

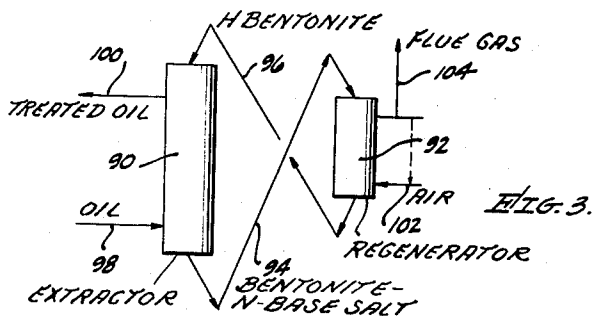
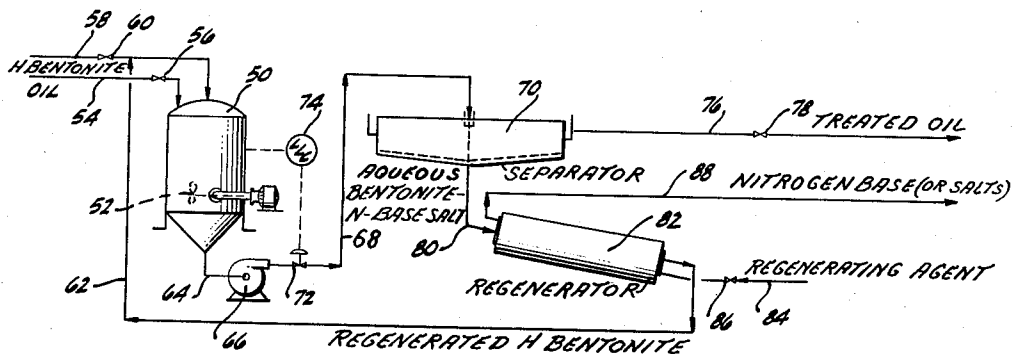
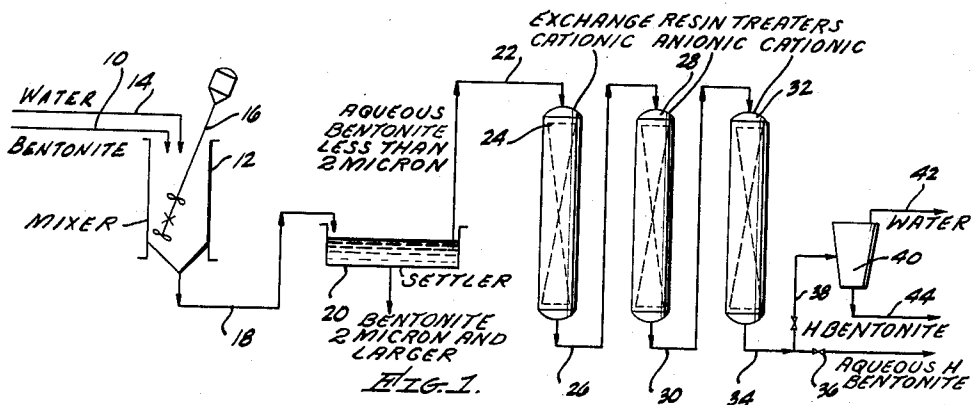
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DENITROGENATION OF HYDROCARBON MIXTURES

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DENITROGENATION OF HYDROCARBON MIXTURES

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12 Claims. (Cl. 208—254)

This invention relates to the purification of contaminated hydrocarbon mixtures and particularly to the removal of hydrocarbon compounds of nitrogen from such mixtures. This invention specifically relates to the denitrogenation of such hydrocarbons by contacting them with a synthetic or natural siliceous mineral with base exchange properties in the "hydrogen" form, such as hydrogen bentonite forming what is apparently a solid salt which is readily and rapidly separable by physical means from the substantially nitrogen-free hydrocarbon.

Many crude petroleum streams are produced from the ground and are found to contain considerable quantities of hydrocarbon derivatives of nitrogen 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 analysis. Mexican and Venezuelan crudes have nitrogen analysis ranging from about 0.2% to about 0.35% by weight. Extensive analysis of these nitrogen-containing crudes indicate that much of the nitrogen occurs in the form of amines or the so-called nitrogen bases. These include pyridine, quinoline, and the mono, di, tri, and tetra-alkylated derivatives of these materials. For example, in California kerosene distillate the di, tri, and tetra-alkylated quinolines and alkylated pyridines are found. There is however considerable non-basic 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 hydrocarbon derivatives of nitrogen that the nitrogen analysis 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 hydrocarbon derivatives of nitrogen 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

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the feed. In a platinum catalyzed gasoline reforming system using a halide promoted catalyst, the nitrogen compounds appear to react with the catalyst or the promoter forming ammonium halides which deposit as solids in the apparatus. This deactivates the catalyst and lowers the yield unless the halide is continuously replenished, and eventually plugs the reactor.

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 readily removable 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 5000 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 the above-mentioned problems in platinum catalyzed reforming.

The present invention is directed to a process for the removal of basic hydrocarbon derivatives of nitrogen from the hydrocarbon fractions associated therewith and derived from virtually any source.

It is a primary object of this invention to provide an improved process for hydrocarbon denitrogenation.

It is a further object of this invention to contact nitrogen-contaminated hydrocarbons with hydrogen bentonite, or more specifically hydrogen montmorillonite, or hydrogen illite, or hydrogen kaolinite to produce a solid salt of nitrogen bases present in the hydrocarbon.

It is a further object of this invention to provide in such denitrogenation processes a regeneration of the solid contact material by high temperature oxidation if the nitrogen bases are of no substantial value, or by extraction and recovery of these nitrogen bases if they constitute a valuable commodity.

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

The present invention comprises an improved process for the separation of basic hydrocarbon compounds of nitrogen, more generally known as nitrogen bases, from hydrocarbon mixtures. The process employs a solid contacting material which appears to react directly in some way as an acid with the nitrogen bases forming a stable product which is a solid. This solid material is very rapidly and completely separable from the liquid hydrocarbon phase. The solid contact material employed in this invention is a natural or synthetic siliceous mineral having base exchange properties converted into the acid or hydrogen ion condition. Hydrogen illite, hydrogen kaolinite, and hydrogen bentonite, which contains a relatively high concentration of hydrogen montmorillonite, are examples of suitable materials. For purposes of the process, these materials appear to behave as a solid acid either in the presence or in the absence of liquid water. They further appear to react directly with nitrogen bases to form a solid salt. The process can be conducted using the solid contacting material in the form of a relatively dilute dispersion in liquid water, or in the "dry" state with the solid either in the form of solid granules or as a dry finely divided powder. With

the water dispersion, the process partakes of a solvent extraction in which solvent is the aqueous dispersion, the raffinate consists of the substantially nitrogen-free hydrocarbon, and the extract comprises an aqueous phase containing the solid reaction product of the nitrogen bases and the solid material. With the granular form of solid contact material, the process may be conducted in a manner analogous to the well known hydrocarbon cracking process in which the hydrocarbon, in either the liquid or vapor phase, is passed through either a static or moving bed of the granules. With the powdered form of solid material, the feed hydrocarbon may be slurried with the powder in the liquid phase or may be fluidized with the powder in the vapor phase according to well known chemical engineering principles. In any of these process modifications, the hydrocarbon after contact with the solid material is freed of the basically reacting hydrocarbon compounds of nitrogen. The spent solid material is then regenerated for reuse in denitrogenating additional feed hydrocarbon and this regeneration may be such as to either recover the nitrogen bases as such or to destroy them as by oxidation as indicated in greater detail below.

The following discussion will refer to hydrogen bentonite or montmorillonite by way of example, it being understood that illite or kaolinite may be treated similarly.

The preferred process for preparing hydrogen montmorillonite and several modifications of the process for using it according to the present invention will be more clearly understood by reference to the accompanying drawing in which:

Figure 1 is a schematic flow diagram of the preferred process for preparing hydrogen montmorillonite,

Figure 2 is a schematic flow diagram illustrating the process of this invention which employs an aqueous dispersion of hydrogen montmorillonite, and

Figure 3 is a highly schematic flow diagram in which the hydrogen montmorillonite is recirculated in the dry state.

Referring now more particularly to Figure 1, bentonite clay, such as commercially available Wyoming bentonite and having a high concentration of montmorillonite, is introduced through line 10 into mixer 12. Water is introduced through line 14 and agitator 16 thoroughly mixes these two materials. Suitable proportions are about one pound of clay per 5 gallons of water. The Wyoming bentonite used in the process is powdered material, 99% of which will pass a 200 mesh screen. These materials are thoroughly mixed in mixer 12 and then passed through line 18 into settler 20. The material is allowed to stand for about 2 hours, or for sufficient time whereby approximately 25% of the original bentonite settles leaving an aqueous dispersion containing 75% of the original clay and including those particles which are less than about 2 microns in size. The settling time is of course a function of the settler geometry and the time necessary to settle out particles above 2 microns varies.

Wyoming bentonite and other naturally occurring montmorillonite clays contain on their crystal surfaces or in the crystalline structure exchangeable cations which may include sodium, calcium, magnesium, and iron. These clays also contain adsorbed salts, principally sodium and calcium chloride, derived from waters which have been originally associated with the clay. In the process of this invention it is necessary to remove not only the adsorbed salts but also the exchangeable cations present in the mineral. In the preferred form for preparing hydrogen montmorillonite this is accomplished in a manner which prevents the conversion of the anions contained in the adsorbed salts into free acids. Thus the preparation of hydrogen montmorillonite may be effected in mild steel equipment.

The settled bentonite dispersion is pumped through line 22 through first ion exchange column 24 in which

it contacts a synthetic cationic exchange resin previously treated with ammonium chloride so that the resin is in the "ammonium" condition. During the contact of the dispersion with this exchange resin, the adsorbed salts on the bentonite are converted to ammonium salts and the sodium and calcium and any other cations accumulate on the resin. Simultaneously the exchangeable cations present in the clay structure are exchanged for ammonium cations producing an ammonium bentonite and the exchangeable cations accumulate on the resin. Since the adsorbed salts are principally chlorides, the adsorbed salts originally on the dry clay are converted to ammonium chloride now principally in the aqueous phase.

The effluent from first column 24 thus consists of ammonium bentonite dispersed in a dilute ammonium chloride solution. It is pumped through line 26 into second ion exchange column 28 containing a synthetic anionic exchange resin previously treated with a strong hydroxide such as caustic soda and is thus in the "hydroxyl" condition. During contact of the dispersion with this resin, the ammonium chloride solution is converted to an ammonium hydroxide solution, the chloride anions being exchanged for hydroxyl ions. The chloride is of course accumulated on the resin. The effluent from exchange column 28 thus consists of a dispersion of ammonium bentonite in a dilute ammonium hydroxide.

This effluent is pumped through line 30 into third ion exchange column 32 and contacts therein a synthetic cationic exchange resin previously treated with strong acid and is thus in the "hydrogen" condition. During this third contact the ammonium bentonite is converted by base exchange with the hydrogen resin to produce hydrogen bentonite. Simultaneously the dilute solution of ammonium hydroxide is converted to water by exchange of the ammonium ion in the solution for hydrogen ion on the resin. The ammonium ion thus accumulates on the resin and the effluent from the third base exchange column comprises a dilute dispersion of hydrogen bentonite in pure water.

For Wyoming bentonite the base exchange capacity is about 100 milliequivalents per 100 grams. This capacity may be entirely exchanged for hydrogen ions. This is the preferable form for denitrogenation of light oils containing relatively low molecular weight nitrogen bases such as methyl and ethyl amine. For heavier oils containing pyridine and quinoline and their alkylated derivatives, a smaller degree of exchange to the hydrogen form can be used because the large hydrocarbon radical of one nitrogen base retained at one active site on the hydrogen bentonite appears to block adjacent sites in a 100% hydrogen bentonite. At least a 20% exchange is required, that is, at least 20% of the base exchange ions are exchanged for hydrogen and the bentonite so treated has a reactive hydrogen ion content of at least about 20 milliequivalents per 100 grams. Because illite and kaolinite have capacities of 20 milliequivalents or less, 100% exchange for hydrogen is highly desirable and the resulting solids are best applied to removal of high molecular weight nitrogen bases from high boiling oils, e.g. boiling above about 500° F. These siliceous minerals are thus not equivalent.

Depending upon the physical form in which the hydrogen bentonite is to be used in the process of this invention, the dispersion is either produced through line 34 through valve 36 in the aqueous form and is sent to storage facilities not shown, or if the hydrogen bentonite is to be used in the dry state, valve 36 is closed and the dilute dispersion is passed through line 38 into separator 40. This may comprise a filter or a centrifuge or other means capable of separating fine solids from liquids. The liquid phase is removed through line 42 and the solid hydrogen bentonite phase is removed through line 44.

Referring now more particularly to Figure 2, a schematic

ic diagram is shown of the process for denitrogenation of hydrocarbons using the aqueous dispersion of hydrogen bentonite. In this process mixer-contactor 50 is provided with a motor driven propeller agitator 52. The contaminated oil is introduced through line 54 at a rate controlled by valve 56 and simultaneously the aqueous dispersion of hydrogen bentonite is introduced through line 58 at a rate controlled by valve 60. This is combined with a recirculated stream of regenerated hydrogen bentonite flowing through line 62. The materials are thoroughly agitated in mixer 50 in proportions sufficient to reduce the nitrogen combination of the hydrocarbon to the desired value. For complete removal of nitrogen bases at least about 1.0 pound of hydrogen bentonite (dry basis) per barrel of oil must be used for each 0.1% by weight of basic nitrogen present in the feed.

The mixed stream of aqueous dispersion and treated oil is removed from mixer 50 through line 64 and pumped by means of pump 66 through line 68 into separator 70. The rate of removal is controlled by valve 72 in accordance with liquid level controller 74. In settler 70 the aqueous and oil phases are allowed to separate and the free oil product is produced through line 76 at a rate controlled by valve 78. If desired, the aqueous dispersion of the bentonite-nitrogen base salt is passed through line 80 into regenerator 82. A regenerating agent is introduced through line 84 at a rate controlled by valve 86 and the effluent removed through line 88. The regenerated hydrogen bentonite is recirculated in the process through line 62.

This regeneration may be a solvent extraction with an aromatic hydrocarbon and an aliphatic alcohol. Thus the nitrogen base is extracted from the salt by solvents such as approximately equal parts of benzene-methyl alcohol, benzene-ethyl alcohol and the like, the extract is separated and the nitrogen base is produced in its original form through line 88 as a product. The regenerating agent may also comprise a strong mineral acid in which case a water soluble nitrogen base salt is produced through line 88. Typically sulfuric or hydrochloric acids are used.

The regenerating agent may also comprise an oxygen-containing gas in which case the nitrogen base-bentonite salt is chemically decomposed and the nitrogen base radical is burned forming nitrogen oxides, carbon oxides, and water.

Referring finally to Figure 3, a highly schematic illustration of a continuous process modification of this invention is shown including extraction zone 90 and regeneration zone 92. Conveyor zones 94 and 96 are provided to maintain a continuous circulation of dry solid hydrogen bentonite. The oil to be purified is introduced in either the liquid or vapor phase through line 98 and the purified oil is removed through line 100. The bentonite-nitrogen base "salt" passes through conveyor 94 to regenerator 92. An oxygen-containing gas such as air, or other, and recirculated cooled flue gas is introduced through line 102. The regeneration is effected at temperatures of 400-800° F. and part of the resulting flue gas is discharged to the atmosphere through line 104. The remaining part may be recycled and cooled to dilute the incoming air through line 102 and to control the regeneration temperature. The regenerated hydrogen bentonite is returned to extraction zone 90 through conveyance zone 96.

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 denitrogenation of hydrocarbons contaminated with nitrogen bases which comprises contacting said hydrocarbons with a siliceous solid having base exchange properties and which has been converted to the hydrogen ion form, and separating hydrocarbon of substantially reduced nitrogen analysis therefrom.
2. A process according to claim 1 wherein said siliceous solid is in the form of an aqueous dispersion.
3. A process according to claim 1 in combination with the steps of regenerating the spent siliceous solid to remove the nitrogen bases therefrom and returning the regenerated siliceous solid to contact further quantities of hydrocarbon.
4. A process according to claim 3 wherein said spent siliceous solid is regenerated by contacting it with an oxygen-containing gas, and controlling the regeneration temperature at between about 400° F. and about 800° F. whereby said nitrogen bases are burned.
5. A process according to claim 3 wherein said spent siliceous solid is regenerated by contacting it with an extractive solvent to dissolve the nitrogen bases, separating the extract from the regenerated siliceous solid, and separating the solvent from said hydrocarbon compounds of nitrogen in said extract.
6. A process according to claim 1 wherein said siliceous solid comprises hydrogen bentonite.
7. A process according to claim 1 wherein said siliceous solid comprises hydrogen illite.
8. A process according to claim 1 wherein said siliceous solid comprises hydrogen kaolinite.
9. A process for denitrogenation of hydrocarbons contaminated with nitrogen bases which comprises contacting the contaminated hydrocarbon with solid hydrogen bentonite having at least about 20 milliequivalents of exchangeable hydrogen ion per 100 grams forming spent hydrogen bentonite and a hydrocarbon product having a substantially reduced nitrogen analysis, regenerating said spent hydrogen bentonite, and contacting additional quantities of hydrocarbons therewith.
10. A process according to claim 9 wherein the solid to hydrocarbon ratio is at least about 1.0 pound of hydrogen bentonite per barrel of hydrocarbon per 0.1% by weight of basic nitrogen in said hydrocarbon.
11. A process according to claim 9 wherein said regeneration is effected by extracting said spent hydrogen bentonite with a solvent mixture of an aromatic hydrocarbon and a water soluble aliphatic alcohol to remove the nitrogen bases therefrom, then separating the nitrogen bases as a product from the solvent mixture, and recirculating said solvent mixture.
12. A process according to claim 11 wherein said solvent mixture comprises an approximately 50-50 mixture of benzene and an alcohol selected from the group consisting of methyl, ethyl, and propyl alcohols.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,943,049

June 28, 1960

Paul G. Nahin et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, lines 26 and 27, strike out "hydrocarbon compounds of"; line 27, after "nitrogen" insert -- bases --.

Signed and sealed this 4th day of April 1961.

(SEAL)

Attest: ERNEST W. SWIDER


Attesting Officer

ARTHUR W. CROCKER
Acting Commissioner of Patents