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This invention relates to processes for the selective hy-
drogenative removal of nitrogen compounds from hydro-
carbon streams. In a particular embodiment, the inven-
tion is concerned with a catalytic process for the substan-
tially complete removal of nitrogenous contaminants from
distillable hydrocarbon oils to be used as feed stocks in
subsequent catalytic conversion processes.

It has long been known that nitrogen compounds could
be removed to some extent from petroleum hydrocarbons
by conventional hydrofining processes. However, even
in the case of relatively low boiling feed stocks, substan-
tially complete nitrogen removal cannot be accomplished
by conventional hydrofining without the use of rather se-
vere conditions of temperature and pressure and a rela-
tively low space velocity. In the hydrofining process the
hydrocarbon oil is treated with hydrogen at elevated tem-
perature and pressure in contact with various catalysts
generally comprising chromium and/or molybdenum ox-
ide together with iron, cobalt, and/or nickel oxides on a
porous oxide support, such as alumina or silica-alumina.
Previous investigations into the effect of the metals con-
tent of the hydrofining catalysts on their activity have in-
dicated that there is little to be gained by the use of metal
contents above about 14%. For example, it is indicated
in Patent Number 2,758,957 to K. Nozaki that increasing
the total metals concentration above 15% by weight is of
little benefit, and that decreasing the nickel content of a
Ni-Mo catalyst to an atomic ratio of 1:3 increased the
activity for hydrogenation.

The present invention is based upon the discovery that
for the purpose of substantially completely removing con-
taminating nitrogen compounds from distillable hydro-
carbon oils to low residual nitrogen levels, catalysts con-
taining large concentrations of both nickel and molybde-
num are outstanding in their properties and are not the
equivalent of the large group of catalytic materials dis-
closed in the prior art. Specifically, the catalysts used in
the hydrodenitrification process of this invention comprise
sulfided nickel and molybdenum on predominantly alu-
mina carriers, containing 4–10% nickel together with
15.5–30% molybdenum by weight, expressed as the
metals. The preferred catalysts contain 6–8% nickel and
21–23% molybdenum. The process comprises contact-
ing the hydrocarbon oil with a sulfided high metals con-
tent nickel-molybdenum-alumina catalyst in the presence
of hydrogen at critical conditions of temperature, pressure,
and space velocity.

There are several aspects to this invention. In one
aspect the invention provides a process whereby more
than 99.9% of the initial nitrogen content of non-refrac-
tory hydrocarbon oils boiling up to about 600° F. may
be readily removed using relatively mild conditions of
temperature and pressure and/or high space velocities.
In many cases 99.99% or more of the nitrogen is re-
moved. In another aspect the invention provides a proc-
ess whereby more than 99.9% of the initial nitrogen con-
tent of highly refractory hydrocarbon oils boiling up to
about 750° F. may be removed using convenient condi-
tions of temperature and pressure and moderate space
velocities, which degree of nitrogen removal was hereto-
fore unattainable in a commercially practical process. In
another aspect the invention provides a process whereby

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more than 99% of the initial nitrogen content of refrac-
tory or high boiling hydrocarbon oils boiling up to about
860° F. may be removed using moderate conditions of
temperature, pressure, and space velocity, which degree
of nitrogen removal was heretofore unattainable at eco-
nomically feasible operating conditions. In still another
aspect the invention provides a process whereby more
than 80% of the initial nitrogen content of heavy hydro-
carbon distillates boiling up to about 1050° F. may be
removed using relatively mild conditions of temperature,
pressure, and/or space velocity, which degree of purifica-
tion was heretofore unattainable without the use of con-
ditions resulting in substantial cracking and coke forma-
tion.

The feed stocks which may be treated by the process
of this invention are distillable hydrocarbon oils. By this
is meant those non-residual hydrocarbon streams normally
processed in petroleum refineries, and including naphthas,
kerosenes, straight run and cracked distillates, distillates
derived from shale oil or gilsonite deposits, light and
heavy cycle oils, and gas oils. In short, the process is
applied to predominantly liquid hydrocarbon streams hav-
ing an initial boiling point above about 180° F. and an
end point below about 1050° F.

Hydrocarbon oils contain varying amounts of nitrogen
compounds, ranging from several parts per million up to
1–3%, depending on the boiling range of the oil and
the nature of the crude petroleum or other hydrocarbona-
ceous deposit from which it was derived. It is not un-
common to report both total nitrogen and basic nitrogen
in analyzing hydrocarbon oils. As used herein, the term
"nitrogen content" refers to total nitrogen, determined by
Kjeldahl analysis, expressed in parts per million of nitro-
gen.

The removal of contaminating nitrogen compounds
from hydrocarbon distillates to very low residual levels
is of particular value where the distillate is to be con-
verted in a low temperature hydrocracking process. In
the low temperature hydrocracking process a hydrocarbon
distillate of low nitrogen content is contacted with certain
dual function catalysts, such as cobalt or nickel sulfide on
a silica-alumina cracking catalyst support, under controlled
conditions of temperature, pressure, hydrogen throughput,
and space velocity, to effect a substantial conversion of
the feed to liquid products boiling below the initial boiling
point of the feed and containing a high ratio of iso- to
normal paraffins, with negligible coke production and only
a very small production of light gaseous hydrocarbons.
Such a process has been denominated by the proprietary
name "Iso cracking." Pretreatment of the feed to a low
temperature hydrocracking process to reduce the nitrogen
content to less than 10 p.p.m. permits the use of lower
operating temperatures (e.g., below 700° F.), extends
the on stream time, and results in a more favorable prod-
uct distribution. More favorable results are obtained
when the feed has a nitrogen content of only 1–2 p.p.m.
Nitrogen contents below 1 p.p.m. are considerably more
advantageous.

A typical light cycle oil derived from a fluid catalytic
cracking process had a gravity of 25.4° API, an initial
boiling point of 415° F., an end point of 550° F., and
an initial nitrogen content of 900 p.p.m. This material
can be virtually quantitatively converted to gasoline boil-
ing range hydrocarbons by low temperature hydrocrack-
ing provided the nitrogen content is first reduced to less
than 10 p.p.m. The inability of conventional hydrofin-
ing catalysts to effect such a degree of nitrogen removal
at ordinary processing conditions is shown by the data
given in Table I. The light cycle oil was contacted with
each of the catalysts described in Table I at 615–620° F.,
800 p.s.i.g., in the presence of 4000 s.c.f. H_2/bbl., at a

liquid hourly space velocity (LHSM) of 1.0 v./v./hr. based on the light cycle oil feed.

TABLE I

Hydrofining of Light Cycle Oil

Catalyst	A	B	C	D	E
Wt. percent Molybdenum	6.8	8.3	6.5	9.2	15.3
Wt. percent Nickel			2.4	3.1	2.7
Wt. percent Cobalt	2.7	2.7	0.3		
Wt. percent Metals, Total	9.5	11.0	9.2	12.3	18.0
Product:					
p.p.m. Nitrogen	244	345	145	108	108
Percent Nitrogen Removal	73	62	84	88	88
Catalyst Relative Activity	1.00	0.75	1.4	1.5	1.5

Catalyst A is a commercially available hydrofining catalyst prepared by the method described in Patent Number 2,878,193 to J. W. Scott. The method comprises solution impregnation of a cobalt salt (followed by calcining to the oxide) on a coprecipitated molybdenum oxide-alumina support. Catalyst B and catalyst C are other commercial hydrofining catalysts wherein the metals molybdenum, nickel, and/or cobalt are supported on alumina. Catalyst D is a nickel-molybdenum-alumina catalyst prepared by impregnating an alumina carrier with an aqueous solution of nickel nitrate, drying and calcining, and then impregnating with aqueous ammonium molybdate, drying and calcining. Catalyst E was prepared in the same manner as catalyst D, but using more concentrated impregnating solutions to provide a total metals content greater than has been found exemplified in the hydrofining or denitrification art. It is apparent that this increase in metal content was of no benefit, as predicted by the prior art. All of the catalysts were sulfided to convert the metal oxides predominantly to metal sulfides prior to contacting with the light cycle oil.

Catalyst A, being intermediate in activity to catalysts B and C, has been assigned a relative activity for hydrodenitrification of 1.00 expressed on a space velocity basis. We have found that the hydrodenitrification reaction closely approximates a pseudo first-order rate reaction with respect to the fractional removal of the initial nitrogen content over the range of operating conditions utilized, i.e., $-\log(1-x) = kt$, where x is the percent nitrogen removal expressed as a decimal, t is the contact time (inversely proportional to LHSV), and k is the reaction rate constant (proportional to relative activity). From this it can be shown that to reduce the nitrogen content of the light cycle oil from the initial 900 p.p.m. to less than 10 p.p.m. would require the use of a catalyst having a relative activity of about 3.5 under the conditions of the above test. For the substantially complete hydrodenitrification of distillates having a greater initial nitrogen content or of a more refractory nature (with respect to ease of denitrification) than the light cycle oil, a catalyst having a relative activity of about 4 or better is required.

We have found that to obtain the high activities required for the substantially complete removal of nitrogen compounds, in accordance with this invention, the catalyst must contain at least 15.5% molybdenum and must also contain at least 4% nickel. Specifically, the highly active catalysts utilized in the process of this invention have nickel contents in the range 4–10% by weight and molybdenum contents in the range 15.5–30% by weight. The catalysts are conveniently prepared by impregnating an alumina support with nickel and molybdenum compounds convertible to the oxides by calcination to give the finished catalyst the desired metals content, calcining, and then sulfiding to convert the nickel and molybdenum oxides predominantly to the sulfides.

When the light cycle oil described previously, having a nitrogen content of 900 p.p.m., was contacted with the nickel-molybdenum-alumina catalysts of this invention under the same operating conditions as were used in the

previous test, the nitrogen was substantially completely removed, as shown in Table II.

TABLE II

Hydrodenitrification of Light Cycle Oil

Catalyst	J	K	L	M	N	P
Wt. percent Molybdenum	18.9	24.3	22.0	21.8	21.8	21.7
Wt. percent Nickel	4.7	4.1	5.9	7.6	10.0	4.9
Wt. percent Metals, Total	23.6	28.4	27.9	29.4	31.8	26.6
Product:						
p.p.m. Nitrogen	4	[1] 4.5	3	1.5	[1] 4	6
Percent Nitrogen Removal	99.55	99.5	99.8	99.8	99.55	99.3
Catalyst Relative Activity	3.8	3.7	4.0	4.6	3.8	3.5

[1] Corrected value based on data at 570–575° F.

As shown by the data of Table II, nickel-molybdenum-alumina catalysts containing 4 to 10% Ni together with from about 19 to 25% Mo are remarkably active with respect to hydrodenitrification, a fact which could not be predicted from a consideration of the catalysts containing lesser quantities of the metals. The molybdenum content may be as low as 15.5% or as high as 30%, but the use of more than 25% Mo is generally unwarranted.

It will be observed that to determine the percent nitrogen removal required the accurate measurement of residual nitrogen concentrations of less than 10 p.p.m. The analyses were made in a "nitrogen-free" laboratory, set aside for the purpose, by a modified Kjeldahl procedure involving the extraction of a fairly large sample (100 gm.) with 92% sulfuric acid. Highly purified water and caustic must be used, and all glassware should be cleaned with hot caustic. At the 1 p.p.m. level the analyses are considered accurate to ±0.1 p.p.m.

Catalysts J, K, L, M, N and P were prepared by substantially the same procedure in order to insure that the results would be indicative solely of the effect of the metals content. Catalysts D and E of Table I were prepared in this same manner, namely, alternate impregnation of alumina with aqueous solutions of nickel and molybdenum compounds convertible to the oxides by calcination. The exact procedure is exemplified by the preparation of catalyst M, described in the following example.

EXAMPLE 1

A high grade alumina, obtained commercially in the form of $\frac{1}{16}''$ extrusions, having a pore volume of 0.65 cc./gm. and a surface area by nitrogen adsorption of 270 m.²/gm. (B.E.T. method), was immersed for 2 hours at room temperature in an aqueous solution of nickel nitrate, prepared by adding 2 parts by weight

$$Ni(NO_3)_2 \cdot 6H_2O$$
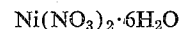
to 1.5 parts H_2O. The pH was about 5.2. The impregnated particles were dried for 10 hours at 400° F., and then calcined for 4 hours at 900° F. The calcined particles were then immersed for 2 hours in an aqueous solution of ammonium molybdate, prepared by mixing 3.9 parts of 20% NH_4OH, 3.2 parts of H_2O, and 2.9 parts of MoO_3, by weight. The pH was maintained at about 8.8 by the addition of more ammonium hydroxide solution. The impregnated particles were dried for 10 hours at 400° F., and then calcined for 4 hours at 900° F. The catalyst was then given a second molybdenum impregnation in the same manner, dried, and calcined as before. The nickel oxide-molybdenum oxide-alumina catalyst so produced contained 7.6% Ni and 21.8% Mo, calculated as the metals, and had a surface area of 119 m.²/gm. The oxide catalyst was then placed in a test reactor, and hydrogen was passed therethrough for about 1 hour, while raising the temperature to 650° F., at a pressure of 800 p.s.i.g. A vaporized solution of dimethyl-disulfide in heptane was added to the H_2 and fed to the reactor for a ten-hour period, at which time approxi-

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mately 2.8 times the amount of sulfur required to convert the NiO and MoO₃ to Ni₃S₂ and MoS₂ had been introduced. The ratio of dimethyldisulfide to hydrogen was about 1 to 12, by volume, at the reactor inlet. The final catalyst had a relative activity of 4.6.

The above order of impregnation, namely, first nickel and then molybdenum, is preferred. When the reverse order was used, there was a tendency for molybdenum to be leached out of the catalyst during the second (nickel) impregnation. In addition, somewhat higher activities are obtained by following the preferred order of impregnation. Catalyst P was prepared by the reverse order of impregnation, as described in the following example.

EXAMPLE 2

Two hundred and fifty cc. of alumina, obtained commercially in the form of 8–14 mesh pieces, having a pore volume of 0.49 cc./gm. and a surface area by nitrogen adsorption of 180 m.²/gm., was immersed for 24 hours at room temperature in a solution of ammonium paramolybdate, prepared by adding to 94.6 gms. of (NH₄)₆Mo₇O₂₄·4H₂O sufficient water to make up 200 ml. of solution. The impregnated alumina was then drained free of excess solution, dried for 24 hours at 250° F., and calcined for 6 hours at 900° F. This material was then vacuum impregnated with molybdenum using an ammonium paramolybdate solution of the same molybdenum content as in the first impregnation, to which 0.2 cc. of concentrated ammonium hydroxide had been added per gram of ammonium molybdate. The once-impregnated alumina was placed in a flask, the flask evacuated, and 200 ml. of the ammonium molybdate solution was introduced. The vacuum was released, and the mixture was allowed to stand for 15 minutes at atmospheric temperature and pressure. After drying and calcining as before, this material was given a third molybdenum impregnation in the same manner as the second impregnation. After drying and calcining as before, the alumina-molybdenum oxide catalyst was vacuum impregnated with nickel, in the same manner, using a solution prepared by adding to 319 grams of

$$Ni(NO_3)_2·6H_2O$$
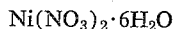
sufficient water to make up 200 ml. of solution. The four-times impregnated catalyst was then dried at 250° F. for 24 hours and calcined at 900° F. for 6 hours. The nickel oxide-molybdenum oxide-alumina catalyst so produced contained 4.9% Ni and 21.7% Mo, calculated as the metals, and had a surface area of 93 m.²/gm. The oxide catalyst was then sulfided with dimethyldisulfide in the same manner as in Example 1. The final catalyst had a relative activity of 3.5.

To obtain high activity for the hydrodenitrification process the high metals content nickel oxide-molybdenum oxide-alumina catalysts must be sulfided prior to contacting with the hydrocarbon oils to be treated. Sulfiding is preferably accomplished in the manner described in Example 1, by passing over the oxide catalyst a sulfiding agent such as H₂S, CS₂, mercaptans, disulfides, and the like. When H₂S is used, the sulfiding may be effected with or without a carrier gas such as hydrogen or nitrogen. High activity catalysts, comparable to those described in Table II, have been prepared by sulfiding directly with pure H₂S. Where sulfur compounds other than H₂S are employed, hydrogen should also be present, preferably under pressure, and the temperature should be sufficiently elevated for ready conversion of the sulfur compound to H₂S, say about 400° F. in the case of mercaptans and disulfides. Extensive reduction of the oxides to the metals is preferably avoided, since usually more active catalysts result if the oxides are sulfided directly. Further, to minimize reduction of the oxides, the temperature during sulfiding preferably should not exceed 750° F., and more preferably is at or below 650° F.

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In a preferred method of sulfiding, mercaptan or organic disulfide addition is continued over a period of about 2–10 hours until at least 1.5 times the theoretical amount of sulfur required to convert the nickel and molybdenum ovides to Ni₃S₂ and MoS₂, respectively, has been added. The exact form of the metals in the final catalyst is not known, and it is not meant to represent that the nickel and molybdenum are quantitatively converted to Ni₃S₂ and MoS₂. However, it is important that an excess of the sulfiding agent be used in order to insure conversion of the metal oxides predominantly to the sulfides. When the oxide catalysts of this invention are contacted directly with the hydrocarbon oil and hydrogen at or slightly below the normal operating temperatures, relying on the inherent sulfur content of the hydrocarbon oil to effect sulfiding, the hydrodenitrification activity is only slightly better than that of the catalysts described in Table I.

The preferred catalyst support is substantially a microporous alumina, such as is commercially available or may be prepared by well known methods. The inclusion in the support of a small amount of silica, say up to 5%, would not be expected to affect the catalyst activity materially, and may be advantageous in stabilizing the catalyst in some cases. Highly active catalysts have also been prepared by impregnating a coprecipitated molybdenum oxide-alumina carrier with nickel and additional molybdenum to provide metal concentrations in the required range, i.e., about 15.5% molybdenum and about 5% nickel. Alumina base hydrofining catalysts of conventional molybdenum and cobalt content may also be utilized as the support if the area and pore volume are adequate. Cobalt cannot be substituted for nickel, as cobalt-molybdenum catalysts containing 4–10% cobalt and 15.5–30% molybdenum are only about half as active for denitrification as the corresponding nickel-molybdenum catalysts. However, the inclusion of a small amount of cobalt in the catalyst in addition to the 4–10% nickel does not materially affect the basic and novel characteristics of the catalyst for denitrification, nor does the inclusion of minor amounts of zinc, copper, or similar metals. The inclusion of such metals appears to be somewhat deleterious, and they are preferably excluded. The support should be predominantly alumina.

To permit the required incorporation in the alumina carrier of more than 19% by weight of the metals, nickel and molybdenum, without substantially filling the pores, the alumina should have an initial pore volume in excess of about 0.2 cc./gm. It is preferred that the alumina have a pore volume of greater than about 0.4 cc./gm. Since the impregnation with large quantities of nickel and molybdenum results in a reduction of the surface area, it is most desirable to start with a carrier having a surface area in excess of about 150 m.²/gm., as determined by nitrogen adsorption; although the surface area may be as low as 75 m.²/gm. if, for example, the catalyst is to contain only 4–5% Ni and 15.5–19% Mo. The alumina may be calcined if desired prior to impregnation with the metals, but precalcining does not appear to be essential.

Where the catalyst is to be employed in a fixed bed process, the alumina is preformed, as in the shape of small spheres, pellets, rods, or irregular pieces. In the preferred method of preparation, a preformed alumina carrier is first immersed in an aqueous solution of a nickel compound readily convertible to the oxide by calcination, such as nickel nitrate, nickel acetate, and the like. Nickel sulfate is a less desirable impregnating compound, and nickel chloride is even less desirable, because of the high temperatures required for decomposition or conversion to the oxide. The preferred medium is an aqueous solution of nickel nitrate containing 2–12% Ni, depending on the final nickel concentration desired in the catalyst. The impregnated carrier is then dried and cal-

cined or otherwise treated to convert the nickel compound to an insoluble form, preferably nickel oxide.

The nickel oxide-alumina catalyst is then impregnated with an aqueous solution of a molybdenum compound convertible to the oxide by calcination, such as ammonium molybdate, or a solution of molybdic acid in an oxalic acid solution containing nitric acid, etc. When ammonium molybdate is used, the pH should be controlled at above about 7.7 to prevent precipitation of molybdenum oxide. Preferably, the pH is maintained at about 8.7 or above to avoid the formation of a molybdenum oxide crust on the outer surface of the catalyst. The twice-impregnated catalyst is then dried and calcined. This catalyst can then be given an additional molybdenum impregnation, again followed by drying and calcining, when it is desired to prepare a catalyst containing above 16% molybdenum. However, molybdenum contents up to about 19% by weight in the finished catalyst have been obtained by a single impregnation with ammonium molybdate.

The final calcination is effected at temperatures in the range 600–1100° F. When a high nickel and molybdenum content catalyst was calcined at or slightly above 1200° F., the relative activity for hydrodenitrification was approximately halved. Thus, when the nickel is incorporated after the molybdenum, the nickel compound used should be one convertible to the oxide at a temperature below 1200° F. The optimum calcining temperature appears to be between 800° F. and 1000° F. The calcinations are usually carried out in the presence of hot air, but an inert gas atmosphere may instead be used since oxygen is already available in the preferred impregnating compounds.

Although the hydrodenitrification process may be carried out in a number of ways, such as by maintaining the catalyst in a fluidized bed or as a downflowing column of granular solids, the process is most suitably carried out using a fixed bed of catalyst in the manner depicted in the attached drawing. Since the nickel-molybdenum catalysts of this invention maintain their high activity over protracted periods of use, a continuous non-regenerative type of operation is obtainable and is normally preferred. The catalysts may be regenerated periodically by the oxidative removal of carbon deposits formed during extended use.

Referring to the drawing, the hydrocarbon oil to be treated enters the process via line 1. Hydrogen-rich gas is admixed with the hydrocarbon oil feed via line 2, and the admixture, after heating to the desired operating temperature, passes to reactor 4 via line 3. Alternately, the hydrocarbon and hydrogen streams may be separately heated before mixing. Reactor 4 is packed with sulfided high metals content nickel-molybdenum-alumina catalyst in the form of small particles such as spheres, pellets, or extrudates. The hydrocarbon oil feed may be completely vaporized in the case of low boiling feed stocks, but mixed phase flow is preferred in the case of higher boiling stocks. In passing through reactor 4 the nitrogen compounds in the hydrocarbon oil are substantially converted to ammonia with concomitant consumption of hydrogen. The reactor effluent leaves via line 5, and is cooled to condense the normally-liquid hydrocarbon portion and then passed via line 7 to separation drum 8. To assist in the removal of ammonia from the effluent, water or acidulated water may be added through line 6. A water phase containing dissolved NH₃ which then separates in drum 8 may be withdrawn via line 14 and discarded. A major portion of the ammonia formed may be removed in this fashion.

Hydrogen-rich recycle gas is separated in drum 8 and withdrawn through line 9 to compressor 10, for return to the reaction zone in combination with additional feed via lines 11 and 12. Make-up hydrogen is introduced through line 13 to compensate for that consumed in the process. It may be desirable to withdraw a small bleed

stream of recycle gas via line 12 to limit the build-up in the recycle stream of light gaseous hydrocarbons, such as may be introduced with the make-up hydrogen.

Liquid hydrocarbon effluent, containing residual ammonia and other hydrogenated impurities, is withdrawn from drum 8 and passed to distillation zone 16 via line 15. Zone 16 is operated at a materially lower pressure than drum 8, and may comprise another simple separation drum, or it may be a stripping column, as shown. Steam, hydrogen, or other inert stripping gas is introduced via line 17 to assist in the complete removal of ammonia and other light gaseous by-products overhead via line 19. Purified hydrocarbon oil substantially free of nitrogen compounds is recovered in line 18. Alternately, or in addition to water washing and/or distillation, equivalent means for removing the NH₃ may be provided, for example, by adsorption on a microporous metal-aluminosilicate (molecular sieve), activated earth, etc.

Conditions of temperature, pressure, hydrogen throughput, and space velocity in the reactor are correlated to provide the desired degree of nitrogen removal. Higher temperatures, pressures, and/or hydrogen throughputs are required when treating the higher boiling feed stocks and those containing the more refractory nitrogen compounds. A particular advantage of the process is that it permits the hydrodenitrification of refractory stocks at comparatively mild conditions of temperature and pressure and/or the use of high space velocities. The term "refractory" is used herein the reference to the relative difficulty with which nitrogen is removed from the respective feed stocks. In general, the complex nitrogen compounds found in high boiling hydrocarbon fractions and cracked cycle oils are more resistant to hydrogenation than the lower boiling compounds.

Temperature has a large influence on the rate of conversion of the nitrogen compounds and is adjusted upwards to maintain the hydrodenitrification rate as the catalyst ages or is deactivated through protracted use. The temperature should be in the range 500–850° F., preferably 600–750° F. The rate of hydrodenitrification is fairly low at temperatures below 550° F. At temperatures much above 800° F. substantial cracking of the hydrocarbon oil and coke formation normally occurs, and the production of light gases increases markedly. With less active catalysts than those of the present invention the temperature at the start of the run must be much higher, and the on stream time between catalyst regenerations is correspondingly reduced. The active hydrodenitrification catalysts of the present invention make possible the use of temperatures at the lower end of the operating range for long periods of time. Hence, a special feature of this invention is the relatively low temperature of operation and the resultant long catalyst life.

Elevated pressures advantageously influence the rate of hydrodenitrification as well as extending the catalyst activity and life. Pressures as low as 200 p.s.i.g. may be employed when treating light naphthas, whereas pressures up to 4000 p.s.i.g. may be advisable for the substantially complete hydrodenitrification of highly refractory and high boiling stocks. Using the highly active catalysts of this invention the pressure will generally be in the range 200–2000 p.s.i.g.

Hydrogen throughput rate is maintained above about 500 s.c.f./bbl. of hydrocarbon oil, and is preferably in the range 1000–10,000 s.c.f./bbl. More generally, at least sufficient hydrogen is provided to supply that consumed in the conversion of the nitrogen compounds and to compensate for incidental hydrogenation of unsaturates and oxygen, sulfur, and halogen compounds, while maintaining a significant hydrogen partial pressure. The use of more than 10,000 s.c.f. of H₂/bbl. does not generally produce sufficient improvement in conversion rate to justify the increased cost.

Table III presents physical inspection data on several

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typical distillable hydrocarbon oils which have been treated by the process of this invention for the substantially complete removal of nitrogen compounds.

TABLE III

| Hydrocarbon Oil | Boiling Range | | | | | Gravity, °API | Initial, p.p.m. N (total) |
	IBP	5%	50%	95%	EP		
Cracked Naphtha	274	291	331	402	419	44.8	220
FCC Light Cycle Oil	415	451	480	523	550	25.4	900
Coker Distillate	380	447	507	582	605	24.8	2,500
Arabian Gas Oil	585	626	671	714	723	29.1	462
Heavy Cycle Oil	565	631	704	790	840	22.6	566
Heavy Gas Oil	513	602	718	818	862	19.5	2,500
Cat. Cracker Feed	385	14% 625	78% 925		1,045	20.6	4,000

The cracked naphtha and the light cycle oil of Table III are examples of relatively non-refractory hydrocarbon oils. The removal of more than 99.9% of the initial nitrogen content from such distillates is readily accomplished by the hydrodenitrification process. For example, Table IV below presents typical and preferred operating conditions which can be used to reduce the nitrogen content of these and similar stocks to less than 1 p.p.m. using the preferred high nickel and molybdenum content catalysts, having relative activities of about 4 or better. Using the highly active catalysts disclosed herein, containing 4–10% Ni and 15.5–25% Mo, feed stocks for low temperature hydrocracking containing less than about 1 p.p.m. nitrogen can be prepared from non-refractory hydrocarbon distillates similar to the cracked naphtha and light cycle oil, boiling up to about 600° F. and having initial nitrogen contents up to about 10,000 p.p.m., by hydrodenitrification under the indicated preferred operating conditions.

TABLE IV

Hydrodenitrification of Non-Refractory Oils

| | Operating Conditions | |
	Typical	Preferred Range
Feed	Cracked Naphtha	<450° F., E.P. Naphthas.
Initial, p.p.m. N	220	<10,000.
Final, p.p.m. N	0 1	<1.
Percent Nitrogen Removal	99.95	99.9-99.99+.
Temperature, °F	575-585	500-700.
Pressure, p.s.i.g	800	200-1,000.
H₂ Throughput, s.c.f./bbl	4,000	500-5,000.
Space Velocity, LHSV	2	1-10.
Feed	Light Cycle Oil	<600° F., E.P. Middle Distillates.
Initial, p.p.m. N	900	<10,000.
Final, p.p.m. N	1	<1.
Percent Nitrogen Removal	99.9	99.9-99.99.
Temperature °F	625-635	550-750.
Pressure, p.s.i.g	800	500-1,500.
H₂ Throughput, s.c.f./bbl	4,000	1,000-10,000.
Space Velocity, LHSV	1	0.5-5.

When the cracked naphtha is contacted with the hydrofining catalyst (catalyst A, as described above) at 800 p.s.i.g., 4000 s.c.f. H₂/bbl., and 2 LHSV, the temperature must be raised to above 650° F. to obtain the same degree of nitrogen removal. At 650° F. a space velocity of about 8 or better can be used with the active catalysts of this invention. Thus, a particular advantage of the invention is that it permits the use of high space velocities in treating light hydrocarbons. Similarly, using catalyst A to treat the light cycle oil at 800 p.s.i.g., 4000 s.c.f. H₂/bbl., and 1 LHSV, the temperature must be raised to above 750° F. to obtain the indicated degree of nitrogen removal.

The coker distillate and the Arabian gas oil of Table III are highly refractory stocks, and they require more severe conditions to effect the removal of more than 99.9% of the nitrogen compounds. Table V presents

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typical and preferred operating conditions which can be employed to reduce the nitrogen content of these stocks to 1 p.p.m. or less when using the high nickel and molybdenum content catalysts of this invention. Feed stocks for low temperature hydrocracking, containing less than 10 p.p.m. nitrogen, can be prepared from such refractory distillates, boiling up to about 750° F. and having initial nitrogen contents up to about 10,000 p.p.m., by hydrodenitrification under the indicated preferred operating conditions and without substantial cracking.

TABLE V

Hydrodenitrification of Refractory Oils

| | Operating Conditions | | |
| | Typical | | Preferred Range |
Feed	Coker Distillate.	Arabian Gas Oil.	<750° F., E. P. Gas Oil Distillates.
Initial, p.p.m. N	2,500	462	<10,000.
Final, p.p.m. N	1	0.5	<10.
Percent Nitrogen Removal	99.96	99.9	99-99.99.
Temperature, °F	700-715	685-700	650-890.
Pressure, p.s.i.g	1,200	1,200	500-2,000.
H₂ Throughput, s.c.f./bbl	6,500	6,000	1,000-10,000.
Space Velocity, LHSV	0.5	0.5	0.2-5.

When the coker distillate or the Arabian gas oil are contacted with the hydrofining catalyst (catalyst A) at 1200 p.s.i.g., 6000–6500 s.c.f. H₂/bbl., and 0.5 LHSV, the temperature must be raised to above 850° F. to obtain the indicated typical nitrogen removal. At such high temperatures excessive cracking of the feed stocks occurs, and the catalyst is rapidly deactivated by coke formation.

Hydrocarbon distillates such as the cracked naphtha, light cycle oil, coker distillate, and Arabian gas oil, after substantially complete removal of the contaminating nitrogen compounds, are particularly good feed stocks for the low temperature hydrocracking process. In that process the purified oil is contacted at 350–750° F., 500–3000 p.s.i.a. H₂ partial pressure, 0.3–5 LHSV, and in the presence of 2000–15,000 s.c.f. H₂/bbl. with a low temperature hydrocracking catalyst. The advantages gained by pretreatment of such hydrocarbon oils in accordance with this invention are illustrated by the following example:

EXAMPLE 3

The FCC light cycle oil of Table III was contacted at 620° F., 800 p.s.i.g., in the presence of 4000 s.c.f. H₂/bbl., and at a space velocity of 1 LHSV with catalyst M, prepared as described in Example 1, comprising 7.6% Ni and 21.8% Mo (calculated as the metals) supported on alumina and presulfided with dimethyldisulfide. After water washing and distilling to remove NH₃ the product oil analyzed 1.5 p.p.m. nitrogen (total). When the temperature was raised to 650° F. the product analyzed only 0.1 p.p.m. nitrogen. Under the latter higher temperature conditions the product contained 100 p.p.m. nitrogen when the conventional hydrofining catalyst (catalyst A) was used. When the light cycle oil containing 1.5 p.p.m. nitrogen is contacted with a low temperature hydrocracking catalyst, comprising 6% nickel sulfide supported on a silica-alumina cracking catalyst, the hydrocracking process may be initiated at 570° F., 1500 p.s.i.g., 8000 s.c.f. H₂/bbl., and 1.0 LHSV, and 60% conversion per pass may be maintained for over 2500 hours by gradually raising the hydrocracking reactor temperature to 715° F. When the feed contains only 0.1 p.p.m. nitrogen, the same conversion may be maintained for over 4000 hours before a temperature of 715° F. is reached. But, if 100 p.p.m. nitrogen were present in the feed, the temperature would have to be raised to above 700° F. very early in the run, and the hydrocracking run length (terminated at 715° F.) would be reduced to less than 100 hours.

In the treatment of high boiling stocks such as the heavy

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cycle oil, heavy gas oil, and cat cracker feed described in Table III, a broad range of conditions may be used depending on the degree of nitrogen removal desired and the use to which the stock is to be put. Table VI presents typical and preferred operating conditions which can be employed to remove more than 99% of the nitrogen from the heavy cycle oil and heavy gas oil using the preferred catalysts of this invention. As shown in Table VI, the nitrogen content of such high boiling oils, boiling up to about 860° F., can be sufficiently reduced by this hydrodenitrification process such that these and similar stocks may also be subjected to low temperature hydrocracking.

TABLE VI

Hydrodenitrification of High Boiling Oils

	Operating Conditions		
	Typical		Preferred Range
Feed	Heavy Cycle Oil.	Heavy Gas Oil.	<860° F., E. P. Gas Oils.
Initial, p.p.m. N	566	2,500	<10,000.
Final, p.p.m. N	1	10	<10.
Percent Nitrogen Removal.	99.8	99.6	99–99.9.
Temperature, ° F.	660–675	735–750	600–800.
Pressure, p.s.i.g.	1,200	1,600	500–4,000.
H₂ Throughput, s.c.f./bbl.	4,100	4,000	1,000–10,000.
Space Velocity, LHSV.	0.5	0.5	0.2–5.

As shown in Table VI the substantially complete hydrodenitrification of refractory and high boiling oils, such as the heavy gas oil, requires rather severe conditions even when using the high metal content catalysts. On the other hand, such a degree of nitrogen removal is incapable of being accomplished at economically feasible operating conditions using the hydrofining catalysts. For example, to obtain the indicated 99.6% nitrogen removal from the heavy gas oil with catalyst A as 1600 p.s.i.g., 4000 s.c.f. H₂/bbl., and 0.5 LHSV, requires the use of a temperature in excess of 900° F. Similarly, to obtain the indicated degree of nitrogen removal from the heavy cycle oil at 1200 p.s.i.g., 4000 s.c.f. H₂/bbl. and 0.5 LHSV with catalyst A, requires the use of a temperature above 800° F.

Although the hydrodenitrification process is of particular value for use in the preparation of a feed stock for low temperature hydrocracking, improved operation and product distribution are also obtained in isomerization, hydrogenation, reforming, catalytic cracking, and like processes when the feed is first pretreated to remove nitrogen. In particular, we have found that isomerization catalysts, especially the solid acid or the dual function type, are rapidly poisoned by basic nitrogen compounds. The ability to remove the nitrogen compounds normally present in hydrocarbon oils makes possible a wide variety of processes for the upgrading of inferior stocks. Thus, high quality jet fuel of low freezing point may be prepared by a process wherein a kerosene boiling range distillate of appreciable n-paraffin content, normally unsuited for jet fuel usage, is first treated for the removal of nitrogen compounds in accordance with the process of this invention. The purified oil is then contacted with an isomerization catalyst, such as halided platinum-on-alumina or nickel-molybdenum on silica-alumina, at 300–700° F., 100–2000 p.s.i.g., at a liquid hourly space velocity of from about 0.1 to 5, and in the presence of added hydrogen. Similarly, lubricating oils of low pour point and high viscosity index may be produced by hydrodenitrification of crude wax or wax-bearing distillates and lubricating oils in the manner set forth herein, followed by isomerization at elevated pressure and temperature, in the range 400–800° F., and at a liquid hourly space velocity of from about 0.01 to 4, in contact with a catalyst such

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as the aforementioned platinum-alumina type or, for example, comprising alumina on which is deposited vanadium or tungsten together with molybdenum, cobalt, or nickel.

For many purposes a lesser degree of nitrogen removal is of considerable value provided that relatively moderate processing conditions can be used. For example, it has been found that when a heavy gas oil, similar to the heavy gas oil of Table III, with its nitrogen content reduced to 100 p.p.m. is fed to a catalytic cracking pilot unit operating at 900° F., a space rate of 1.5, and a catalyst to oil ratio of 1:5, a total conversion of 51 volume percent and a 37 volume percent gasoline yield are obtained. At a nitrogen content of 2500 p.p.m. the stock is only 33 volume percent converted with a 25 volume percent gasoline yield, at the same operating conditions. Table VII presents typical and preferred operating conditions which can be employed to remove the greater portion of the nitrogen contaminants from stocks such as the heavy gas oil and the full boiling range cat cracker feed of Table III using the high activity catalysts of this invention.

TABLE VII

Hydrodenitrification of Heavy Oils

	Operating Conditions		
	Typical		Preferred Range
Feed	Heavy Gas Oil.	Cat. Cracker Feed.	<1,050 ° F., E. P. Heavy Distillates.
Initial, p.p.m. N	2,500	4,000	
Final, p.p.m. N	100	750	
Percent Nitrogen Removal	96	85	80+.
Temperature, ° F.	680–695	735–755	600–800.
Pressure, p.s.i.g.	1,600	2,000	500–4,000.
H₂ Throughput, s.c.f./bbl.	4,000	4,000	1,000–10,000.
Space Velocity, LHSV	0.5	2	0.2–10.

Under the indicated operating conditions of Table VII only about 50% of the nitrogen is removed when the hydrofining catalyst (catalyst A) is used for treating either the heavy gas oil or the cat cracker feed.

In the foregoing comparisons, namely, Tables IV, V, VI and VII, it would appear that substantially complete hydrodenitrification could be accomplished using conventional hydrofining catalysts by resorting to operation at extremely low space velocities, for example, less than 0.2 LHSV. The use of such low space velocities is particularly undesirable not only because of the greatly increased equipment and catalyst costs involved but also because of the necessarily increased time of contact with the catalyst at elevated temperature. Protracted exposure of hydrocarbon oils to high temperatures and catalytic agents in many cases intensifies degenerative side reactions, notably thermal cracking and degradation of color and stability. In contrast thereto, for any desired degree of nitrogen removal the highly active, high nickel and molybdenum content catalysts permit the use of more moderate temperature conditions and higher space velocities. Under such comparatively mild conditions it has been found that many stocks may be substantially decolorized by the hydrodenitrification process. For example, the treatment of the light cycle oil under the conditions of Example 3 yielded a product which was essentially colorless (+15 Saybolt). Thus, it is contemplated that the utilization of the active nickel-molybdenum catalysts in the manner disclosed herein may provide a method whereby many stocks such as stove oils, lube oil fractions, transformer oils, waxes, and special products may be purified to an extent not heretofore considered possible.

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We claim:

1. A process for the substantially complete removal of contaminating nitrogen compounds from a distillable hydrocarbon oil without substantial cracking and coke formation, which comprises contacting said oil at a temperature in the range of from 500° to 800° F. and at a pressure in the range of from 500 to 4000 p.s.i.g., and at a liquid hourly space velocity based on said oil of 0.2 to 10, together with 500 to 10,000 s.c.f. of H_2 per barrel of said oil, with a sulfided nickel-molybdenum-alumina catalyst containing 4 to 10 weight percent nickel and about 19 to 30 weight percent molybdenum, calculated as the metals, removing the resulting ammonia, and recovering denitrified oil.

2. The process of claim 1 wherein the catalyst contains 6 to 8 percent nickel and 21 to 23 percent molybdenum.

3. A process for the substantially complete removal of contaminating nitrogen compounds from a hydrocarbon oil boiling below about 860° F. and having an initial nitrogen content below about 10,000 p.p.m., which comprises passing said hydrocarbon oil at a temperature in the range 500–850° F. together with 500–10,000 s.c.f. H_2/bbl. of said hydrocarbon oil, at a pressure in the range 200–4000 p.s.i.g., and at a liquid hourly space velocity based on the hydrocarbon oil in the range 0.2–10, through a fixed bed of particulate catalyst prepared by impregnating a preformed predominantly alumina carrier with nickel and molybdenum compounds convertible to the oxides by calcination, to provide a nickel content in the range 4–10% by weight, expressed as the metal, and to provide a molybdenum content in the range about 19–30% by weight, expressed as the metal, and calcining to convert the metal compounds to metal oxides, said catalyst having been sulfided prior to contacting with said hydrocarbon oil, cooling the effluent vapors to condense the normally liquid hydrocarbons therein, separating from said liquid hydrocarbons at substantially the reactor pressure a recycle gas comprising hydrogen, removing ammonia from the said hydrocarbons, and recovering as the product a feed stock for a low temperature hydrocracking process containing less than 10 p.p.m. nitrogen.

4. A process for the removal of contaminating nitrogen compounds from a distillable hydrocarbon oil, which comprises contacting said hydrocarbon oil at a temperature in the range 500–850° F. together with 500–10,000 s.c.f. H_2/bbl. of said hydrocarbon oil, at a pressure in the range 200–4000 p.s.i.g., and at a liquid hourly space velocity based on the hydrocarbon oil in the range 0.2–10, with a catalyst prepared by impregnating an alumina support having a pore volume in excess of 0.4 cc./gm. and a surface area in excess of 150 m.²/gm., as determined by nitrogen adsorption, with an aqueous solution of nickel nitrate to provide a nickel content in the finished catalyst in the range 6–8% by weight expressed as the metal, calcining, then impregnating with an aqueous solution of ammonium molybdate to provide a molybdenum content in the finished catalyst in the range 21–23% by weight expressed as the metal, calcining, and contacting the impregnated and calcined alumina with a sulfiding gas to convert the nickel and molybdenum oxides predominantly to the sulfides.

5. A process for the removal of more than 99.9% of the contaminating nitrogen compounds from a non-refractory hydrocarbon middle distillate boiling up to about 600° F. and having an initial nitrogen content below about 10,000 p.p.m., without substantial cracking or coke formation, which comprises contacting said distillate at 550–750° F., together with 500–10,000 s.c.f. H_2/bbl., at a pressure of 200–1500 p.s.i.g. and at a liquid hourly space velocity based on the distillate in the range 0.5–10, with a sulfided nickel-molybdenum-alumina catalyst, separating ammonia from the contacted middle distillate, and

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recovering a feedstock for low temperature hydrocracking containing less than 1 p.p.m. nitrogen, said catalyst having been prepared by impregnating a predominantly alumina carrier with nickel and molybdenum compounds convertible to the oxides by calcination in an amount sufficient to provide a total content of nickel and molybdenum expressed as the metals in the ranges 4–10% by weight nickel and about 19–25% by weight molybdenum, calcining, and sulfiding the impregnated and calcined catalyst to convert the metal oxides predominantly to metal sulfides.

6. A process for the removal of more than 99.9% of the contaminating nitrogen compounds from a refractory hydrocarbon gas oil distillate boiling up to about 750° F. and initially containing from about 400 to about 10,000 p.p.m. nitrogen, without substantial cracking or coke formation, which comprises contacting said distillate at 650–800° F. together with 1000–10,000 s.c.f. H_2/bbl. of said distillate at a pressure of 500–2000 p.s.i.g., and at a liquid space velocity based on the distillate in the range 0.2–5, with a sulfided nickel-molybdenum-alumina catalyst, separating ammonia from the contacted gas oil, and recovering a feedstock for low temperature hydrocracking containing less than 1 p.p.m. nitrogen, said catalyst having been prepared by impregnating a predominantly alumina carrier with nickel and molybdenum compounds convertible to the oxides by calcination, in an amount sufficient to provide a total content of nickel and molybdenum expressed as the metals in the range 4–10% nickel and about 19–25% molybdenum, by weight, calcining, and sulfiding the impregnated and calcined catalyst to convert the metal oxides predominantly to metal sulfides.

7. A process for the removal of more than 99% of the contaminating nitrogen compounds from a refractory hydrocarbon gas oil boiling up to about 860° F., without substantial cracking or coke formation, which comprises contacting said oil at 650–800° F. together with 1,000–10,000 s.c.f. H_2/bbl. of said oil at a pressure of 500–2,000 p.s.i.g., and at a liquid hourly space velocity based on the oil in the range 0.2–5, with a catalyst prepared by impregnating a predominantly alumina support with nickel and molybdenum compounds convertible to the oxides by calcination, in amounts sufficient to provide a total content of nickel and molybdenum expressed as the metals in the range 4–10% nickel and about 19–25% molybdenum, by weight, calcining, and sulfiding the impregnated and calcined catalyst to convert the metal oxides predominantly to metal sulfides, separating ammonia from the contacted gas oil, and recovering contacted gas oil containing less than 10 p.p.m. nitrogen.

8. A process for the removal of contaminating nitrogen compounds from a heavy gas oil catalytic cracker feed stock boiling up to about 1,050° F., which comprises contacting said gas oil at 600–800° F. together with 1,000–10,000 s.c.f. H_2/bbl. of gas oil, at a pressure of 500–4,000 p.s.i.g., and at a liquid hourly space velocity based on the gas oil in the range 0.2–10, with a catalyst prepared by impregnating a predominantly alumina support with nickel and molybdenum compounds convertible to the oxides by calcination, in amounts sufficient to provide a total content of nickel and molybdenum expressed as the metals in the range 4–10% nickel and about 19–25% molybdenum, calcining to convert the nickel and molybdenum compounds to the metal oxides, and sulfiding the impregnated and calcined catalyst to convert said metal oxides predominantly to metal sulfides.

9. A catalyst composition having high activity for the hydrodenitrification of distillable hydrocarbon oils, which comprises sulfided nickel and molybdenum on an alumina support, the quantity of nickel expressed as the metal being in the range 4–10% by weight and the quantity of molybdenum expressed as the metal being in the range 19–25% by weight, prepared by impregnating a preformed alumina support, having a pore volume in excess

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of 0.4 cc./gm. and a surface area in excess of 150 m.²/gm. as determined by N₂ adsorption, with an aqueous solution of a nickel compound convertible to the oxide by calcination, calcining at 600–1100° F., then impregnating with an aqueous solution of a molybdenum compound convertible to the oxide by calcination, calcining at 600–1100° F., again impregnating with an aqueous solution of a molybdenum compound convertible to the oxide by calcination, calcining at 600–1100° F., and

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sulfiding to convert the nickel and molybdenum oxides predominantly to metal sulfides.

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