Feb. 16, 1960 R. N. FLECK ET AL 2,925,379

HYDROCARBON DENITROGENATION

Filed Nov. 13, 1956 2 Sheets-Sheet 1

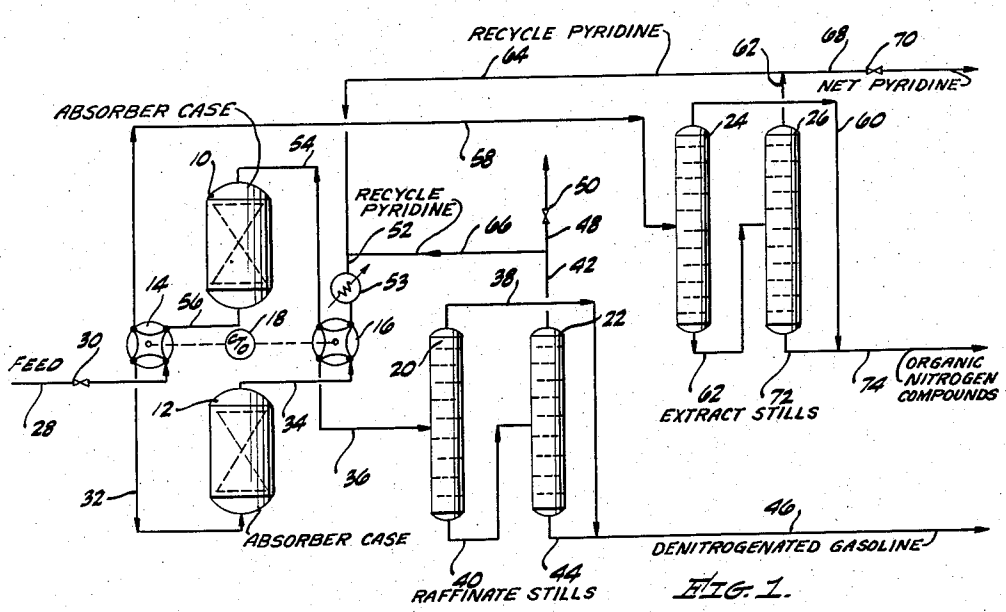


FIG. 1.

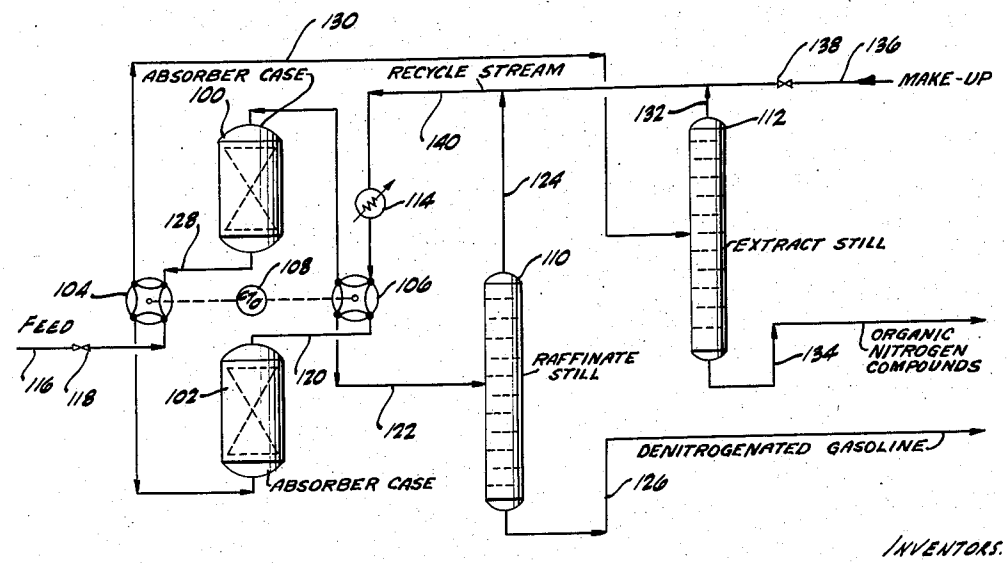


FIG. 2.

INVENTORS.
RAYMOND N. FLECK,
CARLYLE G. WIGHT,
BY
ATTORNEY.

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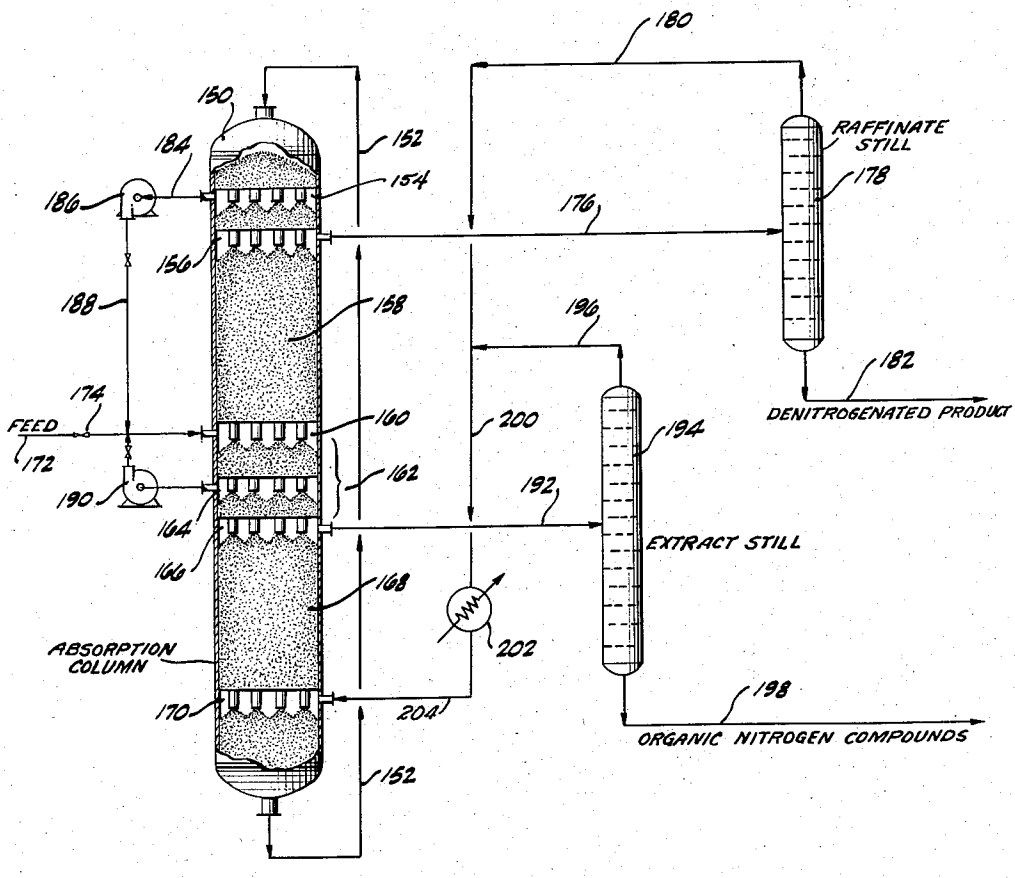


FIG. 3.

INVENTORS.
RAYMOND N. FLECK,
CARLYLE G. WIGHT,

BY

ATTORNEY.

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HYDROCARBON DENITROGENATION

Raymond N. Fleck, Whittier, and Carlyle G. Wight, Fullerton, Calif., assignors to Union Oil Company of California, Los Angeles, Calif., a corporation of California

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15 Claims. (Cl. 208—254)

This invention relates to the refining of hydrocarbons, particularly those contaminated with normally incident organic nitrogen compounds. Such hydrocarbons include those which are produced as petroleum, as well 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 nitrogen compounds in addition to the principal hydrocarbon constituents. In some cases the incidence of these nitrogen compounds is sufficient that the nitrogen content runs as high as 1.0% by weight. California crude oils in many cases contain 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, the di, tri, and tetra alkylated quinolines and alkylated pyridines commonly occur in California kerosene distillates. 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, a well defined adverse effect on such processes as catalytic cracking, catalytic isomerization, and catalytic reforming, particularly platinum catalyzed halide promoted reforming. The nitrogen compounds appear to be adsorbed on the catalyst and selectively deactivate its active cracking centers. In catalytic cracking, for example, the gasoline yield may be reduced as much as 50% by reason of the presence of sufficient organic nitrogen compounds to give the feed a nitrogen content of about 0.3% by weight, and reduced by 75% when the nitrogen content reaches about 0.45%. Platinum catalyzed reforming and other reforming processes in general are also adversely affected by the presence of nitrogen compounds in the feed. In a platinum catalyzed gasoline reforming system using a halide promoted platinum catalyst the nitrogen compounds appear to react with the catalyst 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 most all 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 analysis reduced sufficiently to avoid platinum reforming catalyst poisoning.

The present invention is directed to a highly efficient and improved process for removing and recovering the basic and nonbasic 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 hydrocarbon compounds contaminated with nitrogen.

It is a more specific object of this invention to denitrogenate hydrocarbons through contact with a solid contact material which exhibits specific adsorption properties for nitrogen compounds in preference to hydrocarbons of the same boiling range, which process includes a step conducted at substantially the same temperature as the hydrocarbon contact and in which the organic nitrogen compounds are displaced by and exchanged for different organic nitrogen compounds which is separable by distillation from not only the displaced nitrogen compounds but also the unadsorbed hydrocarbons.

It is a more specific object of this invention to provide for hydrocarbon denitrogenation through contact with a metallo alumino silicate adsorbent of a specific type to produce a nitrogen-free hydrocarbon, displacement of the adsorbed nitrogen compounds isothermally by means of nitrogen compounds of different boiling range, the distillation of the adsorption effluent and of the displacement exchange effluent to produce a hydrocarbon stream substantially free of nitrogen compounds and a hydrocarbon-free stream containing the nitrogen compounds, and recycling a selected fraction of the organic nitrogen compounds in the process as a displacement exchange stream.

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 denitrogenation process for treating hydrocarbon streams derived from virtually any source and which are contaminated with organic nitrogen compounds. The process consists of a combination of cyclic contact of the feed stream and a recycled displacement exchange stream with a granular solid zeolitic metallo alumino silicate contact material, more precisely defined and described below. The effluent fluids from these contacts are fractionated separately whereby the organic nitrogen compounds are separated from the feed stream and recovered as a product of the process in their original form. The present invention will be described in connection with the denitrogenation of various shale oil fractions whose

nitrogen content is particularly high and which present probably the most difficult feed streams to denitrogenate completely. The process is equally applicable to the complete denitrogenation of various petroleum and coal tar oil hydrocarbon streams containing nitrogen compounds.

The feed mixture is first passed through contact with a compact bed of the granular solid metallo alumino silicate which retains the organic nitrogen compounds leaving the hydrocarbon constituents substantially unaffected as an effluent or raffinate phase. Instead of heating the spent contact material and attempting to strip it with a fluid such as steam as in the conventional adsorptive fractionation processes, the spent contact material is then contacted with a recycled displacement exchange stream comprising selected organic nitrogen compounds whose boiling point or boiling range is such that they are readily fractionated as by distillation from the displaced nitrogen compounds and from the raffinate. During this contact an active displacement exchange takes place in the presence of the contact material whereby the organic nitrogen compounds present on the contact material are displaced by and exchanged for the recycled organic nitrogen compounds which are retained on the contact material. This displacement exchange contact is preferably conducted at substantially the same temperature and pressure as the contact with the feed stream. There is produced by this displacement exchange an extract or displacement exchange effluent stream which comprises a mixture of the displaced organic nitrogen compounds and part of the selected displacement exchange nitrogen compounds, the remainder being retained by the adsorbent leaving it saturated with the selected organic nitrogen compounds which are recycled in the process. The extract stream is then fractionated as by distillation to recover the recycle component from the organic nitrogen compounds displaced from the metallo alumino silicate. The material is then contacted, repeating a cyclic process, with the feedstock to remove therefrom the organic nitrogen compounds referred to above. During this feed contact and continuing through the process, a reverse displacement exchange occurs in which the organic nitrogen compounds present in the feedstock displace and are exchanged for the selected organic nitrogen compounds recycled as the displacement exchange stream in the process and which is present on the metallo alumino silicate. The raffinate thus contains the displaced recycled component or components and is separated therefrom for recycle in the process.

The recycle stream employed in the process of this invention for displacement exchange of the organic nitrogen compounds accumulated from the feedstock on the metallo alumino silicate may be a mixture of selected organic nitrogen compounds or a single pure compound of this type. Further, the selected material or materials for recycle may be the same as one which occurs in the feedstock or may be different therefrom. The recirculated material however must have a boiling point or boiling range, or another physical property, relative to that of the feedstock so that it is readily and economically separable from both the raffinate and extract streams. In this process both the raffinate and extract streams contain recycled displacement exchange nitrogen compounds, each of these streams is separately fractionated, as by distillation preferably, and the displacement exchange components so recovered are recirculated.

This fractionation produces a substantially nitrogen-free hydrocarbon stream and a substantially hydrocarbon-free nitrogen compound stream as separate process products. The nitrogen compound stream may be disposed of if necessary, but it constitutes a desirable concentrated stream of organic nitrogen compounds suitable for further purification or as feed material to various chemical synthesis processes well known to those skilled in organic chemistry. The nitrogen-free hydrocarbon stream is suitable as feedstock to the various hydrocarbon refining and conversion processes well known to those skilled in those arts and which avoids therefore the catalyst poisoning referred to previously. If the boiling range and chemical constituents of the feed material are properly selected this hydrocarbon stream may constitute as such a suitable solvent which is free of the odor and other problems mentioned.

The adsorbent employed in the process of this invention is a solid granular material having a mesh size range between about 2 and 100 mesh or smaller and preferably between about 4 and about 30 mesh for static or moving solids bed contact. It is used in the form of a dense compact bed of material through which the feed and displacement and exchange recycle streams pass, either in the vapor phase or in the liquid phase. The process may employ the adsorbent in the form of a single static bed of material in which case the process is only semi-continuous. Preferably a plurality of two or more static beds of adsorbent are employed with appropriate remotely operable valving so that the feed stream is passed through one or more of the contacting vessels in a set while the exchange displacement 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. When the granular solids are sufficiently rugged physically then the moving solids bed modification may be employed in which flow of feed is maintained continuously through a first contacting or adsorption zone, the flow of displacement exchange fluid is maintained continuously through a second contacting or displacement exchange zone, and the granular adsorbent is recirculated successively through these two zones. With the smaller sized mesh ranges of adsorbent, the material may be fluidized in and by the fluid streams contacting it, although the compact bed modifications are preferred since a greater number of theoretical and actual contact stages are more readily obtained in smaller and simpler equipment.

The present invention may not be carried out with the commonly available solid granular adsorbents. It has been found that particular adsorbents which are highly efficient and preferred in the hydrocarbon denitrogenation process of the present invention are the natural or synthetic zeolitic crystalline partially dehydrated metallo alumino silicates. 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 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 and thereby change the pore size. For purposes of denitrogenation of hydrocarbon mixtures in the process of this invention, the pore size must be at least 7 A. The metallo alumino silicates having such pore sizes exert preferential adsorptive forces for organic nitrogen compounds in great preference to the hydrocarbons of the same boiling range.

The synthetic crystalline partially dehydrated metallo alumino silicate zeolitic adsorbents 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 of 10 A. and 13 A. respectively.

In the process of this invention the solid contact material utilized for the hydrocarbon denitrogenation appears to be deactivated only very slowly. Ultimately in a long continued process the material may require regeneration due to the accumulation on the material of traces of very high molecular weight hydrocarbonaceous materials

present in the feed stream. Since the temperature at which the feed contact and the displacement exchange contact is relatively low, little if any chemical reaction ordinarily occurs in contact with the material. The accumulated deactivating materials may be removed from the metallo alumino silicate by heating to temperatures of the order of those customarily employed in the oxidative regeneration of spent hydrocarbon conversion catalysts and passing a dilute oxygen-containing stream in contact therewith. Regeneration may also be effected by stripping with steam followed by contact at this temperature with an anhydrous gas.

The process of this invention and the various modifications and applications thereof, as well as several forms of the apparatus in which the process may be effected, will be more readily understood by reference to the accompanying drawings in which:

Figure 1 is a schematic flow diagram of the denitrogenation process of this invention employing a recycled displacement exchange organic nitrogen compound fraction which has a boiling range within the boiling range of the hydrocarbon feed stream to be treated,

Figure 2 illustrates a schematic flow sheet of the same process in which the displacement exchange stream has a boiling range below that of the feed stream, and

Figure 3 is a schematic flow diagram of the process of this invention in which a recirculating stream of the preferred contact material in the form of a downwardly moving dense solids bed is shown.

Referring now more particularly to Figure 1, the essential equipment elements of the process include adsorber cases **10** and **12** provided with four-way flow control valves **14** and **16** operated by cycle timer operator **18**, first and second raffinate distillation columns **20** and **22**, and first and second extract distillation columns **24** and **26**. Various pumps, valves, reboilers, and overhead condensers are conventional items and are not shown here for purposes of clarity of illustration. The description of Figure 1 will be conducted in the form of a specific example of the process of this invention applied to the denitrogenation of shale oil coker gasoline. The material is produced by retorting shale to yield crude shale oil followed by coking this material in any of the several conventional ways to produce a coker distillate, of which the gasoline fraction boiling between about 120° F. and about 400° F. comprises the feedstock in the present example. The nitrogen analysis of this coker gasoline is 0.8% by weight. The displacement exchange stream employed is pyridine having a boiling point of about 240° F.

The coker gasoline feed is introduced through line **28** at a rate controlled by valve **30** in the vapor phase at a temperature of about 403° F., just above the dew point of the feed. It passes through first control valve **14** and line **32** upwardly through adsorber case **12**. It contacts the static bed of metallo alumino silicate having pore diameters of the order of 10 A. and in which the organic nitrogen compounds are adsorbed. In this particular feedstock there appears to be few nitrogen compounds with boiling points below pyridine. The contact material, previously treated with the pyridine displacement exchange stream, retains the organic nitrogen compounds present in the feed stream while liberating by displacement exchange the pyridine present on the contact material. The raffinate comprising a gasoline stream, now freed of the original organic nitrogen compounds and containing the displaced pyridine, flows through line **34** provided with second control valve **16** and through line **36** into the raffinate distillation equipment.

The raffinate distillation equipment consists of first and second distillation columns connected to produce a heart cut. In first column **20** materials boiling below 240° F. are produced overhead as a vapor which flows through line **38**. This comprises light coker gasoline free of organic nitrogen compounds and of the displacement exchange pyridine. The pyridine passes from the bottom of first column **20** through line **40** into second distillation column **22** along with the heavy gasoline boiling above about 240° F. In second column **22** the pyridine vapor is taken overhead through line **42** and the nitrogen-free heavy gasoline is produced from the bottom thereof through line **44**. The light and heavy nitrogen-free gasolines may be produced as separate streams in the obvious manner, namely from the top of column **20** and the bottom of column **22**, or they may be combined as shown in Figure 1 to produce a full range gasoline which is sent through line **46** to storage or further processing facilities not shown. The pyridine overhead from second column **22** comprises part of the displacement exchange stream and this is returned by means subsequently described to treat the contact material. Since in this modification pyridine also occurs in the feedstock there is a net production of pyridine in the process which tends to accumulate in the displacement exchange stream. This material may be removed at a rate equivalent to the rate at which pyridine is fed to the system in the feed stream by removing it through line **48** at a rate controlled by valve **50**. It may be combined as desired with the oil-free organic nitrogen compounds separated in the process as described immediately below.

Simultaneously with the aforementioned contact of the feed stream with the 10 A. silicate, another mass of the same contact material present in adsorber case **10** is being contacted, preferably in the reverse flow direction from that of the feed stream passing through the contact material, with the stream of pyridine as the displacement exchange material. This stream is introduced through line **52** and vapor heater **53**, passes through second control valve **16** and through line **54** downwardly through the solid material in contacting vessel **10**. The purpose of heater **53** is to raise the temperature of the displacement exchange vapor if necessary from that of its distillation to approximately the same temperature as that at which the feed contacts the 10 A. metallo alumino silicate. In adsorber case **10** the active displacement exchange takes place in which pyridine accumulates on the 10 A. silicate in exchange for and displacing the organic nitrogen compounds previously accumulated while it was contacting the feed stream. An extract stream comprising a mixture of pyridine and the displaced organic nitrogen compounds flows out through line **56**, and first control valve **14**, and through line **58** to the first and second distillation columns **24** and **26** making up the extract distillation system. The distillation here is entirely analogous to that in the raffinate distillation step of the process. The extract is distilled to remove overhead any organic nitrogen compounds boiling below 240° F. and these materials are removed through line **60**. The displacement exchange pyridine and higher boiling organic nitrogen compounds are introduced from the bottom of column **24** through line **62** into column **26**. The pyridine which boils about 240° F. is taken overhead through line **62** and recirculated through line **64** into combination with the pyridine separated from the raffinate as previously described, which latter fraction flows through line **66**. The combined stream comprises the displacement exchange recycle stream introduced through line **52** as indicated above.

Optionally the net production of pyridine in the process may be removed from the overhead from column **26** through line **68** at a rate controlled by valve **70**. If desired, only a sufficient quantity of the pyridine present in the feed to second column **26** may be taken overhead so that the total quantity in combination with the material produced overhead from second raffinate distillation column **22** will produce the desired quantity of pyridine for displacement exchange. Then the net production of pyridine is taken from the system together with the

higher boiling organic nitrogen compounds from the bottom of column 26 through line 72. The nitrogen compounds boiling below pyridine flowing through line 60 and the compounds boiling above pyridine, and which may include some net production of pyridine flowing through line 72, may be produced as separate product streams or may be combined. In the latter case the combined free organic nitrogen compounds are produced from the system through line 74 and sent to storage or to further processing facilities not shown.

In the process described above in which a shale oil coker gasoline is denitrogenated, the denitrogenation efficiency is 99.7% and the denitrogenated gasoline contains 0.003 weight percent nitrogen (Kjeldahl).

The same process conducted at the same temperature but using a 13 A. silicate is applied to denitrogenate a hydrogenated shale oil coker gasoline analyzing 0.222 weight percent nitrogen (Kjeldahl). The displacement exchange stream is pyridine and the denitrogenation gasoline product analyzed less than 0.001 weight percent nitrogen (Kjeldahl). The denitrogenation efficiency is therefore somewhat above 99.6%.

Either of the foregoing processes may be effected with substantially the same denitrogenation efficiency employing any of the alkylated pyridines, such as the 2-, 3-, and 4-methyl pyridines boiling respectively at 264° F., 290° F., and 289° F. Of course when this substitution is made appropriate changes in the heart cutting points must be made when distilling the extract and raffinate.

The same process is repeated using ethylene diamine as the exchange stream. The 13 A. silicate saturated with ethylene diamine is contacted at atmospheric pressure and 405° F. with a stream of 120° F.–400° F. shale oil coker gasoline analyzing 0.961% by weight nitrogen. The feed gravity is 47.0° API. Of 423 volumes of feed introduced, 420 volumes of raffinate including displaced ethylene diamine are obtained. This is distilled to heart cut the ethylene diamine boiling at about 242° F. from the nitrogen-free oil. The silicate saturated with nitrogen compounds is then contacted with 71 volumes of ethylene diamine at the same conditions of temperature and pressure to produce 71 volumes of extract. This is also heart cut to separate the ethylene diamine from the nitrogen compounds displaced from the silicate, and the contacts are continued alternately. The raffinate contains 0.002% nitrogen by weight.

In the process of this invention as previously indicated, the preferred contact material is the metallo alumino silicate defined above having pore diameters of about 13 A. Other similar forms of this silicate are available having smaller pore sizes such as 5 A. material. The denitrogenation capacity of this latter contact material is considerably less than that of the 13 A. material when treating gasoline boiling range hydrocarbons. The following data indicate that the capacity is limited to less than 1.5% of that of the 13 A. materials when denitrogenating gasolines. The same hydrogenated shale oil coker distillate referred to above is contacted with metallo alumino silicate contact material having 5 A. pores at a temperature of 403° F. Analytical distillation of the denitrogenated gasoline indicates that although the lower boiling cuts contain 0.002 to 0.0092% nitrogen (Kjeldahl) succeeding cuts indicates substantially no nitrogen removal since the nitrogen content rapidly rises to 0.163 and 0.212 weight percent. The latter figure is substantially the same as that of the feed stream. For pyridine adsorption, the 5 A. material will adsorb 0.167 ml. per 100 grams whereas the 13 A. material adsorbs 13.3 ml. per 100 grams. Thus the 13 A. silicate adsorbent is preferred in the present invention since it has substantially greater adsorption capacity for the organic nitrogen compounds present in these feed streams than the 5 A. zeolite.

As a further example of the separation of nitrogen bases from gasoline boiling range materials and of the tenacity with which the 13 A. silicates adsorb and retain organic nitrogen compounds, the following data are given. A mixture of equal volumes of 95% normal octane having a refractive index of 1.3989 and of pyridine having refractive index of 1.509 is passed in the vapor phase at a temperature of about 280° F. over the 13 A. metallo alumino silicate. The raffinate product has a refractive index of 1.3992 indicating it is essentially pure normal octane. The raffinate is so completely purified of pyridine that no odor of the latter compound can be detected in the product.

Referring now more particularly to Figure 2, a somewhat modified process of the present invention is shown in which the selected displacement exchange material employed to remove organic nitrogen compounds from the contact material is selected so as to have a boiling point or boiling range which is different from that of the feed material. In such an instance the displacement exchange material is readily separated as an overhead or as a bottoms product from both the raffinate and extract streams. The description of Figure 2 is in the form of an example of the process applied to the denitrogenation of a light gasoline derived from petroleum and having a boiling range of from 120° F. to 300° F. The displacement exchange material selected in this application is isopropylamine having a boiling range of 91° F. to 92° F.

In Figure 2 the essential components of the apparatus include adsorber cases 100 and 102 provided with four-way control valves 104 and 106 operated remotely by cycle timer operator 108, raffinate distillation still 110, and extract still 112. Again for simplicity of illustration most of the conventional valves, pumps, reboilers, and overhead condensers have been omitted. Also provided is displacement exchange vapor reheater 114 provided for the same purpose as reheater 53 in Figure 1.

The light gasoline having a nitrogen analysis of 0.14% by weight (Kjeldahl) is introduced through line 116 at a rate controlled by valve 118 and passes upwardly in contact with the 13 A. metallo alumino silicate in adsorber case 102 in which the nitrogen compounds are exchanged for and displace the isopropylamine displacement exchange material present on the contact material. The denitrogenated light gasoline together with the displaced isopropylamine flows on through line 120, control valve 106, and line 122 into raffinate still 110. The overhead vapor from still 110 passing through line 124 consists of the isopropylamine whose boiling point is some 30° F. below the initial boiling point of the light gasoline feed. The bottoms product comprises the denitrogenated light gasoline and it is removed through line 126 to further processing facilities or storage facilities not shown. The nitrogen content of this light gasoline product is 0.0001% by weight indicating a nitrogen removal efficiency of 99.9%.

Simultaneously with this part of the process the 13 A. metallo alumino silicate in adsorber case 100 is being contacted with a downwardly moving stream of isopropylamine vapor at a temperature of about 405° F. A displacement exchange takes place in this vessel whereby the organic nitrogen compounds accumulated during contact of the solid material with the light gasoline in the previous step of the cycle, are displaced from the adsorbent in exchange with part of the isopropylamine in the displacement exchange recycle stream. The extract, comprising a mixture of the displaced nitrogen compounds and the recycle stream, passes through line 128, control valve 104, and line 130 into extract still 112. In this distillation column the isopropylamine having a boiling point of 91° F. to 92° F. is taken overhead through line 132 while the higher boiling organic nitrogen compounds originating in the light gasoline feed and having a boiling range between the limits given above for the gasoline feed are removed as a bottoms product through line 134. Any additional isopropyl-

amine for makeup necessary in the process introduced through line 136 controlled by valve 138.

The isopropylamine produced overhead from stills 110 and 112 is combined in line 140, substantially at the overhead temperatures of the two columns. This material is reheated in heater 114 to about 405° F. and it is used at this temperature for the displacement exchange contact.

In the foregoing example the isopropylamine may be substituted with normal propylamine, ethylamine, or methylamine. Methylamine boils at 20° F. and accordingly is suitable for displacement exchange of organic nitrogen compounds occurring in hydrocarbon streams boiling between about 40° F. and 200° F. Monoethylamine boils at about 63° F. and is suitable for displacement exchange of nitrogen compounds contained in light gasoline boiling between about 80° F. and 250° F. Normal propylamine has a boiling point of 120° F. and is suitable for displacement exchange of nitrogen compounds in light gasolines boiling between about 140° F. and 300° F.

As further examples of the application of the process of this invention as illustrated in Figure 2 above, the following data are given.

The process of Figure 2 is applied to the denitrogenation of heavy gasoline derived from petroleum, having a boiling range of 300° F. to 400° F., and having a nitrogen content of 0.1% by weight. Contacting this feed stream in the vapor phase with the 13 A. metallo alumino silicate produces denitrogenated heavy gasoline having a nitrogen content of 0.001% by weight. The displacement exchange stream employed with this feed stream, and with other nitrogen compound contaminated hydrocarbon streams boiling between about 300° F. and 400° F. is pyridine. This displacement exchange material has a normal boiling point of about 239° F. and is easily produced as an overhead distillate from both the denitrogenated heavy gasoline and from the alkylated pyridines and similar materials separated in admixture therewith as the extract from the process. In this application the denitrogenation efficiency is about 99.0%.

The process described in connection with Figure 2 is applied to the denitrogenation of the fraction of Colorado shale oil boiling between about 400° F. and 500° F. The 13 A. metallo alumino silicate is again employed, the contacting temperature for both steps of the process is about 510° F., and the displacement exchange stream recycled is 1,1-dimethylhydrazine. This raw shale oil fraction has a nitrogen content of about 1.7% by weight. The displacement exchange material has a boiling range of 200° F. to 205° F., and the denitrogenated shale oil product analyzes 0.002% by weight nitrogen. The denitrogenation efficiency is above 99%.

It has been found in the application of the process of this invention to the denitrogenation of hydrocarbon fractions boiling in the range of from 300° F. to 600° F. and particularly within the range of from 400° F. to 500° F. as in the foregoing example that the alkylated hydrazines such as methylhydrazine, ethylhydrazine, iso and normal propylhydrazine, 1,2-dimethylhydrazine, 1,2-diethylhydrazine, methyl ethylhydrazine, and the other mono and dialkylated hydrazines having up to three carbon atoms per alkyl radical may be substituted as the displacement exchange stream. It has also been found that the aliphatic diamines such as diaminoethane, 1,2 and 1,3-diaminopropane may be employed as the displacement exchange stream.

Ethylene diamine is effective in displacing higher boiling nitrogen compounds. The 13 A. silicate saturated with ethylene diamine is contacted at 405° F. and 0.26 atmosphere in the vapor phase with the fraction of shale oil coker distillate normally boiling between 400° F. and 500° F. The gravity of the feed is 30.2° API and it has a 1.76% by weight nitrogen analysis. Of 203 volumes of feed 201 volumes of raffinate are obtained. The ethylene diamine is distilled overhead from the nitrogen free oil which contains 0.0025% by weight nitrogen. Subsequently the 13 A. silicate is contacted at the same temperature and pressure conditions with 105 volumes of ethylene diamine to produce 106.5 volumes of extract. From this is distilled, as bottoms product, 35 volumes of nitrogen oil having a gravity of less than 15° API. The process is continued by repeating these steps in alternation. The ethylene diamine so separated from the raffinate and extract is recycled in the process as the displacement exchange stream as indicated previously.

A raw shale oil fraction boiling between 500° F. and 600° F. and having a nitrogen analysis of 2.0% by weight nitrogen is contacted for about one hour in the liquid phase with the 13 A. metallo alumino silicate at a temperature of 490° F. The displacement exchange material employed in this application of the process is diethylenetriamine having a normal boiling point of about 400° F. It is found that this polyamino material is capable of displacing and being displaced by the organic nitrogen compounds in this 500° F. to 600° F. fraction respectively in the displacement exchange and contacting portions of the cycle. A denitrogenated raffinate, freed of the diethylenetriamine by distillation is produced having a nitrogen content of about 0.002% by weight. The degree of denitrogenation is 99%.

The process of this invention is applied to a heavy gas oil and residual fraction of shale oil boiling above 600° F. The 13 A. metallo alumino silicate adsorbent is employed, the contact is in the liquid phase at a temperature of 525° F., and the displacement exchange material recycled in the process is triethylenetetramine. This material has a normal boiling range of about 460° F. and in this modification of the process the displacement exchange is contacted in the vapor phase at a temperature of about 500° F. The feed material has a nitrogen content of about 2.0% by weight nitrogen and the denitrogenated product contained 0.1% by weight nitrogen.

Although the foregoing examples have served to illustrate the application of this invention to shale oil and petroleum oil fractions, this is not to be construed as a limitation since it is applicable in general to any hydrocarbon mixture contaminated with organic nitrogen compounds. In general, the selection of the displacement exchange stream is determined after a consideration of the boiling range of the feedstock to be denitrogenated. Primarily, the displacement exchange stream should have a normal boiling point somewhat below or above the initial boiling point or end point respectively of the hydrocarbon stream to be treated to permit distillation separations of the extract and raffinate streams. At least about 10° F. and preferably 25° F. or more is the preferred difference. It has been found however that in most cases the preferred displacement exchange materials have boiling points below the initial boiling temperature of the feedstock. For feedstocks boiling up to about 300° F. the aliphatic primary amines having between about 1 and about 3 carbon atoms per molecule are the preferred displacement exchange materials. For hydrocarbon materials boiling in the range of from 300° F. to 400° F. the preferred displacement exchange material is pyridine, although ethylene diamine can also be employed successfully. The preferred displacement exchange materials are the lower aliphatic diamines and the mono and disubstituted hydrazines whose constituent groups contain from 1 to about 3 carbon atoms per group in the case of hydrocarbon mixtures boiling in the range of from about 400° F. to 500° F. Again ethylene diamine can be used. For treatment of hydrocarbon streams boiling in the range of from 500° F. to 600° F. the preferred displacement exchange materials are the aliphatic triamines such as diethylenetriamine and the line. For materials including the residual oils boiling above about 600° F. the

various tetramines such as triethylenetetramine are preferred as the displacement exchange material. Thus for materials boiling above about 500° F., the displacement exchange components are preferably polyamines having up to about 6 carbon atoms per molecule. Because of the cyclic reverse adsorption steps which take place in the process of this invention it is preferred to fractionate in a preliminary way wide boiling range oils to be dehydrogenated so that fractions boiling approximately between the limits given above can be treated with an adsorbent which in turn is subjected to the displacement exchange step using the preferred displacement exchange material. Therefore the present invention contemplates such a preliminary fractionation step and the individual treatment of each fraction according to the principles of the invention as defined above.

As indicated above, the solid granular contact material used in this denitrogenation process is a zeolitic material comprising a metallo alumino silicate and prepared from natural minerals or synthetically and which has fairly uniformly sized pores of at least 7 A.

The preferred flow directions for the displacement exchange and the feed streams are indicated in Figures 1 and 2. It has been found that an increased efficiency of displacement exchange and reverse displacement exchange during the feed contact is obtained when these materials flow through the adsorbent bed in the opposite directions. This is not intended to exclude the passage of these two streams in the same direction since the displacement exchange still occurs, although somewhat additional quantities of material are required to effect the same degree of displacement.

Referring finally to Figure 3, the moving solids bed modification of the process described in connection with Figure 2 is shown. In this process adsorption column **150** is provided with a means **152** for removing the solid contact material from the bottom of column **150** and returning it to the top of the same column so as to maintain a downwardly moving dense solids bed in the column. The nature of this conveyor depends to some extent upon whether vapor phase or liquid phase contacting is employed within the column but may include bucket elevators, pneumatic solids conveyance such as the well known gas lift suspension system, the conveyance of these solids as a slow moving dense packed mass, and others. Adsorption column **150** is provided at successively lower levels with first seal gas disengaging zone **154**, raffinate disengaging zone **156**, contacting zone **158**, feed engaging zone **160**, sealing zone **162** including second seal gas disengaging zone **164**, extract disengaging zone **166**, displacement exchange zone **168**, and displacement exchange recycle engaging zone **170**. A 13 A. metallo alumino silicate contact material passes downwardly as a moving bed through these zones in succession.

The feed stream to be denitrogenated is introduced through line **172** at a rate controlled by valve **174** into engaging zone **160**, passes upwardly countercurrent to the descending solids bed in zone **158**, and substantially all of the denitrogenated feed stream is removed from zone **156**. The raffinate passes through line **176** into raffinate still **178** in which the lower boiling displacement exchange component is taken as an overhead product by means of line **180**. The denitrogenated hydrocarbon product is produced through line **182** as a bottoms product.

A small amount of the raffinate is allowed to pass upwardly countercurrent to the solids toward first seal gas disengaging zone **154**; this produces an impure mixture of the raffinate together with materials which inevitably are reintroduced into the system with the recycled solids. Most often this is the fluid which last contacts the solids at the bottom of the column, namely the displacement exchange recycle stream. Removal of the said mixture from zone **154** by means of line **184** and pump **186** prevents contamination of the raffinate and loss of raffinate from the top of the column. This material is recirculated through line **188** and combined with the feed.

The nitrogen compound saturated contact material passes downwardly through sealing zone **162** from which a seal stream is removed consisting of a mixture of the feed stream introduced into zone **160** and the extract stream removed from zone **166**. This material is also recycled to the feed stream by means of pump **190**.

The contact material is next contacted with the displacement exchange recycle stream in zone **168** to produce the extract comprising the displacement exchange component and the displaced organic nitrogen compounds from the adsorbent. The extract flows through line **192**, is distilled in extract still **194** to produce the displacement exchange component overhead through line **196** and the displaced nitrogen compounds as a product of the process through line **198** as bottoms product.

As in the process previously illustrated in Figures 1 and 2, the displacement exchange components separated from the raffinate and the extract are combined in line **200**, reheated in heater **202** to an appropriate contacting temperature substantially equal to that at which the feed stream passes through contacting zone **158**, and are passed through line **204** into recycle engaging zone **170** and thence into the displacement exchange zone **168**.

The process of this invention thus consists of an improved denitrogenation process for contaminated hydrocarbon mixtures employing the principles of solid adsorption and fluid fractionation in such a way so as to remove organic nitrogen compounds from the feed stream and whereby the ordinary heating and gas stripping or liquid washing steps customary in prior adsorption processes have been completely eliminated. The process of this invention may be operated under pressure or under vacuum, and the actual operating pressures are actually determined by the pressure at which the feed stream is available and its boiling range, and whether the material being contacted is desirably in the vapor phase or the liquid phase. The proper operating pressure can be determined by those skilled in the art from known physical characteristics of the materials to be separated; namely the bubble point and dew point of complex hydrocarbon mixtures and the known way in which these change with pressure. The operating temperatures employed in the process of this invention are also determined by the physical characteristics of the feed stream and the operating pressure and also whether a vapor phase or a liquid phase contact is desired. In the complex gasoline streams the operating temperature is largely determined by the dew point and the bubble point of the stream at a given operating pressure. For example, contacting temperatures above the dew point will obviously be in the vapor phase while operating temperatures below the bubble point will be in the liquid phase. It is within the contemplation of the present invention to treat the feed stream at a temperature between its bubble point and its dew point so that mixed phase contacting will be maintained for some special streams. Obviously the feed contact may be in the vapor phase followed by recycle stream contact in the liquid phase, or vice versa, if desired.

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 cyclic process for denitrogenating a hydrocarbon mixture containing normally incident organic nitrogen compound contaminants which comprises: (1) contacting said mixture with a lean granular solid adsorbent essentially comprising a partially dehydrated zeolitic metallo alumino silicate having substantially uni-

form pores between about 7 A. and about 13 A. in diameter and having adsorbed thereon a displacement exchange medium essentially comprising an organic nitrogen base, whereby there is formed a rich adsorbent essentially comprising said silicate having adsorbed thereon the organic nitrogen components of said mixture and a raffinate product comprising non-adsorbed hydrocarbon components of said mixture and desorbed displacement exchange medium; (2) separating said raffinate product from said rich adsorbent; (3) contacting said rich adsorbent with said displacement exchange medium, whereby said adsorbent is returned to the aforesaid lean state and there is obtained an extract product comprising desorbed organic nitrogen components of said mixture and said displacement exchange medium; (4) separating said extract product from said lean adsorbent; (5) returning the lean adsorbent to step (1); (6) separately treating said separated raffinate and extract products to separate the displacement exchange medium therefrom; and (7) returning separated displacement exchange medium to step (3).

2. A process according to claim 1 wherein said displacement exchange medium has a boiling point such that it is readily distilled from said raffinate and said extract products.

3. A process according to claim 2 wherein the boiling point of said displacement exchange medium is within the boiling range of said mixture and is separated from the extract and the raffinate products by means of a heart-cutting distillation.

4. A process according to claim 1 in combination with the step of periodically raising the temperature of said metallo alumino silicate and contacting it with a gas containing oxygen thereby burning residual hydrocarbonaceous materials therefrom.

5. A process according to claim 1 in combination with the steps of flowing the hydrocarbon mixture in contact with said silicate in a direction opposite to that at which the displacement exchange medium is passed in contact therewith.

6. A process according to claim 1 wherein said hydrocarbon mixture and said displacement exchange medium are passed alternately through at least two contacting zones each containing a static bed of said metallo alumino silicate.

7. A process according to claim 1 in combination with the step of recirculating said metallo alumino silicate successively through a contacting zone in contact with said hydrocarbon mixture and then through a displacement exchange zone in contact with the recycled stream of said displacement exchange medium.

8. The cyclic process for denitrogenating a normally liquid hydrocarbon mixture containing normally incident organic nitrogen base contaminants which comprises: (1) contacting said mixture with a lean granular solid adsorbent essentially comprising a partially dehydrated zeolitic metallo alumino silicate having substantially uniform pores between about 7 A. and about 13 A. in diameter and having adsorbed thereon a displacement exchange medium essentially comprising an organic nitrogen base which is separable from said hydrocarbon mixture by distillation, whereby there is formed a rich adsorbent essentially comprising said silicate having adsorbed thereon the organic nitrogen base components of said hydrocarbon mixture and a raffinate product comprising non-adsorbed hydrocarbon components of said hydrocarbon mixture and desorbed displacement exchange medium; (2) separating said raffinate product from said rich adsorbent; (3) contacting said rich adsorbent with said displacement exchange medium, whereby said adsorbent is returned to the aforesaid lean state and there is obtained an extract product comprising desorbed organic nitrogen base components of said hydrocarbon mixture and said displacement exchange medium; (4) separating said extract product from said lean adsorbent; (5) returning the lean adsorbent to step (1); (6) separately distilling the separated raffinate and extract products to separate said displacement exchange medium therefrom; and (7) returning separated displacement exchange medium to step (3).

9. A process according to claim 8 wherein said metallo alumino silicate has a pore size of about 10 A. in diameter.

10. A process according to claim 8 wherein said metallo alumino silicate has a composition corresponding substantially to $5Na_2O \cdot 6Al_2O_3 \cdot 15SiO_2$, and has a pore size of about 13 A. in diameter.

11. A process according to claim 8 wherein said hydrocarbon mixture comprises a light gasoline fraction boiling below about 300° F., and wherein said displacement exchange medium is a primary alkylamine containing from 1 to 3 carbon atoms.

12. A process according to claim 8 wherein said hydrocarbon mixture comprises a gasoline fraction boiling below about 400° F. and wherein said displacement exchange medium comprises a pyridine compound selected from the group consisting of pyridine 2-methyl pyridine, 3-methyl pyridine, and 4-methyl pyridine.

13. A process according to claim 8 wherein said hydrocarbon mixture has a boiling range of from about 400° F. to about 500° F. and wherein said displacement exchange medium is an alkyl hydrazine containing from 1 to 2 alkyl groups each containing from 1 to 3 carbon atoms.

14. A process according to claim 8 wherein said hydrocarbon mixture boils above about 500° F. and wherein said displacement exchange medium comprises a polyethylene polyamine containing from 3 to 4 amino groups.

15. A process according to claim 8 wherein said hydrocarbon mixture has a boiling range between about 400° F. and about 500° F., and said displacement exchange medium is a diamino-alkane containing from 2 to 3 carbon atoms and having the amino groups attached to different carbon atoms.

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