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PROCESS OF REMOVING NITROGEN COMPOUNDS BY OXIDATION

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This invention relates to a process for the selective oxidation of nitrogen-containing compounds present in petroleum fractions.

It has been found that nitrogen-containing compounds are deleterious in certain refining processes, such as the cracking and hydrocracking processes, because of their poisonous effect on the catalysts. It is also speculated that nitrogen-containing compounds contribute to discoloration, formation of sludges and gum, and general instability of petroleum products. It is, therefore, desirable to remove these nitrogen-containing compounds from the petroleum fractions. In general, there are two types of nitrogen-containing compounds present in petroleum fractions. These are designated as basic and non-basic nitrogen-containing compounds. It has been found that methods suggested in the art for the removal of nitrogen-containing compounds from petroleum fractions suffer from certain disadvantages, such as the use of expensive solvents or reactants, which are difficult to separate and recover from the product streams, or the processes are not selective enough for the removal of nitrogen-containing compounds, particularly the basic nitrogen-containing compounds and the high molecular weight highly alkylated nitrogen-containing compounds. It has now been found that nitrogen-containing compounds, particularly the basic type and those of high molecular weight, may be selectively removed by a mild oxidation process utilizing an easily recoverable solid catalyst.

In accordance with the invention, the nitrogen content of a nitrogen-containing petroleum fraction is reduced by contacting the nitrogen-containing petroleum fraction with an oxygen-containing gas in the presence of a solid oxidation catalyst comprising an oxide of phosphorus. In one preferred embodiment of this invention it has been found that the activity of the solid phosphorus oxide oxidation catalyst for the selective oxidation of nitrogen-containing compounds is unexpectedly promoted by the addition of an oxide of vanadium, and more particularly, the solid phosphorus oxide oxidation catalyst is promoted when the atomic ratio of vanadium to phosphorus is between about 0.02:1 and 5:1. In yet another embodiment of this invention, it has been found that essentially complete removal of nitrogen-containing compounds can be effected by a combination process comprising mild oxidation followed by hydrogenation.

The charge stocks for the process of this invention comprise any nitrogen-containing petroleum fraction. By "nitrogen-containing petroleum fraction" is meant any petroleum fraction comprising nitrogen-containing compounds in admixture with other compounds and hydrocarbons. In particular, the charge stock can comprise any nitrogen-containing petroleum fraction boiling between about 250° F. and 1100° F. or higher at atmospheric pressure. For example, virgin or catalytic naphthas, furnace oils, or gas oils; full range crudes, lubricating oils, residuums; or shale oils may be employed. Nitrogen-containing petroleum fractions boiling above about 400° F. and particularly boiling between about 550° to 1100° F., i.e., heavy furnace oils and gas oils are preferred charge stocks for the process of this invention since the method of this invention is particularly applicable for preparing such charge stocks for further catalytic treatment as noted above.

The function of the catalyst is to aid in the removal of the nitrogen-containing compounds. The catalyst is believed to function in part as a true catalyst in initiating the reaction, but it may also be acting as a reactant and forming, for example, phosphorus-nitrogen bonds. The catalyst is solid and comprises an oxide of phosphorus, for example, phosphorus pentoxide. The other oxides of phosphorus are also suitable, for example, phosphorus trioxide; however, these oxides will probably be converted to the higher oxidation stage during processing. The oxides of phosphorus can be used unsupported or distended on a suitable carrier. The unsupported form of the catalyst is preferred. However, any of the common carriers, either natural or synthetic, may be employed, for example, alumina, silica, magnesia, or mixtures thereof, diatomaceous earth, kieselguhr, kaolin, and others. If a supported form of the catalyst is employed, it is preferred that a non-cracking carrier be employed, especially at the higher reaction temperatures, in order to avoid the degradation of products by cracking. Any amount of the phosphorus oxides may be distended on the carrier and employed successfully in the process of this invention. For example, the amount of phosphorus oxides to be distended on the carrier may vary up to 50 weight percent, or more, of the final catalyst. The function of the carrier, however, is to extend the available surface area of the phosphorus oxide, and it is therefore preferred that the final catalyst contain between about one and 30 weight percent of the phosphorus oxides.

While a catalyst comprising an oxide of phosphorus is suitable for the process of this invention, it has been found that the activity of the phosphorus catalyst for the removal of nitrogen-containing compounds by selective oxidation is unexpectedly promoted by the addition to the phosphorus oxide of an oxide of vanadium. In order to achieve a promotional effect, it has been found that sufficient vanadium, as the oxide, should be added so that the mixture has an atomic ratio of vanadium to phosphorus of between about 0.02:1 and 5:1 with preferred atomic ratios between 0.06:1 and 0.5:1. The most preferred atomic ratio of vanadium to phosphorus is 0.2:1. Mixtures of vanadium and phosphorus oxides, wherein the atomic ratio of vanadium to phosphorus is greater than about 5:1 but less than about 50:1, may also be employed successfully, for the presence of the oxide of phosphorus tends to activate the oxide of vanadium to the level of activity of the oxide of phosphorus catalyst alone. The mixture of phosphorus and vanadium compounds can also be distended on a suitable support similar to the supports listed for the phosphorus catalyst above. The total amount of metal oxides dis-

tended on the support may again vary up to 50 weight percent, or more, with preferred amounts of metal oxides between 1 to 30 weight percent.

The oxidant employed may be any oxygen-containing gas. By an "oxygen-containing gas" is meant any gas containing free molecular oxygen or ozone. Examples of suitable oxygen-containing gases include, for example, oxygen and air. It has been found that the removal of nitrogen-containing compounds will not occur unless there is at least some amount, even though small, of an oxygen-containing gas present in the reaction. Although smaller amounts of an oxygen-containing gas can be used, it is preferred that the rate of addition of the oxygen-containing gas be at least one cubic foot per hour per barrel of feed. It is more preferred to have the rate of addition of the oxygen-containing gas between 5 and 1000 cubic feet per hour per barrel of feed. The oxygen or ozone concentration is not critical and can be at any level, for example, from 0.1 to 100 percent, with preferred oxygen or ozone concentrations between 1 and 50 percent.

Any suitable means may be employed to contact the charge stock, catalyst and oxidant to selectively oxidize the nitrogen-containing compounds in the charge stock. For example, a fixed bed operation may be employed utilizing the solid phosphorus oxide or phosphorus oxide and vanadium oxide catalyst, or the phosphorus and vanadium compounds may be distended on a support and the supported catalyst used in the fixed bed reaction. The oxidant may flow either co-currently or counter-currently to the liquid feed.

A batch-type slurry operation may also be employed. In this operation an amount of catalyst is mixed with the nitrogen-containing petroleum fraction and the mixture is stirred while an oxidant is continuously added over a desired time period under mild oxidation conditions. The product is separated from the catalyst by any suitable means, such as distillation, filtration or centrifugation.

As a further example, a continuous slurry type of operation may also be employed if desired. In this type of operation fresh feed is continuously pumped into a reactor containing a small amount of the desired oxidation catalyst and maintained at the desired reaction conditions while an oxygen-containing gas is continuously added and the product is continuously withdrawn. In this type of operation small amounts of catalyst may be withdrawn with the product and may be separated therefrom by any suitable means, such as distillation, filtration or centrifugation.

In the slurry type of operation, the concentration of catalyst is not critical and may vary over wide limits. It is preferred, however, that the catalyst concentration be at least about 0.1 weight percent of the charge. The most preferred catalyst concentrations are between 0.3 and 15 weight percent of the charge stock. Since a mixture of phosphorus and vanadium in the proper atomic ratios is more effective than phosphorus alone, lesser amounts of the mixed catalyst over phosphorus alone need be used to achieve similar results. In general, higher catalyst concentrations should be employed with the charge stocks containing the greater amounts of nitrogen.

In the presence of the catalysts of this invention it has been found that removal of nitrogen-containing compounds is selective under the mild oxidation reaction conditions to be described below. By mild oxidation reaction conditions is meant reaction conditions such that the production of oxygenated compounds is minimized. Now petroleum oils as found contain certain amounts of oxygen-containing compounds, but usually the total weight percent oxygen is less than about 0.5 percent. Under the mild oxidation reaction conditions of this invention, the products will contain no more than about two weight percent oxygen and usually no more than about 0.5 to 1 percent oxygen.

The function of temperature in the selective oxidation of nitrogen-containing compounds is to activate the catalyst and thereby accelerate the reaction. The lower limit for the reaction temperature is determined only by the desired rate of reaction. In general, reaction temperatures below about 100° F. are undesirable due to the slow reaction rates. The upper temperature limit is determined by the degradation of the charge stock, for example by cracking, or over oxidation to undesired products. In general, it is preferred that the oxidation temperature not exceed about 650° F. The preferred oxidation reaction temperatures are between 250° and 500° F. It is also preferred to maintain the charge stock in the liquid phase for improved contacting among the reactants. In general, therefore, the lighter charge stocks will require the lower reaction temperatures.

Atmospheric pressure is the preferred reaction pressure, but pressures less than atmospheric or pressures up to 100 pounds per square inch gauge or higher may be employed if desired.

The effective removal of nitrogen-containing compounds will also be a function of contact time. The reaction under the conditions of this invention has been found to be selective for the oxidation of nitrogen-containing compounds with excellent product yields. While some removal of nitrogen-containing compounds will occur at even very short contact times, it is preferred to employ a contact time of at least one minute with the more preferred contact times between 30 minutes and 4 hours. In general, the shorter contact times are employed with the higher temperatures. Longer contact times than four hours may also be employed, but further removal of nitrogen-containing compounds by this procedure is slow.

As a further description of this invention the following examples are given.

The reaction procedure, unless indicated otherwise, comprises adding the desired amount of catalyst and liquid charge stock to a reactor, continuously stirring and continuously adding 400 cubic feet of air per hour per barrel of feed at atmospheric pressure for a given reaction time while maintaining the reactor at the desired reaction temperature.

A series of nine experiments were performed using a fluid catalytically cracked furnace oil as the charge whose inspections are given in Table I below.

Table I

INSPECTIONS OF FLUID CATALYTICALLY CRACKED FURNACE OIL

Inspection:	
Gravity, ° API	20.8
Sulfur, percent by weight	2.03
Total nitrogen, p.p.m	340
Basic nitrogen, p.p.m	52
Distillation, ° F.:	
Overpoint	446
10%	506
50%	548
90%	610
Endpoint	636

The catalysts employed in this first series of nine experiments were phosphorus pentoxide, vanadium pentoxide and mixtures of the two. The catalyst concentration was

two percent by weight of the charge in all of these nine experiments. All of the nine experiments were made for a time period of four hours while the temperature in most runs was 300° F. The pertinent information for the nine runs is summarized in Table II below.

Table II

EFFECT OF V_2O_5:P_2O_5 RATIO ON DENITROGENATION

Example No	1	2	3	4	5	6	7	8	9
Catalyst:									
Phosphorus Pentoxide, Percent by Wt	2.0	0.0	1.9	1.75	1.5	1.25	1.0	0.5	0.1
Vanadium Pentoxide, Percent by Wt	0.0	2.0	0.1	0.25	0.5	0.75	1.0	1.5	1.9
Atomic Ratio, Vanadium to Phosphorus			0.03:1	0.09:1	0.23:1	0.36:1	0.61:1	1.85:1	12.5:1
Time, Hours	4	4	4	4	4	4	4	4	4
Temperature, ° F	303	350	300	300	300	300	300	300	300
Product Analyses:									
Total Nitrogen, p.p.m	180	250	170	140	120	130	160	160	180
Basic Nitrogen, p.p.m	<5	50	<5	<5	<5	<5	<5	<5	6
Sulfur, Percent by Wt	2.03	2.00	1.89	2.03	1.91	2.03	1.93	1.91	2.03
Yield,[1] Percent by Wt	97.40	93.33	95.90	93.53	95.06	91.83	97.00	94.90	96.2

[1] Yield is calculated by dividing the weight of oil out by the weight of oil in and multiplying by 100.

Example 1 shows two percent phosphorus pentoxide results in essentially complete removal of the basic nitrogen-containing compounds and over 60 percent removal of the non-basic nitrogen-containing compounds in the furnace oil.

Example 2 shows the use of two percent vanadium pentoxide resulted in essentially no removal of the basic nitrogen-containing compounds and only 14 percent removal of the non-basic nitrogen-containing compounds despite the use of higher reaction temperatures than were used with the phosphorus pentoxide catalyst. Since vanadium pentoxide is a known oxidation catalyst, this result was somewhat unexpected.

A comparison of Examples 3 through 9 shows the unexpected effect of utilizing a catalyst comprising a two weight percent mixture of the oxides of phosphorus and vanadium at various atomic ratios of vanadium to phosphorus. The atomic ratio of vanadium to phosphorus varies from a high of 12.5:1 in Example 9 to a low of 0.03:1 in Example 3. A comparison of Example 3 with Example 1 shows that even small amounts of vanadium pentoxide, i.e., 0.03 atom to 1 of phosphorus, has a promotional effect on the phosphorus pentoxide for lowering the level of nitrogen in the product. Example 5 shows the optimum atomic ratio of vanadium to phosphorus is about 0.2:1. Example 9 shows that a mixture of vanadium and phosphorus pentoxides, wherein the atomic ratio of vanadium to phosphorus is 12.5:1, reduces the total nitrogen content of the charge to 180 parts per million, which is about equivalent to the use of phosphorus pentoxide alone.

A series of experiments were run to determine the effect of reduced catalyst concentration on the removal of nitrogen from the same FCC furnace oil as used above. A catalyst comprising phosphorus pentoxide and vanadium pentoxide was employed wherein the atomic ratio of vanadium to phosphorus was the same as in Example 5 above. These runs are summarized in Table III below.

Table III

EFFECT OF VARYING CATALYST CONCENTRATION ON OXIDATIVE DENITROGENATION AT A CONSTANT V_2O_5:P_2O_5 ATOMIC RATIO OF 0.23:1

Example No	5	10	11	12	13	14
Catalyst:						
Phosphorus Pentoxide, Percent by Wt	1.5	0.75	0.30	0.225	0.15	0.10
Vanadium Pentoxide, Percent by Wt	0.5	0.25	0.10	0.075	0.05	0.03
Total Concentration, Percent by Wt	2.0	1.0	0.40	0.300	0.20	0.13
Time, Hours	4	4	4	4	4	4
Temperature, ° F	300	300	300	300	300	300
Product Analyses:						
Total Nitrogen, p.p.m	120	170	180	210	265	245
Basic Nitrogen, p.p.m	<5	<5	<5			
Yield,[1] Percent by Wt	95.06	95.53	97.33	96.5	97.2	97.06

[1] Yield is calculated by dividing the weight of oil out by the weight of oil in and multiplying by 100.

Example 5 is the same Example 5 as reported on Table II above. Reducing the catalyst concentration to one percent as shown in Example 10 results in the removal of lesser amounts of the non-basic nitrogen-containing compounds in the charge.

Example 11 compared with Example 1 on Table II shows again the unexpected promotional effect of vanadium pentoxide on the phosphorus pentoxide catalyst. Thus, a mixture of phosphorus pentoxide and vanadium pentoxide in an atomic ratio of vanadium to phosphorus of about 0.2:1 can be used in a concentration of only 0.4 weight percent and achieve essentially the same denitrogenation results as a two weight percent concentration of phosphorus pentoxide alone.

It should be particularly noted that in almost all of the experiments shown in Tables II and III above, the yields of denitrogenated products were over 95 percent by weight of the charge, which shows the excellent selectivity for nitrogen removal achieved by the procedure of this invention. It should also be noted that sulfur removal was not great, which emphasizes again the selective nature of the catalysts of this invention for nitrogen removal.

It has also been found that the selective oxidation procedure of this invention is equally applicable to the treatment of the heavier type of nitrogen-containing petroleum fractions. Two experiments were performed charging two different stocks, i.e. an atmospheric gas oil and a heavy Kuwait gas oil, using air as the oxidant at the rate of 400 cubic feet per hour per barrel of feed.

Analyses of these charge stocks and results of these experiments are given in Table IV below.

Table IV

Example Number	Charge Stock	15	Charge Stock	16
Catalyst:				
P_2O_5—Wt. Percent	Light, Gas, Oil, From Atmospheric Tower.	1.5	Heavy Kuwait Gas Oil.	1.5
V_2O_5—Wt. Percent		0.5		0.5
Atomic Ratio, V:P		0.23:1		0.23:1
Reaction Time, Hours		4		4
Reaction Temperature, ° F		350		400
Analyses:				
Gravity, ° API	32.4		21.4	
Sulfur, Percent by Wt	0.91	0.91	3.05	2.96
Total Nitrogen, p.p.m	450	150	890	590
Basic Nitrogen, p.p.m	126	6	265	47
Boiling Range:				
Overpoint, ° F	268		329	
Endpoint, ° F	760			
90% point	726		934	
Yield,[1] Percent by Wt		96.28		96.94

[1] Yield is calculated by dividing the weight of oil out by the weight of oil in and multiplying by 100.

Example 15 shows the total nitrogen content was reduced 66⅔ percent, while the basic nitrogen-containing compounds were almost completely removed. The yield of denitrogenated oil was over 96 percent by weight of the charge, showing again the excellent selectivity of the process.

The heavy Kuwait gas oil charged in Example 16 was more difficult to treat. Still, the total nitrogen content was lowered by about 34 percent with a yield of product of 96 percent by weight of the charge. In addition, over 80 percent of the basic nitrogen-containing compounds were removed.

EXAMPLE 17

In this example, an FCC furnace oil whose inspections are given in Table I above was preheated to 350° F. and charged upflow at the rate of 2.0 vol./vol./hr. to a 100 cc. column filled with 22.1 grams of a catalyst comprising 20 percent by weight phosphorus pentoxide and 10 percent by weight vanadium pentoxide distended on a kieselguhr base.

The column was heated to 350° F. When no air was present in the column, the nitrogen content of the product was the same as that of the charge.

After a 20.0 throughput, air at the rate of 400 cubic feet per hour per barrel of feed was passed upflow together with the FCC furnace oil charge through the column. The nitrogen content of the product was found to be 260 parts per million indicating a reduction in nitrogen content of about 24 percent.

When the column temperature was subsequently increased to 500° F., the nitrogen level in the product was further reduced to 110 parts per million or a reduction of 68 percent.

EXAMPLE 18

Example 17 was repeated employing air at 350° F. except the catalyst was anhydrous unsupported phosphorus pentoxide. The nitrogen content of the product was 140 parts per million representing a nitrogen reduction of 59 percent.

EXAMPLE 19

In this example an FCC furnace oil whose inspections are given in Table I above was preheated to 300° F. and pumped at the rate of 250 cc. per hour continuously into a 2000 milliliter flask containing 20.0 grams of anhydrous phosphorus pentoxide and 1000 milliliters of the FCC furnace oil. Product was continuously withdrawn from the flask at the rate of 250 cc. per hour. The reaction flask was maintained at atmospheric pressure and 400° F. The operation was continued for 28 hours. Analysis of the total product shows a nitrogen level of 170 parts per million or a nitrogen reduction of about 50 percent. The total amount of catalyst employed amounted to only 0.28 percent by weight of the oil charged. This operation is therefore equivalent to the batch-type of process described above.

It has further been found, quite unexpectedly, that the selective oxidation procedure of this invention is peculiarly adapted to be used in combination with subsequent hydrogenation to achieve still further reductions in nitrogen content. It has also been found, quite unexpectedly, that the combination of selective oxidation according to the method of this invention and hydrogenation enhances the removal of sulfur compounds. The use of hydrogenation alone to remove nitrogen-containing compounds from petroleum fractions requires relatively severe conditions. Pre-oxidation of the nitrogen-containing petroleum fractions in accordance with the method of this invention, as contrasted with other methods of pre-oxidation, appears to remove those nitrogen-containing compounds which are the most difficult to remove by hydrogenation, and consequently, a less severe type of hydrogenation is required to remove substantially all of the nitrogen-containing compounds from the petroleum fractions. It has been found that the removal of nitrogen-containing compounds is particularly applicable by the method of this invention to the higher boiling petroleum fractions, such as those having a boiling range between 550° and 1100° F.

It has also been found that mild pre-oxidation in accordance with the method of this invention results in very little sulfur removal, but pre-oxidation followed by hydrogenation results in unexpected decreases in the sulfur level of the product.

EXAMPLE 20

An FCC furnace oil whose inspections are given in Table I above was subjected to hydrogenation. The FCC furnace oil was charged at a liquid-hourly space velocity of 2.0 downflow through a bed of a catalyst comprising 16 percent nickel and 16 percent tungsten as their oxides on alumina. The reactor was held at 650° F. and a pressure of 1000 pounds per square inch gauge. A hydrogen rate of 4000 cubic feet per barrel of feed was employed. The product contained 3.3 parts per million of nitrogen.

EXAMPLE 21

Example 20 was repeated except the charge stock was the oxidized FCC furnace oil product from Example 5 above. The oxidized FCC furnace oil was filtered to remove the oxidation catalyst, washed with water and dried before being charged to the hydrogenation unit. It was found that the liquid-hourly space velocity could be increased to 3.0 while achieving below 3.3 parts per million of nitrogen in the product.

EXAMPLE 22

A heavy Kuwait gas oil whose inspections are given in Table V below was charged downflow through a bed of a catalyst comprising 16 percent nickel and 16 percent tungsten as their oxides on alumina at a liquid-hourly space velocity of 2.0, a temperature of 700° F. and a pressure of 1000 pounds per square inch gauge. Hydro-

gen was charged with the feed at the rate of 4000 cubic feet per barrel. The nitrogen content of the product was 570 parts per million, representing a nitrogen reduction of 36 percent. The sulfur content of the product was 0.41 percent, representing a sulfur reduction of 86 percent.

Table V

INSPECTIONS OF HEAVY KUWAIT GAS OIL

Gravity, ° API	21.4
Sulfur, percent by weight	3.05
Total nitrogen, p.p.m	890
Basic nitrogen, p.p.m	265
Distillation:	
10%	651
30%	758
50%	825
90%	934

EXAMPLE 23

A heavy Kuwait gas oil whose inspections are given in Table V above was subjected to mild oxidation by a slurry reaction with 2.0 percent by weight of a phosphorus pentoxide-vanadium pentoxide catalyst having an atomic ratio of vanadium to phosphorus of 0.61:1 at 400° F. and atmospheric pressure for four hours while passing 400 cubic feet of air per hour per barrel of feed through the slurry. The nitrogen content of the charge was reduced from 890 parts per million to 590 parts per million while no reduction in sulfur level was achieved. The product from this oxidation was filtered, washed with water, dried, and hydrogenated by passage downflow at a liquid-hourly space velocity of 2.0 vol./vol./hr. through a bed of a nickel oxide and tungsten oxide on alumina catalyst while the temperature was maintained at 700° F. and the pressure at 1000 pounds per square inch gauge. The nitrogen content of the product was reduced to 240 parts per million, representing a nitrogen reduction of 59.3 percent. Thus, the pre-oxidized heavy gas oil resulted in a greater percentage nitrogen removal under essentially the same hydrogenation conditions, as well as resulting in a product having a much lower total nitrogen level. The sulfur was unexpectedly reduced to 0.17 percent, representing a reduction of 95 percent of the sulfur in the charge.

EXAMPLE 24

Example 23 was repeated except the liquid-hourly space velocity of the charge stock in the hydrogenation stage was reduced to 0.2 vol./vol./hr. The nitrogen content of the product was found to be only 6.1 parts per million. This level of nitrogen in the product would be virtually unattainable without pre-oxidation at these mild hydrogenation conditions.

EXAMPLE 25

Example 20 was repeated except the charge stock was the atmospheric gas oil whose inspections are given in Table IV above and the space velocity was 1.85 volumes of oil per volume of catalyst per hour. A product was obtained having a nitrogen level of 240 parts per million.

EXAMPLE 26

Example 25 was repeated except the charge stock was the filtered and washed oxidized atmospheric gas oil product from Example 15 above, whose inspections are given in Table IV. At a space velocity of 1.9 volumes of oil per volume of catalyst per hour, a product having only 20 parts per million of nitrogen was obtained.

It is estimated that a liquid-hourly space velocity of about 0.3 to 0.4 would be required to obtain a product having 20 parts per million of nitrogen for the non-oxidized atmospheric gas oil used in Example 24 above.

Examples 25 and 26 show the particular applicability of the process of this invention to the treatment of the heavier type of hydrocarbon charge stocks for the removal of nitrogen-containing compounds.

EXAMPLE 27

In this example 7000 grams of an FCC furnace oil whose inspections are given in Table I were oxidized using one percent by weight of a soluble oxidation catalyst, namely, manganese naphthenate. The oxidation was carried out at 300° F. for four hours while continuously stirring and adding 400 cubic feet of air per hour per barrel of feed. The product was distilled to separate the catalyst and high boiling nitrogen concentrate from the lower boiling materials. Analysis of the product showed a reduction in nitrogen from 340 parts per million to 60 parts per million in about a 92 percent yield.

The product from this oxidation was hydrogenated by passage downflow at a liquid-hourly space velocity of 2.0 through a bed of catalyst comprising 16 percent nickel and 16 percent tungsten as the oxides on alumina while the temperature was maintained at 700° F. and the pressure at 1000 pounds per square inch gauge. The nitrogen content of the product was only reduced to 40 parts per million. Hydrogenation of the untreated FCC furnace oil at these conditions would decrease the nitrogen from 340 parts per million to about 2 parts per million. These results show, therefore, that a manganese naphthenate catalytic pre-oxidation treatment in some manner inhibits the subsequent hydrogenation operation.

The catalysts which can be employed for the hydrogenation stage include at least one of the metals from group VIB of the periodic table and the iron group metals, their oxides or sulfides. These metals include chromium, molybdenum, tungsten, iron, cobalt and nickel, their oxides and sulfides. These catalysts are suitably distended upon solid, natural or synthetic carriers, such as silica, alumina, magnesia or mixtures thereof, kieselguhr or steam deactivated silica-alumina cracking bases. While it is preferred that the catalyst carrier be a non-cracking base, a conventional cracking carrier can be used, if desired, for the cracking character of the base will be quickly lost due to the poisoning effect of the nitrogen in the charge stock. The total amount of metals which may be deposited on the carrier may vary over wide limits. Suitable amounts of metals may be between 3 and 40 weight percent of the catalyst with preferred amounts of metals ranging between 5 and 35 weight percent. The most preferred catalyst is one comprising 16 weight percent nickel and 16 weight percent tungsten in the form of their oxides distended on an alumina support.

The reaction conditions for this hydrogenation stage are relatively mild. Suitable reaction temperatures may be between 550° and 750° F. with preferred reaction temperatures between 600° and 700° F.

The reaction pressure is advantageously maintained between about 200 and 2000 pounds per square inch gauge. Pressures between about 1000 and 2000 pounds per square inch gauge are preferred for the treatment of the higher boiling charge stocks, i.e., those boiling in the range from about 700° to 1100° F. or higher. Pressures between 400 and 1,000 pounds per square inch gauge are preferred for the hydrogenation of the lower boiling charge stocks, i.e., those boiling between 250° and 700° F. These lower pressures are also satisfactory with higher boiling fractions which do not contain excessively large amounts of nitrogen or when utilizing highly active catalysts with lower space velocities.

As with the oxidation step above, the removal of nitrogen-containing compounds will be a function not only of temperature and pressure, but also of contact time. The reciprocal of contact time or the space velocity may be between 0.1 and 10 volumes of oil per volume of catalyst per hour with preferred space velocities between 0.2 and 6. The hydrogen recycle rate is maintained between about 1,000 and 20,000 standard cubic feet per barrel, with preferred rates between about 2,000 and 10,000 standard cubic feet per barrel. The particular pressure, temperature, space velocity and hydrogen rate to be employed for any particular reaction, will depend upon the degree

of nitrogen removal desired. In general, the higher the temperature and pressure and the lower the space velocity, the greater will be the removal of nitrogen-containing compounds.

Resort may be had to such variations and modifications as fall within the spirit of the invention and the scope of the appended claims.

We claim:

1. A process for reducing the nitrogen content of a nitrogen-containing petroleum fraction which comprises contacting said nitrogen-containing petroleum fraction with an oxygen-containing gas in the presence of a solid catalyst comprising an oxide of phosphorus under mild oxidation conditions including a temperature between 100° and 650° F. to minimize the production of oxygenated compounds.

2. A process according to claim 1 wherein the catalyst is phosphorus pentoxide.

3. A process according to claim 2 wherein the nitrogen-containing petroleum fraction boils between about 250° to 1100° F. at atmospheric pressure.

4. A process for reducing the nitrogen content of a nitrogen-containing petroleum fraction boiling between 250° and 1100° F. at atmospheric pressure which comprises admixing said nitrogen-containing petroleum fraction and a solid catalyst comprising an oxide of phosphorus and contacting said admixture with an oxygen-containing gas under mild oxidation conditions including a temperature between 100° and 650° F. to minimize the production of oxygenated compounds.

5. A process according to claim 4 wherein the catalyst is phosphorus pentoxide.

6. A process for reducing the nitrogen content of a nitrogen-containing petroleum fraction which comprises contacting said nitrogen-containing petroleum fraction with an oxygen-containing gas in the presence of a solid catalyst comprising a mixture of the oxides of phosphorus and vanadium wherein the atomic ratio of vanadium to phosphorus is between 0.02:1 and 5:1 under mild oxidation conditions including a temperature between 100° and 650° F. to minimize the production of oxygenated compounds.

7. A process according to claim 6 wherein the catalyst is a mixture of phosphorus pentoxide and vanadium pentoxide and wherein the atomic ratio of vanadium to phorus is between 0.02:1 and 5:1.

8. A process for reducing the nitrogen content of a nitrogen-containing petroleum fraction boiling between 250° and 1100° F. at atmospheric pressure which comprises admixing said nitrogen-containing petroleum fraction and a solid catalyst comprising a mixture of the oxides of phosphorus and vanadium wherein the atomic ratio of vanadium to phosphorus is between 0.02:1 and 5:1 and contacting said admixture with an oxygen-containing gas under mild oxidation conditions including a temperature between 100° and 650° F. to minimize the production of oxygenated compounds.

9. A process according to claim 8 wherein the catalyst is a mixture of phosphorus pentoxide and vanadium pentoxide and wherein the atomic ratio of vanadium to phosphorus is between 0.06:1 and 0.5:1.

10. A process for reducing the nitrogen content of a nitrogen-containing petroleum fraction which comprises contacting said nitrogen-containing petroleum fraction with an oxygen-containing gas in the presence of a solid catalyst comprising an oxide of phosphorus under mild oxidation conditions and thereafter subjecting the mildly oxidized nitrogen-containing petroleum fraction to hydrogenation.

11. A process according to claim 10 wherein the oxide of phosphorus catalyst comprises phosphorus pentoxide.

12. A process according to claim 10 wherein the catalyst comprises a mixture of the oxides of phosphorus and vanadium wherein the atomic ratio of vanadium to phosphorus is between 0.02:1 and 5:1.

13. A process according to claim 12 wherein the catalyst is a mixture of phosphorus pentoxide and vanadium pentoxide and wherein the atomic ratio of phosphorus to vanadium is between 0.06:1 and 0.5:1.

14. A process for reducing the nitrogen content of a nitrogen-containing petroleum fraction which comprises contacting said nitrogen-containing petroleum fraction with an oxygen-containing gas in the presence of a solid catalyst comprising a mixture of phosphorus pentoxide and vanadium pentoxide wherein the atomic ratio of vanadium to phosphorus is between 0.02:1 and 5:1 under mild oxidation conditions including a temperature of between 100° F. and 650° F. and a contact time of at least one minute and thereafter contacting the mildly oxidized nitrogen-containing petroleum fraction with a hydrogenation catalyst under hydrogenation conditions including a temperature between 550° and 750° F., a pressure between 200 and 2,000 pounds per square inch gauge and a space velocity between 0.1 and 10 vol./vol./hr.

15. A process according to claim 14 wherein the charge stock is a mixture of nitrogen-containing petroleum hydrocarbons boiling between 400° and 800° F.

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