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DENITROGENATION OF PETROLEUM WITH POTASSIUM HYDROXIDE OF LOW WATER CONTENT

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This application is a continuation-in-part of our copending application Serial Number 160,339, filed December 18, 1961, now abandoned.

This invention pertains to the removal of nitrogen-containing compounds from petroleum fractions and in particular to the removal of nitrogen compounds from petroleum fractions which are to be subsequently hydrocracked.

It is known that nitrogen compounds occur in many petroleum fractions. These nitrogen compounds have various deleterious effects. For instance, these nitrogenous materials have a poisoning effect on cracking catalysts and the removal of nitrogen-containing substances from catalytic cracking feed stocks has been quite thoroughly investigated. Also these nitrogenous materials have a poisoning effect on hydrocracking catalysts and there has been fairly extensive investigation of these effects and of methods for removal of nitrogen compounds from hydrocracking feed stocks. The problems involved in such removal have not been completely overcome. This is particularly true with respect to hydrocracking procedures for medium or heavy feed stocks. These higher boiling feeds contain higher boiling nitrogen compounds which are exceedingly difficult to remove; at least their removal to a sufficient degree to avoid poisoning of the hydrocracking catalyst has been a difficult problem. It is of course known that these poisonous materials can be removed by hydrogenation treatment. However the thorough-going removal required for hydrocracking feed stocks has necessitated relatively high pressures of above about 2000 p.s.i. and relatively low space velocities.

This invention has for its object to provide improved procedure for separation of nitrogen-containing contaminants from petroleum fractions. Another object is to provide improved hydrocracking procedure. Other objects will appear hereinafter.

It has now been discovered that these and other objects may be achieved by treating a petroleum fraction, which contains nitrogen compounds, with solid potassium hydroxide which has a water content of 0–10% at elevated temperatures and separating the petroleum fraction from the potassium hydroxide and nitrogen reaction products. It has been discovered that potassium hydroxide, with less than 10% water content, and especially with about 5% water content, is extraordinarily effective in removing nitrogenous compounds from petroleum fractions. It has been further discovered that the process which includes subjecting a petroleum fraction which contains nitrogenous compounds to be removed to treatment with potassium hydroxide which contains 0–10% water, preferably 5% water, at elevated temperature; separating the petroleum fraction from the solid potassium hydroxide and solid precipitated nitrogenous material formed by reaction with the potassium hydroxide; and then hydrogenating the separated petroleum fraction, is a new and effective method for eliminating the most difficult to remove nitrogenous compounds which remain. The hydrogenation treatment is carried out in the presence of a hydrogenation catalyst at elevated temperature and at moderate pressures. It results in hydrogenation of nitrogen compounds which remain in the petroleum fraction after the potassium hydroxide treatment. In the event that the petroleum fraction treated as above is to be hydrocracked, the so treated fraction is then subjected to hydrocracking. This procedure results in thorough removal of nitrogen compounds to such an extent that the activity of the hydrocracking catalyst is not deleteriously affected.

The feed stocks to our process may be any hydrocarbon mixture, which is substantially free of asphaltic material, having a boiling point above about 250° C., which contains above about 25 p.p.m. of nitrogen. The feed stock must be substantially free of asphaltic materials since such substances have a harmful effect on the catalyst used in the second or hydrogenation stage of our process (and in the third stage when a hydrocracking operation follows the nitrogen removal). Our invention is of particular value for the treatment of furnace oil, especially catalytic furnace oil. Light and heavy catalytic cycle stocks and deasphalted residuum are examples of other feed stocks that can be advantageously employed. Also our invention is applicable to solvent extracts of various petroleum fractions. For instance, our process is applicable to a sulfur dioxide extract of a catalytic cycle stock. Also our invention is applicable to products produced by pyrolysis of carbonaceous material such as creosote oil or shale oil.

The solid potassium hydroxide used in our process must contain from 0–10% water. It is preferred that the water content be about 5%. Solid potassium hydroxide containing above 10% water is not satisfactory in that it does not result in a thorough removal of the most difficultly removable nitrogen compounds. Therefore when this commercial product is used substantial amounts of these most difficultly removable nitrogen compounds remain in the petroleum fraction. The subsequent moderate pressure hydrogen treatment will not adequately remove these difficultly removable nitrogenous substances and therefore the preparation of a satisfactory final product for hydrocracking or for other purposes does not result. There is a sharp increase in the capacity for nitrogen removal when the water content of the solid potassium hydroxide is less than 10%. The most effective level is about 5%. There is some lessening of denitrogenative capacity as water is removed further. The solid KOH is employed in an amount of between about 0.1 and 15 percent and preferably between about 2 and 5 percent by weight of the petroleum fraction. An elevated temperature is employed during the treatment with solid potassium hydroxide. A temperature above about 200° F. but below the cracking temperature of the oil, and preferably between about 250° and 350° F. may be employed. The treatment with the solid potassium hydroxide is continued for a period of between about 10 minutes and 4 hours. Actually a longer time than 4 hours may be used but is accompanied by no advantage since the beneficial results of the treatment are fully obtained with the shorter periods mentioned. A time of treatment of between about one-half and 1 hour is usually most advantageous. The contacting of the petroleum fraction with the solid potassium hydroxide may be accomplished using any method which will result in thorough contact between a solid and a liquid. For instance, the contacting may be accomplished in batch fashion by simply stirring the two reactants together in a container. A much more satisfactory procedure is to flow the petroleum fraction through a stationary mass of particles, pellets or beads of the solid potassium hydroxide. If desired, the two reactants can be passed countercurrently to each other. After the treatment with the potassium hydroxide the petroleum fraction is filtered, distilled, settled or otherwise treated to remove any solid potassium hydroxide which might be suspended therein and to remove nitrogenous reaction products. These reaction products are usually solid materials and can be advantageously removed by filtering or decanting. If there are traces of

potassium hydroxide left in the feed it is advantageous to remove them by washing with water. The potassium hydroxide cannot be reused in the process unless it is first regenerated at elevated temperature to thermally decompose the nitrogenous salts formed. It can be reactivated by calcining at a temperature above about 800° F. After calcining, water may be added as desired.

The hydrogen treatment to remove the remaining nitrogen compounds is advantageously carried out at a temperature between about 550° and 750° F. and preferably between about 600° and 700° F. The pressure is advantageously maintained between about 200 and 1500 p.s.i.g. The required degree of nitrogen removal usually can be obtained utilizing pressures of between about 400 and 1000 p.s.i.g. A space velocity of between about 0.5 and 10 and preferably between about 1 and 6 is generally used. The hydrogen recycle rate is maintained between about 1000 and 20,000 s.c.f./bbl. and preferably between about 2000 and 10,000 s.c.f./bbl. The catalyst employed in this first stage is advantageously a mixture of nickel and tungsten oxides or sulfides, of nickel and molybdenum oxides or sulfides. The most effective catalyst of this group is a mixture of nickel and tungsten oxides and a catalyst having a particularly high activity for nitrogen removal is one containing a mixture of 16 parts nickel and 16 parts tungsten in the form of the oxides. While we have found these catalysts to be unusually effective for nitrogen removal, we can in general employ metal oxides or sulfides of metals of Group VI left-hand column of the Periodic System or iron group oxides or sulfides or mixtures thereof. These catalysts are deposited upon solid porous carriers such as alumina, kieselguhr or steam deactivated silica-alumina cracking catalyst. As a matter of fact, since the nitrogen deactivates the cracking activity, these catalysts may be deposited upon a conventional cracking catalyst. Thus the cracking activity of the carrier is very quickly lost due to the poisoning effect of the nitrogen in the feed stock and the poisoned carrier then serves as a satisfactory porous non-cracking carrier.

The product from the above hydrogenation may be used for any purpose in which a low nitrogen feed is advantageous. Thus it may be subjected to a hydrocracking operation. This is accomplished by contacting the denitrogenated feed with hydrogen in the presence of a hydrogenation catalyst deposited upon a silicious carrier having cracking activity. A temperature of between about 450° and 800° F. and preferably between 550° and 750° F. is used, and a pressure of between about 500 and 2000 and preferably between about 700 and 1500 p.s.i.g. is employed. A space velocity of between about 0.1 and 10 and preferably between about 0.5 and 3 will in general be found satisfactory. The hydrogen recycle rate may be between about 2000 and 20,000 and preferably 6000 and 10,000 s.c.f./bbl. The hydrogenating component of the hydrocracking catalyst may be a noble metal or an iron group metal. Also an oxide or sulfide of metals of Group VI left-hand column may be used, alone or in combination with a noble metal or an oxide or sulfide of an iron group metal. Examples of satisfactory catalysts are tungsten oxide or sulfide, molybdenum oxide or sulfide, nickel, nickel oxide or nickel sulfide, platinum, palladium and mixtures of Group VI left-hand column oxides or sulfides with iron group metal oxides or sulfides such as nickel tungstate and cobalt molybdate. The carrier for the hydrogenating component may be any known silicious cracking catalyst such as a silica-alumina cracking catalyst. These cracking catalysts may also contain activators such as are commonly used in cracking catalysts, for instance magnesium oxide or strontium oxide. Also these catalysts may be activated with halides such as fluorine.

EXAMPLE I

A commercial grade of potassium hydroxide (nominally containing 15% water) was calcined at 1000° F. for 16 hours to render it completely anhydrous. It was then placed under a nitrogen atmosphere to prevent any water absorption. Five batches of nine grams each of the anhydrous potassium hydroxide were weighed out under a nitrogen blanket. Calculated amounts of water were added so that five lots of potassium hydroxide were available, one being anhydrous and the others containing 5%, 10%, 15% and 25% water, respectively.

A fluid catalytically cracked furnace oil which contained 360 p.p.m. of nitrogen in the form of nitrogenous compounds was selected for treatment with each of the potassium hydroxide samples. The complete inspection data on this charge stock are contained in Table I. Each of the previously prepared samples of potassium hydroxide was added to 300 grams of the furnace oil. The mixtures were heated rapidly to 300° F. with constant agitation. The temperature was maintained at 300° F. for four hours. The oil was then filtered and washed twice with water. It was then analyzed for nitrogen. Each analysis was run in duplicate. The results are summarized in Table II.

Table I

INSPECTIONS OF FCC FURNACE OIL

Gravity, ° API	23.1
Nitrogen, p.p.m.	360
Nitrogen, basic, p.p.m.	86
Sulfur, percent by wt.	0.98
FIA analysis, percent by vol.:	
Aromatics	61.4
Olefins	7.0
Saturates	31.6
Distillation, D–86, ° F.:	
Over point	386
10%	462
30%	496
50%	524
70%	558
90%	604
End point	650

Table II

DENITRIFICATION OF FCC FURNACE OIL WITH POTASSIUM HYDROXIDE

Water in Potassium Hydroxide	Nitrogen Analysis (p.p.m.)	Nitrogen Analysis (p.p.m.)	Nitrogen Analysis Average
0	180	190	185
5	60	100	80
10	200	210	205
15	240	260	250
25	250	260	255

EXAMPLE II

The same furnace oil was treated in a manner identical with that in Example I except that only four samples of potassium hydroxide were tested. One was an anhydrous sample. Water concentration, in the others, was 5%, 10% and 15%. The potassium hydroxide samples were also prepared identically with those in Example I.

After the oil product was filtered and washed, it was analyzed for nitrogen. The results of this testing are contained in column 1 of Table III.

The oil was then subjected to a hydrogenation treatment over a sulfided nickel-cobalt-molybdenum catalyst at a pressure of 1000 p.s.i.g. and at 650° F. The liquid hourly space velocity was 5 and the hydrogen recycle rate, 4000 standard cubic feet per barrel of feed. The oil was again tested after the hydrogenation for nitrogen content. These results are in column 2 of Table III. The oil that had been treated with anhydrous potassium hydroxide was not tested after hydrogenation but it is estimated that about 12 p.p.m. of nitrogen would remain. This estimate is based on the other data in Table III.

Table III

HYDROGENATION OF KOH-TREATED FCC FURNACE OIL

Water in KOH Used to Treat Sample (percent)	N-Level Before Hydrogenation (p.p.m.)	N-Level After Hydrogenation (p.p.m.)
15	240	49.
10	220	14.
5	80	Less than 5.
0	185	No test (estimated 12).

What we claim is:

1. A process for removing nitrogen compounds from a petroleum fraction which comprises contacting said fraction with potassium hydroxide containing less than 10% water and separating the potassium hydroxide and nitrogen reaction products.

2. A process for removing nitrogen compounds from a petroleum fraction which comprises contacting said fraction with potassium hydroxide containing about 5% water and separating the potassium hydroxide and nitrogen reaction products.

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