly desirable with heavier feeds such as coker distillate bottoms and other heavy oils. This feed stream is mixed with the silicate adsorbent flowing through line **30** at a rate of 115 tons per day and the mixture passes through line **32** into first contactor recycle line **34**. This material passes through first contactor heater **36** which serves to heat the feed and maintain the slurry during the contact at about 248° F. The slurry is recirculated by means of pump **38** at a rate of 25,000 barrels per day by means of valve **40** upwardly into and through first contactor **10** from which it overflows through line **42**, and is recycled.

The first stage effluent is removed from first contactor **10** through line **44** at a rate controlled by valve **46** and is introduced into first effluent separator **48**. In the drawing this is indicated as a centrifuge although conventional settlers and thickeners commonly used for this purpose may be substituted. The centrifuge indicated is preferred because of high throughput relative to the small physical size of the equipment. In separator **48** the spent solids are separated from the oil, they are washed by means of normal pentane or other light solvent introduced at a rate of 500 barrels per day controlled by valve **52**. Solvent-to-solids ratios of between about 1.0 and about 10.0 barrels per ton may be used. The spent washed solids saturated with pentane are removed through line **54** and are treated as hereinafter described. The solvent and solids-free oil are removed from separator **48** through line **56** and pass through solvent vaporizer **58** into separator **60**. The solvent is re-

moved therefrom as a vapor through line **62** and passes into solvent recycle manifold **64**. The first stage effluent oil flows through line **66** at a rate of about 4971 barrels per day and analyzing 0.113 weight percent nitrogen.

In the second stage of the process this effluent is combined with 115 tons per day of silicate adsorbent flowing through line **68** and is introduced through second contactor recycle line **70**. It is herein mixed with the overflow or second contactor recycle stream flowing through line **72**. It is reheated to a temperature of about 248° F. in recycle heater **74** and is recirculated through the contactor at a rate of about 24,855 barrels per day by means of recycle pump **76** controlled by valve **78**. The second contactor effluent is removed through line **80** at a rate controlled by valve **82** and enters second separator **84**. Again the spent solids are separated from the oil, are washed with pentane at a rate of 500 barrels per day introduced through line **86** at a rate controlled by valve **88**, and the washed solids are passed through line **30** at a rate of 115 tons per day into the first contactor **10** in the manner described. The solvent and oil mixture is removed from second separator **84** through line **92**, is passed through solvent vaporizer **94** and introduced into second vapor liquid separator **96**. The evolved solvent vapor flows through line **98** into the recycle solvent manifold **64**. The second stage hydrocarbon effluent flows through line **100** and valve **101** at a rate of about 4927 barrels per day and analyzes 0.044% nitrogen by weight (Kjeldahl).

The second stage effluent oil comprises the feed to the third contactor **14**. It is mixed with 115 tons per day of silicate adsorbent flowing through line **102** and this mixture is introduced into third contactor recycle line **104** together with third contactor overflow passing through line **106**. The mixture flows through third recycle heater **108** and is recirculated through third contactor **14** by means of third recycle pump **108** at a rate of about 24,635 barrels per day controlled by valve **110**. Slurry from the third contacting zone **14** is passed through line **112** into third separator **114**. The spent solids are washed free of occluded oil as before by means of 500 barrels per day of pentane introduced through line **116** at a rate controlled by valve **118**. The washed solids are removed through line **120** and constitute the feed solids to the second contacting zone **12**. The solvent and oil mixture is removed from third separator **114** through line **122**, and is heated in heater **124**, and the mixture is introduced into the third vapor separator **126**. Vaporized pentane flows into manifold **64** through line **128** and the effluent oil from the third contacting zone is removed therefrom through line **130** at a rate controlled by valve **132**. This oil flows at a rate of about 4900 barrels per day and has a nitrogen analysis of 0.003 weight percent nitrogen (Kjeldahl).

This oil constitutes the feed to the fourth contacting stage and it is mixed with 115 tons per day of regenerated silicate adsorbent flowing through line **134**. This slurry is introduced into fourth contacting zone recycle line **136** into admixture with the fourth contacting zone overflow which passes through line **138**. This mixture is reheated in fourth contacting heater **140** and is recirculated at a rate of about 24,500 barrels per day by means of pump **142** controlled by valve **144**. The oil and solids slurry from the fourth contacting zone is removed therefrom through line **146** at a rate controlled by valve **148** and is introduced into fourth separator **150**. The spent solids are again washed with pentane flowing through line **152** at a rate of about 500 barrels per day controlled by valve **154**. The washed solids are passed by means of line **102** and constitute the feed solids to the third contacting stage. The solvent and oil mixture is removed from separator **150** through line **156**, the pentane is vaporized in heater **158**, and the vaporized pentane is separated from the oil in fourth vapor liquid separator **160**. The solvent vapor is introduced into manifold **64** by means of line **162**. The oil product flows through line **164** through cooler **166** and is sent to further processing or storage facilities, not shown, through line **168** at a rate of 4899 barrels per day. This oil stream analyzes 0.0005 weight percent nitrogen (Kjeldahl).

The normal pentane solvent vaporized from each of the solvent-oil mixtures passes from manifold **64** through solvent condenser **170** and is recirculated as wash liquid through liquid solvent manifold **172** to each of the four separators.

Invariably a small quantity of the adsorbent is lost in the system through the formation of fines and otherwise. Accordingly makeup metallo alumino silicate is introduced through line **174** at a rate of about 200 pounds per day controlled by valve **176**. These solids are passed through line **178** into admixture with regenerated silicate solids flowing through line **136**.

Completely spent solids are removed from first separator **48** and flow through line **54** as previously indicated. These solids are introduced into a flow of inert gas such as steam flowing through line **180** at a rate controlled by valve **182**. A suspension of solids is thus formed which passes continuously through line **184** and is introduced upwardly into the bottom of solvent vaporizer **18**. Hot regenerated adsorbent at a temperature of about 1050° F. maximum is introduced into solvent vaporizer **18** at a rate of 115 tons per day through line **186** controlled by valve **188**. This serves to raise the temperature of the spent silicate adsorbent to a temperature of about 650° F. The rate of steam introduction is controlled relative to the size of the solids and the cross sectional area of solvent vaporizer **18** so that a fluidized suspension of solids is maintained in vaporizer **18**. With the aid of the steam and the increase in temperature, the pentane solvent is vaporized completely from the solids and the vapor leaves through line **190**. This material is condensed in condenser **192** and is introduced into vapor liquid separator **194**. Steam condensate is removed from the bottom of the separator through line **196** and the recovered solvent is decanted from the upper part of separator **196**, and is passed through lines **198** and **200** to liquid solvent manifold **172** by means of pump **202**. Stripped solids collect in drawoff line **204**, are purged of traces of pentane vapor by means of steam introduced through line **206** at a rate controlled by valve **208**, and the stripped spent solids are removed from solvent vaporizer **18** through line **210** at a rate of 230 tons per day controlled by valve **121**.

The stripped spent solids are suspended in line **214** in a mixture of recirculated flue gas flowing through line **216** and fresh air introduced into line **214** at a rate controlled by valve **218** sufficient to maintain a regeneration temperature in regenerator **20** not exceeding about 1100° F. The suspension is passed upwardly into regenerator **20** and again the rate is controlled so as to maintain therein a fluidized suspension of the solids. The organic nitrogen compounds present in the solids are burned from the spent silicate adsorbent by means of the air. Additional fuel, if needed to maintain the elevated regeneration temperature, may be added through line **219** at a rate controlled by valve **221**. Flue gas flows from the top of regenerator **20** through line **220**, and a portion thereof is vented to the atmosphere through line **218** at a rate controlled by valve **222**. The remainder is recirculated in the regenerator for purposes of temperature control and this material passes through line **224** through recycle gas cooler **226** wherein its temperature is reduced to about 750° F. This cooled gas is recirculated by means of blower **228** through line **216** to line **214** into which air is added as previously indicated.

Hot regenerated silicate adsorbent is drawn off from regeneration zone **20** through standpipe **230**. A stripping or seal gas, such as steam, is introduced into the bottom

of the standpipe by means of line 232 serving to prevent traces of flue gas from flowing into the solvent vaporizer 18 via line 186.

Through standpipe 234, into which a seal gas such as steam is introduced through line 236 for the same purpose as before, are removed 115 tons per day of regenerated silicate adsorbent. These materials are passed through line 238 into combination with fresh solids introduced through line 178. The mixture of solids is recirculated in the process through line 136 as described.

In the foregoing example the metallo alumino silicate adsorbent had a composition corresponding to

$$5Na_2O \cdot 6Al_2O_3 \cdot 15SiO_2$$

and had substantially uniform pores of about 13 A. in diameter. Substantially equivalent results are obtained when using other metallo alumino silicates having pores approximating 10 A. in diameter. It is required for effective denitrogenation that these pores have diameter of at least 7 A. for it has been determined that substantially no effective denitrogenation results with these metallo alumino silicates when the pores are 4 or 5 A. in diameter.

In the foregoing process, four contact stages were employed. This number is seen to be sufficient to reduce the nitrogen analysis from 0.160 weight percent to 0.0005% or 5 p.p.m. In those situations where it is not necessary that the product oil have such a low nitrogen analysis or in which the feedstock does not have such a high nitrogen analysis, then fewer than four contact stages may be employed. It is obvious from the previous description the manner in which more or fewer than four contact stages would be employed. In the event that a single contact stage is sufficient, the oil feed indicated as in the drawing as being introduced through line 22, may be introduced instead into the single contacting zone at point F indicated in the drawing at line 138. Spent washed silicate adsorbent is removed from separator 150 at point R at line 102 and introduced into the solvent vaporizer 18 in the same manner. Recycled regenerated solids are introduced into the system at the same points shown. In this single stage modification, the first, second, and third contacting zones, and the associated elements are not necessary and may be eliminated.

The process of this invention is readily applicable in the denitrogenation of very heavy oil feeds contaminated with organic nitrogen compounds. In the preliminary distillation of cracking stock fed to a fluid catalytic cracking unit, approximately 9.5% by volume of a heavy bottoms material is produced. This material has an initial boiling point of 715° F., the end point being unknown since cracking begins at about 850° F. The API gravity is 33°. The nitrogen analysis (Kjeldahl) is 0.198%. This material was diluted with an equal volume of toluene. This 50–50 mixture was contacted in a single contacting stage with 105 pounds of 10 A. metallo alumino silicate solids per barrel of oil-solvent mixture. The contacting temperature was maintained at about 248° F. The product oil after separation of the solvent analyzed 0.068% by weight nitrogen (Kjeldahl). This constitutes a 66% removal of the organic nitrogen compounds in a single contacting stage. In those cases where lower nitrogen analysis is desirable in the subsequent use of the feedstock, additional contacting stages are readily utilized to the point that substantially complete removal of nitrogen compounds is effected if necessary.

In the foregoing example in which toluene was used as a diluent, and in the description of the drawing in which pentane was used to wash spent solids and as a diluent if required, in each case the solvent employed was a relatively low boiling hydrocarbon solvent. Preferably, the solvent should have a boiling point or range which is substantially below the initial boiling point of the hydrocarbon being treated for denitrogenation. Aromatic, paraffinic, naphthenic, or olefinic hydrocarbon solvents may be employed. Hydrocarbon solvents are preferred since they are highly compatible with virtually every hydrocarbon feedstock treated according to the present invention. In some cases other organic solvents may be substituted such as the alcohols, liquid aldehydes, ketones, and the like.

The process of the present invention is particularly applicable to the denitrogenation of the hydrocarbons in the gasoline boiling range. The removal of organic nitrogen compounds 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.

A gasoline feedstock intended for catalytic dehydroaromatization had a nitrogen analysis of 9.7 p.p.m. This material was treated in the process according to the present invention to reduce the nitrogen content to levels sufficient to avoid detrimental effects in the subsequent treatment. The feedstock was contacted in the vapor phase in a single contacting stage with the 13 A. metallo alumino silicate at a liquid hourly space velocity of 14 volumes per volume per hour. The temperature was 425° F. The product oil analyzed 0.5 p.p.m. of nitrogen.

It has been found that in the embodiment of the process of this invention in which the denitrogenation is conducted in the liquid phase, contacting temperatures on the order of 80° F. are adequate to effect a substantial degree of denitrogenation. It has been found also that at higher temperatures the rate of denitrogenation is considerably higher as indicated by the lower nitrogen analyses of the products, particularly in the liquid phase with fairly heavy feedstocks. Preferred contacting temperatures are from about 80° F. to about 500° F. It should be understood that the process of the present invention may likewise be applied with fine or powdered solids in the vapor phase, exactly as was done in the vaporization of solvent and in the regeneration of spent solids in the description of the drawing. A certain amount of multi-stage contacting may be obtained in this manner, although it is more readily obtained using a pluraltiy of fluidized contacts.

The solids-fluid contact may also be conducted using a static bed of the metallo alumino silicate, and if desired a moving solids bed may be employed with countercurrent fluid flow so that a greater plurality of contact stages may be obtained. These contacts may also be effected in either the vapor or liquid phase. 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 adsorbent. 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 nonvaporizable. 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. A process for the denitrogenation of a normally liquid hydrocarbon mixture derived from a material selected from the class consisting of petroleum, shale oil and coal tar oil, said mixture being contaminated with normally incident organic nitrogen compounds of substantially the same boiling range, which process comprises contacting said mixture with a solid partially dehydrated zeolitic metallo alumino silicate adsorbent having substantially uniform pores at least 7 A. in diameter, thereby sorbing said organic nitrogen compounds; separating a hydrocarbon mixture of reduced nitrogen content from the adsorbent; and contacting the adsorbent containing sorbed nitrogen compounds with an oxygen-containing gas while controlling the temperature at values below about 1100° F. sufficient to burn said sorbed nitrogen compounds therefrom and regenerate said adsorbent.

2. A process according to claim 1 wherein the said contacting step is carried out at a temperature between about 80° F. and about 500° F.

3. A process according to claim 1 in combination with the steps of diluting said hydrocarbon mixture with a light hydrocarbon solvent boiling below the initial boiling point of said mixture, and separating the said solvent from said hydrocarbon effluent.

4. A process according to claim 1 wherein said metallo alumino silicate has a composition corresponding substantially to $5Na_2O \cdot 6Al_2O_3 \cdot 15SiO_2$ and has pores of about 13 A. in diameter.

5. A process according to claim 1 wherein said hydrocarbon mixture is a petroleum hydrocarbon distillate.

6. A process according to claim 1 wherein said hydrocarbon mixture is derived from shale oil.

7. A process for the denitrogenation of a normally liquid hydrocarbon mixture derived from a material selected from the class consisting of petroleum, shale oil, and coal tar oil, said mixture being contaminated with normally incident organic nitrogen compounds of substantially the same boiling range, which process comprises establishing a plurality of serially connected contacting zones; maintaining within each of said contacting zones a bed of a solid partially dehydrated zeolitic metallo alumino silicate adsorbent having substantially uniform pores at least 7 A. in diameter; passing said hydrocarbon mixture into the first of said contacting zones and thence through the remaining of said contacting zones in series, whereby said mixture is brought into intimate contact with the adsorbent contained in each of said zones and the said nitrogen compounds are sorbed on said adsorbent; passing said adsorbent through said contacting zones in series counter-current to the flow of said hydrocarbon mixture; withdrawing from the last of said contacting zones a hydrocarbon mixture of substantially reduced nitrogen content; withdrawing adsorbent containing sorbed nitrogen compounds from the first of said contacting zones; contacting said adsorbent containing sorbed nitrogen compounds with an oxygen-containing gas at a temperature below about 1100° F. sufficient to burn said sorbed nitrogen compounds from said adsorbent and regenerate the same; and recirculating said regenerated adsorbent to the last of said contacting zones to complete the circulation of adsorbent.

8. A process according to claim 7 in combination with the steps of circulating a liquid slurry of said adsorbent in the hydrocarbon mixture in each contacting zone, and heating the recirculating stream to maintain a contacting temperature between about 80° F. and about 500° F.

9. A process according to claim 8 in combination with the step of removing a slurry stream from each contacting zone, introducing it into a communicating solids-fluid separator zone, and separating the solid adsorbent from said hydrocarbon therein.

10. A process according to claim 9 in combination with the step of applying centrifugal forces to said solid adsorbent during separation of the same from said hydrocarbon.

11. A process according to claim 9 in combination with the steps of washing said solid adsorbent with a low boiling solvent to remove occluded hydrocarbon therefrom, heating the effluent from each of said separator zones to vaporize said low boiling solvent, and separating the solvent vapor from said hydrocarbon.

12. A process according to claim 11 in combination with the steps of passing the solvent-washed spent adsorbent into a vaporizor zone, and heating said adsorbent therein to vaporize solvent therefrom prior to passing said adsorbent into contact with the oxygen-containing regeneration gas.

13. A process according to claim 12 in combination with the steps of maintaining a fluidized body of said spent adsorbent in said vaporizor zone, maintaining a fluidized body of said silicate solids in a regeneration zone during contact with the oxygen-containing gas, and recirculating a sufficient amount of hot regenerated adsorbent from said regeneration zone to said vaporizer zone to heat said spent adsorbent and vaporize said solvent therefrom.

14. A process according to claim 13 wherein said adsorbent in said vaporizer zone is maintained in the fluidized state by controlling the upward velocity of steam therethrough.

15. A process according to claim 7 wherein said metallo alumino silicate has a composition corresponding substantially to $5Na_2O \cdot 6Al_2O_3 \cdot 15SiO_2$ and has substantially uniform pores of about 13 A. in diameter.

16. A process for the denitrogenation of a normally liquid hydrocarbon mixture derived from a material selected from the class consisting of petroleum, shale oil, and coal tar oil, said mixture being contaminated with normally incident organic nitrogen compounds of substantially the same boiling range, which process comprises passing said hydrocarbon mixture through a plurality of solid-fluid contacting zones, contacting said mixture therein with a partially dehydrated zeolitic solid metallo alumino silicate adsorbent having substantially uniform pores of at least 7 A. in diameter to sorb the said organic nitrogen compounds and produce a hydrocarbon product of substantially reduced nitrogen content, and spent adsorbent, removing occluded hydrocarbon from said spent adsorbent, regenerating said adsorbent by contact with an oxygen-containing gas to burn said organic nitrogen compounds therefrom, and contacting additional hydrocarbon mixture with the regenerated adsorbent.

17. A process according to claim 16 wherein said mixture contacts said metallo alumino silicate in the vapor phase.

18. A process according to claim 16 wherein said mixture contacts said metallo alumino silicate in the liquid phase.

19. A process according to claim 16 in combination with the steps of circulating a liquid slurry of said hydrocarbon mixture and said metallo alumino silicate adsorbent through each of the contacting zones, flowing a slurry stream from each contacting zone into a centrifugal separator zone, contacting said adsorbent separated therein with a low boiling hydrocarbon solvent obtain extracted adsorbent and a solvent-hydrocarbon mixture, separating and recycling the solvent leaving a hydrocar-

bon effluent of reduced nitrogen content, introducing the extracted adsorbent from all but the first separator zone into the previous contacting zone, introducing the hydrocarbon effluent from all but the last separator zone into the subsequent contacting zone, producing the hydrocarbon effluent from the last separator zone as said hydrocarbon product of substantially reduced nitrogen content, introducing the extracted adsorbent from the first separator zone into a solvent vaporizer zone, heating and stripping said extracted adsorbent therein to separate residual solvent from the adsorbent, recycling the recovered solvent, introducing the stripped adsorbent into a regeneration zone wherein the adsorbent is contacted with said oxygen-containing gas, controlling the temperatures therein below about 1100° F. to burn sorbed organic nitrogen compounds therefrom forming regenerated solids, said regenerated adsorbent being introduced into the last contacting zone completing the adsorbent cycle.

20. The process for denitrogenating a normally liquid hydrocarbon feed mixture derived from a material selected from the class consisting of petroleum, shale oil, and coal tar oil, said feed mixture being contaminated with normally incident organic nitrogen compounds of substantially the same boiling range, which process comprises introducing said feed mixture into a contacting zone and therein contacting it with a solid partially dehydrated zeolitic metallo alumino silicate molecular sieve adsorbent having substantially uniform pores at least 7

A. in diameter, whereby said organic nitrogen compounds are sorbed; and withdrawing from said contacting zone a hydrocarbon product mixture having an organic nitrogen compound content substantially lower than that of said hydrocarbon feed mixture.

21. A process as defined by claim 20 wherein said feed mixture is contacted with said adsorbent while in the vapor phase.

22. A process as defined by claim 20 wherein said feed mixture is contacted with said adsorbent while in the liquid phase.

23. A process as defined by claim 20 wherein said hydrocarbon feed mixture is a petroleum hydrocarbon mixture of the gasoline boiling range.

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