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IN BOTH STAGES TO PRODUCE A HIGH OCTANE GASOLINE
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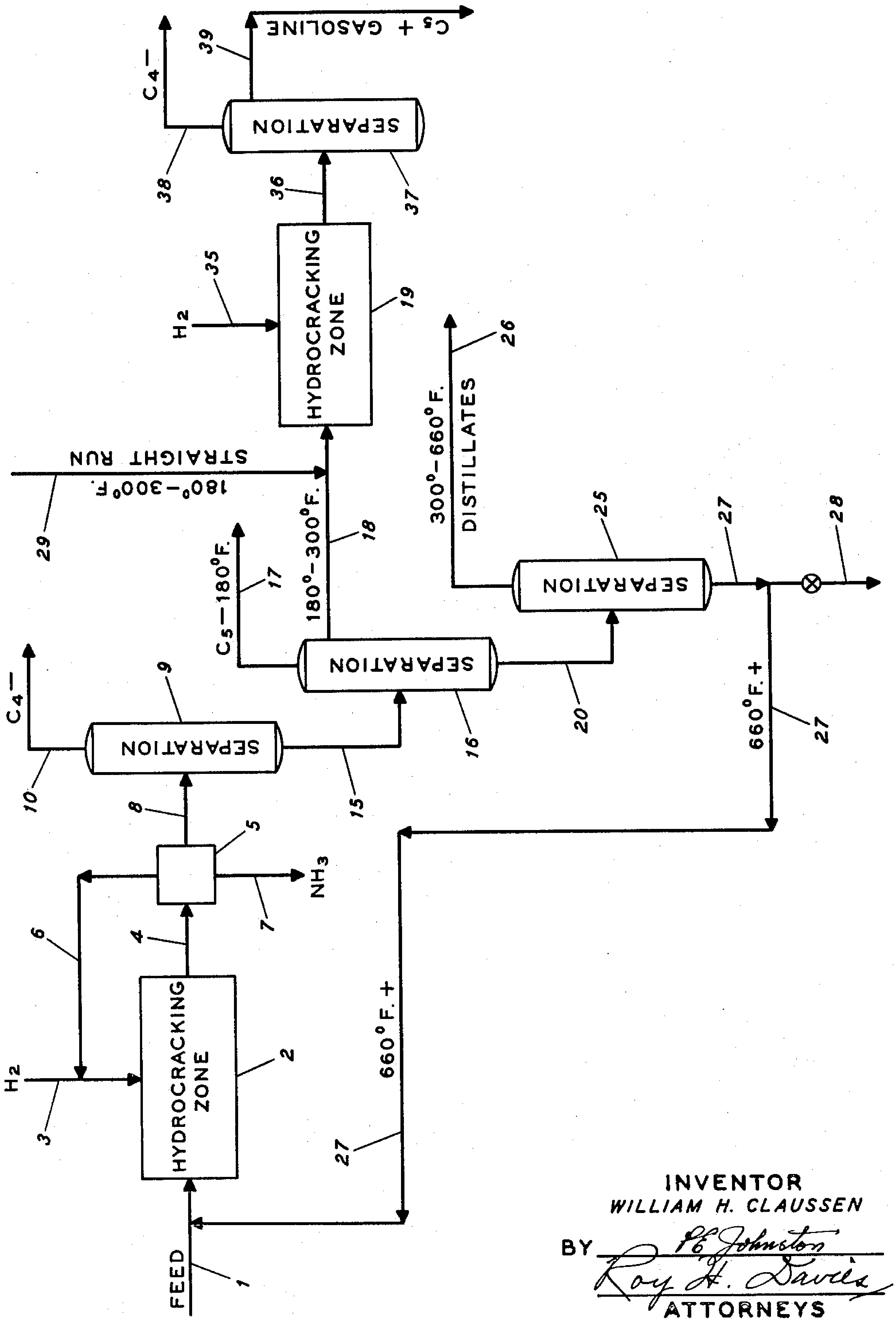

INVENTOR
WILLIAM H. CLAUSSEN

BY P. E. Johnston
Roy H. Davis
ATTORNEYS

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TWO STAGE HYDROCARBON CONVERSION PROCESS WITH HYDROCRACKING IN BOTH STAGES TO PRODUCE A HIGH OCTANE GASOLINE

William H. Claussen, Berkeley, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware

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INTRODUCTION

This invention relates to a hydrocarbon conversion process, more particularly to a hydrocarbon conversion process for converting petroleum distillates and residua into various valuable products, and still more particularly to a catalytic conversion process capable of producing middle distillates, light gasoline and isobutane.

PRIOR ART HYDROCRACKING OF HYDROCARBON FEEDS TO PRODUCE MIDDLE DISTILLATES AND GASOLINE, AND PROBLEMS INVOLVED

A. *Nitrogen content of feed.*—It is well known that nitrogen in a hydrocarbon feed is deleterious to certain hydrocracking catalysts, particularly highly acidic hydrocracking catalysts, and that, in order to provide a practical process for producing middle distillates from a feed containing substantial amounts of nitrogen, a catalyst having no more than weak acidity has been necessary so that the deleterious effect of nitrogen on the catalyst would be minimized. However, catalysts having no more than weak acidity frequently result in the production of substantial quantities of heavy gasoline, which often is a less desirable product than middle distillates, light gasoline and isobutane.

B. *Ratio of iso-C_4 to normal-C_4 product.*—It is well known that a high iso-C_4 to normal-C_4 product from a hydrocracking zone is highly desirable. Isobutane, for example, is a valuable product for use in motor gasoline blending, whereas normal butane is less valuable. A low iso-C_4 to normal-C_4 product ratio has been a disadvantage of many prior art processes.

C. *Paraffinicity of unconverted bottoms fraction recycled to reactor.*—It is well known that various prior art catalysts, particularly catalysts of extremely low activity which are useful in the production of middle distillates and catalysts of extremely high activity which are useful in the production of gasoline, produce an unconverted bottoms fraction having a high content of normal paraffins. It is known that these normal paraffins are deleterious to the hydrocracking operation because they are extremely refractory to further hydrocracking and therefore, particularly where high middle distillate production is desired, as a practical matter, cannot be recycled. It would be desirable if a two-stage process were available for producing middle distillates, light gasoline and isobutane in a first stage and light gasoline and isobutane in a second stage without producing a first stage bottoms product having a normal paraffin content too high to permit a practical recycle thereof to the first stage.

D. *Regeneration.*—It is known that many prior art hydrocracking catalysts lose a great deal of their fresh catalyst activity upon regeneration, and it would be very desirable if the catalysts used in processes for meeting the foregoing prior art problems were regenerable.

OBJECTS

In view of the foregoing, it is an object of the invention to provide a two-stage process using selected catalysts, capable of converting both hydrocarbon feed stocks that have a high nitrogen content and those that have been denitrified, to produce middle distillates, light gasoline and isobutane in large quantities, while minimizing heavy gasoline production, at reasonable starting and operating temperatures.

It is a further object of the present invention to provide such a process capable of producing large quantities of isobutane.

It is a further object of the present invention to provide such a process and catalysts wherein the unconverted bottoms fraction from the first stage has a sufficiently low content of normal paraffins to permit recycling a selected portion of this fraction to the first stage reactor in sustained recycle operation, to increase the overall yield of light gasoline and isobutane.

It is a further object of the present invention to provide such a process wherein the catalysts in each stage may be regenerated to reimpart to them a substantial portion of their original fresh activity.

DRAWING

The invention will best be understood, and further objects and advantages thereof will be apparent, from the following description when read in conjunction with the accompanying drawing which is a diagrammatic illustration of process units and flow paths suitable for carrying out the process of the present invention.

STATEMENT OF INVENTION

In accordance with the present invention, there is provided a process for producing gasoline and middle distillates from a hydrocarbon feed selected from the group consisting of petroleum distillates boiling from 200° to 1100° F. and petroleum residua boiling above 500° F., which comprises contacting said feed and from 1000 to 10,000 s.c.f. of hydrogen per barrel of said feed in a first conversion zone at a temperature from 500° to 950° F., a pressure above 500 p.s.i.g. and an LHSV of 0.1 to 4.0 with a catalyst comprising at least one hydrogenating component selected from the Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from the Group VIII metals and compounds of Group VIII metals intimately associated with a catalyst support comprising silica-magnesia, recovering from the effluent from said first conversion zone a middle distillate product and a light gasoline product, hydrocracking in a second conversion zone in the presence of an active acidic hydrocracking catalyst at a pressure of 500 to 3000 p.s.i.g. and a temperature of 550° to 850° F. a portion of the effluent from said first conversion zone boiling from about 180° to 300° F., to produce a light gasoline product having an increased isoparaffin content and recovering said light gasoline product from said second conversion zone.

Further in accordance with the present invention, there is provided a process for producing gasoline and middle distillates which comprises converting a heavy gas oil feed in a first conversion zone in the presence of a catalyst comprising nickel and tungsten on a silica-magnesia support at a temperature of from 500° to 950° F., a pressure above 500 p.s.i.g. and an LHSV of from 0.4 to 2.0, to a total product containing above 60 volume percent, based on feed converted, of 320° to 650° F. middle distillate, separating said total product into fractions including a middle distillate fraction and a gasoline fraction, recovering said middle distillate and gasoline fractions as products, hydrocracking in a second conversion zone in the presence of an active acidic hydrocracking catalyst at a pressure of 500 to 3000 p.s.i.g. and a temperature of 500° to 850° F. a portion of the effluent from said first conversion zone boiling from about 180° to 300° F., recovering a gasoline product from said second conversion zone, and recycling to said first conversion zone at least a portion of the effluent from said first conversion zone boiling above about 660° F.

Still further in accordance with the present invention, there is provided a process for converting a nitrogen-containing hydrocarbon feed selected from the group consisting of petroleum distillates boiling from 500° to 1100° F. and petroleum residua boiling above 500° F. which comprises concurrently hydrofining and hydrocracking said feed by contacting with feed in a first stage in the presence of from 1000 to 10,000 s.c.f. of hydrogen per barrel of said feed and in the presence of a catalyst comprising at least one hydrogenating component selected from the group consisting of Group VI metals and compounds thereof and at least one hydrogenating component selected from the group consisting of Group VIII metals and compounds thereof intimately associated with a silica-magnesia catalyst support at a temperature of 500° to 950° F., a pressure above 500 p.s.i.g. and an LHSV of from 0.1 to 4.0, recovering a gasoline product and a middle distillate product, hydrocracking in a second stage in the presence of an active acidic hydrocracking catalyst at a pressure of 500 to 3000 p.s.i.g. and a temperature of 550° to 850° F. at least a substantial portion of the liquid effluent from said first stage, recovering a gasoline product from said second stage, and recycling to said first stage at least a portion of the effluent from said first stage boiling above about 660° F.

Still further in accordance with the present invention, there is provided a process as aforesaid wherein at least two reactors are used in said first conversion zone, each containing said silica-magnesia supported catalyst, and wherein said reactors are so arranged that they can be switched from parallel, for maximizing middle distillate production, to series, for maximizing either gasoline or middle distillate production, whereby the ratio of middle distillate product to gasoline product can be varied.

HYDROCARBON FEEDS SUITABLE FOR USE IN THE PROCESS OF THE PRESENT INVENTION

Suitable feeds for use in the process of the present invention are petroleum distillates boiling from 200° to 1100° F., preferably petroleum distillates boiling from 500° to 1100° F., and petroleum residua boiling above 500° F., and mixtures of the foregoing. Heavy gas oils and catalytic cycle oils are excellent feeds to the process as well as conventional FCC feeds and portions thereof. Residual feeds may include Minas and other paraffinic-type residua.

Particularly when it is desired to produce middle distillates, including jet fuels, which are exceptionally high in naphthene content and low in aromatic content (therefore having high smoke points) and low in normal paraffin content (therefore having low freeze points), it is preferable to use a feed in the process of the present invention which has an initial boiling point of 500° F. or above. Where the feed has an initial boiling point above 500° F., it is converted in the process of the present invention directly to a synthetic material, i.e., one boiling below the initial boiling point of the feed, which is a preferred jet fuel or middle distillate having high naphthene content, low normal paraffin content and therefore low freeze point, and low aromatic content and therefore exceptionally high smoke point. It has been found that feeds having lower initial boiling points, for example around 300° to 400° F., tend to produce excessive quantities of nonsynthetic products having a high aromatics contents and therefore exceptionally low smoke points, although the freeze point may be satisfactory. Such a nonsynthetic product also tends to have a high pour point.

FIRST CONVERSION ZONE IN PROCESS OF PRESENT INVENTION, AND NITROGEN CONTENT OF FEED THERETO

It has been found that the silica-magnesia supported hydrocracking catalyst in the first conversion zone of the process of the present invention is relatively nitrogen insensitive, compared with conventional acidic hydrocracking catalysts such as nickel sulfide on silica-alumina. Accordingly, the nitrogen content of the feed used in the process of the present invention may be relatively high, and excellent hydrocracking results still may be obtained in said conversion zone at reasonable temperatures, without the necessity for rapidly raising the temperature to maintain conversion as is necessary when hydrocracking a high nitrogen content feed over a conventional acidic hydrocracking catalyst such as nickel sulfide on silica-alumina. Although high nitrogen content feeds can be tolerated by said first conversion zone hydrocracking catalyst, it will be noted that said catalyst also is an excellent hydrodenitrification catalyst, and is efficient in concurrently hydrofining as well as in hydrocracking the feed. Nevertheless, the process of the present invention may be rendered even more efficient if the feed either is low in nitrogen content or first is hydrofined by conventional methods prior to being hydrocracked in said first conversion zone in accordance with the process of the present invention. And in certain applications a conventional hydrofining zone following said first conversion zone is desirable; as will be discussed below, in one embodiment of the present invention, wherein very heavy feeds, for example propane deasphalted residua, are used, the feed may be processed in three stages; in the first stage, the feed may be concurrently hydrocracked and denitrified to a large extent over a silica-magnesia supported catalyst, following which a portion of the effluent from the first stage may be further denitrified in a second stage before being hydrocracked over an acidic hydrocracking catalyst in a third stage.

Generally speaking, it is possible to operate the first conversion zone in the process of the present invention at slightly lower temperatures when the feed has a low nitrogen content, for example, from 0 to 10 p.p.m. total nitrogen, than temperatures that are necessary for the same conversion when the feed has a high nitrogen content, for example from 10 to 1000 p.p.m. total nitrogen. However, even feeds containing considerably higher levels of nitrogen than 1000 p.p.m. total nitrogen may be satisfactorily converted in the process of the present invention to valuable products, contrary to conventional prior art processes wherein acidic hydrocracking catalysts, such as nickel sulfide on silica-alumina, are used. In such conventional processes, it is impossible as a practical matter to use feeds with such high nitrogen contents.

The catalyst in the first conversion zone in the process of the present invention is capable of concurrently accomplishing both denitrification and hydrocracking. The hydrocracking facilitates the concurrent denitrification because, upon the breaking of carbon-to-carbon bonds, nitrogen is more easily removed. At higher levels of cracking conversion, somewhat higher pressures may be desired to counteract catalyst fouling and deactivation.

The nitrogen compounds tend to concentrate in the heavier portions of the feed; accordingly, such heavier portions are more difficult to denitrify. However, it will be noted from the foregoing that such heavier portions also are easier to crack.

OPERATING CONDITIONS IN FIRST CONVERSION ZONE

The first conversion zone of the process of the present invention, which contains a silica-magnesia supported catalyst, discussed below, is operated at combinations of conditions selected from within the varying ranges that will produce the desired degree of hydrocracking: a temperature of about 500° to 950° F., preferably 650° to 850° F.; a hydrogen partial pressure of 500 to 3500 p.s.i.g., preferably 1000 to 2500 p.s.i.g.; and an LHSV of from about 0.1 to 4.0, preferably 0.4 to 2.0. The hydrogen flow to said conversion zone may be from 1000 to 10,000 s.c.f. per barrel of feed, preferably 2500 to 8000 s.c.f per barrel of feed. The higher hydrogen partial pressures, particularly with unrefined feeds, give lower catalyst fouling rates and therefore for longer catalyst lives it is preferable to operate above 2000 p.s.i.g. In general, the hydrogen partial pressure will depend upon a number of factors, including type of feed stock and nitrogen content thereof, degree of denitrification required, etc.; however, in general, a hydrogen partial pressure of 1000 to 2000 p.s.i.g. is highly desirable if practicable in any given instance.

CATALYST IN FIRST CONVERSION ZONE

A. *Composition of catalyst.*—It is essential that the catalyst in the first conversion zone in the process of the present invention have (*a*) a silica-magnesia support, and (*b*) at least two hydrogenating components, at least one of which must be a Group VI metal or compound thereof and at least one of which must be a Group VIII metal or compound thereof. It has been found that, where the catalyst comprises a Group VI metal or compound thereof alone, without a Group VIII metal or compound thereof, the catalyst has an unacceptably low activity. It has been found that, where the catalyst comprises a Group VIII metal or compound thereof alone, without a Group VI metal or compound thereof, the catalyst has an exceptionally high fouling rate. However, where the catalyst comprises at least one Group VIII metal or compound thereof, and also at least one Group VI metal or compound thereof, the catalyst has a high activity and a low fouling rate. The Group VI metals and compounds thereof that may be used include chromium, molybdenum and tungsten and compounds thereof. The Group VIII metals and compounds thereof that may be used include iron, cobalt, nickel, platinum and palladium and compounds thereof. The most preferred catalysts comprise nickel and either tungsten or molybdenum on a silica-magnesia support, the catalyst in each case preferably being sulfided. The single main preferred catalyst which has been found to have the most outstanding qualities in the process of the present invention comprises nickel and tungsten on silica-magnesia, preferably sulfided. The Group VI metal or compounds thereof may be present in the catalyst in an amount from 1 to 40 weight percent, preferably from 2 to 25 weight percent, based on the total catalyst composite; the Group VIII metal or compounds thereof may be present in an amount of from 1 to 20 weight percent, preferably from 2 to 12 weight percent, based on the total catalyst composite. The magnesia content of the silica-magnesia support may range from 5 to 75 weight percent, preferably from 15 to 50 weight percent, and still more preferably from 20 to 35 weight percent.

B. *Preparation of catalyst.*—The silica-magnesia support of the catalyst can be prepared by any conventional method, and the plurality of hydrogenating components may be incorporated in the catalyst by any conventional method. A particularly effective method for preparing the catalyst is set forth in the following example.

Example 1

A powdery silica-magnesia material containing about 28% magnesia was compressed, together with about 5% by weight of a conventional glue-type bonding material used in catalyst preparation, into $\frac{3}{16}''$ x $\frac{3}{16}''$ pellets, and was calcined in air at 950° F. for six hours.

1000 cc. of the aforesaid calcined material were impregnated for four hours with 800 cc. of a solution of nickel nitrate containing 11.2% nickel, and the impregnated material was dried for 24 hours at 250° F. and then calcined for four hours at 900° F. The resulting product was a catalyst support containing 9.43% nickel.

The aforesaid catalyst support was impregnated three times with separate 800 cc. portions of a solution consisting of 960 g. of tungstic acid (H_2WO_4) dissolved in a mixture of 1152 cc. of 30% ammonia (NH_3) and 3460 cc. of water. After each of the aforesaid impregnation treatments, the impregnated composite was dried at 250° F. for 20 hours, and calcined at 900° F. for four hours. The catalyst resulting from the foregoing operations contained 7.02 weight percent nickel and 19.3 weight percent tungsten, and had a nitrogen surface area of 316 $m.^2/g$.

C. *Sulfiding the catalyst.*—Although the catalyst of the present invention may be used in the unsulfided form, the sulfided form is preferable. With feeds containing any substantial amounts of sulfur compounds, the catalyst automatically will tend to become sulfided on the surface under the operating conditions of the process. It is somewhat more preferable to presulfide the catalyst before placing it on-stream, and such sulfiding may be accomplished by any conventional method.

D. *Regeneration of the catalyst.*—It is an outstanding advantage of the catalyst of the present invention that it may be regenerated, particularly in view of the difficulties that have been met by the art in the regeneration of many prior art catalysts. While regeneration may be accomplished by any conventional method, and while the relative effectiveness of such methods may be readily determined by those skilled in the art, the regeneration method set forth in Table IV below is a highly effective one.

E. *Preferred catalyst.*—The preferred catalysts for use in the process of the present invention are set forth above.

F. *Activity of catalyst for dentrification.*—The catalyst of the present invention is a dentrification catalyst, as well as a hydrocracking catalyst, and in the process of the present invention performs both functions under the conditions of the process. The catalyst has excellent denitrification activity, but it is relatively insensitive to nitrogen, and is highly insensitive to nitrogen compared with a conventional acidic hydrocracking catalyst such as nickel sulfide on silica-alumina.

Not only are a plurality of hydrogenation components, at least one of which must be a Group VI metal or compound thereof and at least one of which must be a Group VIII metal or compound thereof, essential to the hydrocracking activity of the catalyst of the present invention, but this same plurality of hydrogenation components is essential to the dentrification activity of the catalyst of the present invention. For example, the preferred nickel-tungsten on silica-magnesia catalyst of the present invention would not have good denitrification activity if only nickel or only tungsten were present; single hydrogenating components, for example molybdenum or tungsten from Group VI or nickel or cobalt from Group VIII, are relatively ineffective for denitrification when not accompanied by a hydrogenating component from the other one of the two groups. Further information regarding the denitrification activity of the catalyst is set forth in Table V below.

G. *Selectivity of catalyst for middle distillate production.*—The catalyst of the present invention has a high selectivity for the production of middle distillates from various hydrocarbon feeds. It has a much greater selectivity for the production of middle distillates than conventional acidic hydrocracking catalysts, such as nickel sulfide on silica-alumina. The high yields of middle distillates resulting from the selectivity of the catalyst of the present invention for middle distillate product is unexpected in view of the selectivity for gasoline production that is characteristic of many prior art hydrocracking catalysts, for example nickel sulfide on silica-alumina. Further information regarding the selectivity of the present invention catalyst for the production of middle distillates is set forth in Table III below.

DESCRIPTION OF PROCESS FLOW ARRANGEMENTS SUITABLE FOR CARRYING OUT THE PROCESS OF THE PRESENT INVENTION

Referring now to the drawing, there shown is a diagrammatic illustration of an embodiment of process units and flow paths suitable for carrying out the process of the present invention.

A hydrocarbon feed is passed through line **1** into contact in hydrocracking zone **2** with the aforesaid silica-magnesia supported catalyst and with hydrogen entering zone **2** through line **3** under the hydrocracking conditions previously discussed. From zone **2** an effluent is passed through line **4** to separation zone **5** from which hydrogen is recycled through line **6**, ammonia is withdrawn through line **7**, and remaining materials are passed through line **8** to separation zone **9**. From separation zone **9** a C_4 and lighter stream, including isobutane, is withdrawn through line **10**, and remaining materials are passed through line **15** to separation zone **16**. From separation zone **16**, a light gasoline product is withdrawn through line **17**, a heavy gasoline boiling from about 180° to 300° F. is passed through line **18** to hydrocracking zone **19**, and materials heavier than about 300° F. are passed through line **20** to separation zone **25**.

From separation zone **25** middle distillate products boiling from about 300 to 660° F. are withdrawn through line **26** and materials boiling above about 660° F. are recycled through line **27** to hydrocracking zone **2**. If desired, a minor portion of the materials in line **27** may be withdrawn from the system through line **28**. If desired the hydrocarbon feed to hydrocracking zone **19**, entering that zone through line **18**, may be augmented by additional hydrocarbon stocks boiling between about 180° and 300° F., for example straight run stocks, through line **29**. Hydrocracking zone **19** may contain a conventional acidic hydrocracking catalyst, for example nickel sulfide or silica-alumina, platinum on silica-alumina, etc., and may operate under conventional hydrocracking conditions, for example a pressure of from 500 to 3000 p.s.i.g. and a temperature of from 550° to 850° F. It is well known that such catalysts can be subjected to regeneration with an oxygen-containing gas under conventional regeneration conditions. Hydrocracking zone **19** is supplied with hydrogen through line **35**. Zone **19** effluent is passed through line **36** to separation zone **37**. From separation zone **37**, C_4 and lighter hydrocarbon gases, including isobutane, are withdrawn through line **38**, and a C_5 plus light gasoline product is withdrawn through line **39**.

Hydrocracking zone **2** may comprise two hydrocracking reactors, each containing the catalyst of the present invention and each operating under the aforesaid process conditions. These two reactors may be arranged in a known manner so that alternately they can be connected in parallel and in series. When connected in parallel, they will operate to maximize middle distillate production, and when switched to series operation they may maximize gasoline or middle distillate production. In series operation, middle distillate production may be maximized by withdrawing middle distillate as a product from the first reactor as well as from the second, for example from an inter-reactor fractionation zone. In series operation, gasoline production may be maximized by including the middle distillate produced in the first reactor in the feed to the second reactor. In either series arrangement, it is preferred to remove from the system any ammonia produced in the first reactor, rather than permitting it to pass to the second reactor. Such switching arrangements will enable the ratio of middle distillate to gasoline product to be varied in order to achieve further process application flexibility. In series operation to produce gasoline, where ammonia formed in the first reactor has been removed, the second reactor, because it is operating with a feed that has been denitrified in the first reactor, is operable at lower temperatures, thus providing leeway for increase in severity of the operating conditions in the second reactor to increase gasoline production. The resulting gasoline, produced over the catalyst of the present invention, is isoparaffinic and of high quality, in contrast to the normal paraffinic character of gasoline produced over hydrocracking catalysts having weak acidity.

Because the catalyst in zone **2** serves as an effective hydrofining catalyst, the materials in line **8** are low in nitrogen and therefore are specially suitable for further hydrocracking in the presence of the acidic catalyst in zone **19**.

The process of the present invention is specially effective for converting heavy feed such as residua and propane deasphalted oils when a conventional denitrification zone is inserted between the first hydrocracking zone and the second hydrocracking zone of the process. Because such feeds generally are specially difficult to denitrify, and because for most efficient results the feed to the second conversion zone **19** here, containing an acidic hydrocracking catalyst, should have a minimum nitrogen level, the insertion of a conventional denitrification zone between the two hydrocracking zones in the present process can be of significant value.

The conventional denitrification zone may be inserted for example in line **8** or line **15**, and may be operated under conventional denitrification conditions with either the silica-magnesia supported catalyst used in hydrocracking zone **2**, or with any conventional denitrification catalyst. Such a three-stage process enables the heavier feeds to be hydrocracked and partially denitrified in the first stage, thereby reducing both the molecular weight and the nitrogen level of the feed and greatly accelerating the rate of the remaining denitrification to be accomplished in the second, or conventional, denitrification zone.

TABLE I.—COMPARISON OF FIRST STAGE CATALYST OF PROCESS OF PRESENT INVENTION WITH CONVENTIONAL CATALYSTS RE STARTING TEMPERATURES AND FOULING RATES

The following table sets forth on a comparative basis single stage hydrocracking results of processing a 650° to 980° F. heavy Arabian gas oil having a total nitrogen content of 660 to 700 p.p.m. at the indicated average catalyst temperature, about 50 to 55 volume percent substantially constant per-pass conversion to products boiling below the initial boiling point of the feed, 1.0 LHSV, 2000 p.s.i.g. and a hydrogen rate sufficient to permit withdrawal from the hydrocracking zone of 4500 s.c.f. of hydrogen per barrel of feed, over the first stage catalyst of the present invention compared with hydrocracking the same feed under the same conditions over various prior art catalysts. The factors compared are: (1) the average catalyst temperature necessary to give said substantially constant 50 to 55% per-pass conversion, which substantially constant conversion is indicated by the substantially constant product gravity shown; and (2) the catalyst fouling rate.

Cat. No.	Support		Hydrogenating component, percent				Area, M^2/g.	Av. cat. temp., °F. necessary for desired conversion	Product gravity	Fouling rate
	SiO_2-Al_2O_3	SiO_2-MgO	Ni	W	Mo	Pt				
1		27% MgO	7.0	19.3			316	759	40.0	None observable.[1]
2		27% MgO	4.9		22.8		254	755	40.3	Do.[1]
3		27% MgO	5.0		5.0			756	39.9	Moderate.[2]
4		27% MgO	5.0	1.8				767	39.5	Do.[2]
5		27% MgO		8.5			437	790	39.5	High.[3]
6		27% MgO	9.0				445	765	40.3	Very high.[4]
7		27% MgO				0.5		845	38.5	Do.[4]
8	25% Al_2O_3		4.5	12.2			134	790	40.3	None observable.[1]
9	28% Al_2O_3		3.9	10.4			130	792	40.0	Moderate.[2]
10	47% Al_2O_3		5.0	7.0				780	40.0	Do.[2]
11	47% Al_2O_3		4.4		9.4		92	790	39.8	Do.[2]
12	10% Al_2O_3			18.0			116	805	39.8	.[3]

[1] 0.05° F. per hour. [2] 0.10–0.15° F. per hour. [3] 0.5° F. per hour. [4] 1.0° F. per hour.

From the above table, it will be noted that only catalysts 1 to 4 resulted in *both* (1) the desired conversion rate at a reasonably low average catalyst temperature, in each case 767° F. or below, *and* (2) a reasonably low catalyst fouling rate, in each case, moderate, as defined, or less. It will be noted that catalysts 5 to 7, each having one hydrogenating component only, on a silica-magnesia support, resulted in an excessive catalyst fouling rate, i.e., one that was high, as defined, or higher. It will be noted that catalysts 8 to 12, each having a silica-alumina support rather than the silica-magnesia support of the first stage catalyst of the present invention, resulted in the desired conversion being obtained only at an unreasonably high average catalyst temperature, in each case 780° F. or above.

TABLE II.—COMPARISON OF FIRST STAGE CATALYST OF PRESENT INVENTION WITH CONVENTIONAL CATALYSTS RE ACIDITY, STARTING TEMPERATURE, ISO TO NORMAL C_4 PRODUCT RATIO, MIDDLE DISTILLATE TO GASOLINE PRODUCT RATIO AND NORMAL PARAFFIN CONTENT OF UNCONVERTED BOTTOMS

The following table sets forth on a comparative basis single-stage hydrocracking results of processing an Arabian straight run feed, at 0.5 LHSV, 2000 p.s.i.a., 60% per-pass conversion to products boiling below the initial boiling point of the feed, and extinction recycle, over the first stage catalyst of the present invention, compared with hydrocracking the same feed under the same conditions over various prior art catalysts. The factors compared are: (1) starting temperature necessary to give said 60% per-pass conversion; (2) the ratio of iC_4 to nC_4 in the product; (3) the ratio of 400° to 650° F. product to C_5 to 400° F. product, i.e., the ratio of middle distillate production to gasoline production; (4) the hydrogen consumption, in s.c.f. per barrel of feed; and (5) the change, in ° F., of the pour point of the same bottoms fraction in each case, from the pour point of the feed, as an indication of the effect of the reaction in each case on normal paraffins in the system.

Cat.	Cat. comp.	Start. T.,° F.	iC_4/nC_4	400–650° F./ C_5–400° F.	H_2, s.c.f./ bbl.	Bottoms pour point change, ° F.
A	6% Ni+22% Mo on Al_2O_3	850	0.2	1.4	1,300	+13
B	NiMo on SiO_2—Al_2O_3, 30% SiO_2	765	0.6	1.4	1,700	−38
C	NiW on SiO_2—MgO, 27% MgO	720	1.1	1.4	2,000	−25
D	NiMo on SiO_2—Al_2O_3, 90% SiO_2	790	0.6	0.9	1,800	−15
E	6% Ni on SiO_2—Al_2O_3, 90% SiO_2	740	1.1	0.4	2,600	+19

The catalysts in the above table are set forth in order of increasing acidities, with Catalyst A having the lowest acidity and Catalyst E having the highest acidity. Catalyst C is an example of the first stage catalyst of the present invention, while the other catalysts indicated are representative of various prior art catalysts.

From the above table it will be noted that: (1) as acidity increases, the product iso to normal ratio increases smoothly, except in the case of the first stage catalyst of the present invention, with which is obtained a higher ratio than would be expected from inspection of the prior art catalysts alone; (2) as acidity increases, the product middle distillate to gasoline ratio decreases, but remains as high with the first stage catalyst of the present invention as with catalysts of weaker acidity, which is entirely unexpected; heretofore, it has been believed that a catalyst of higher acidity would produce less middle distillate per unit of gasoline production than a more weakly acidic catalyst; (3) as acidity increases, hydrogen consumption increases smoothly, except in the case of the first stage catalyst of the present invention, with which is obtained a higher hydrogen consumption and improved product quality; (4) as acidity increases, the normal paraffin content of the unconverted bottoms material, as indicated by the ° F. change in bottoms pour point from the pour point of the feed, decreases and then increases; with Catalysts A and E the bottoms material is indicated to have a greater normal paraffin content than the feed. With Catalysts B, C and D the unconverted bottoms material is less paraffinic than the feed, which is extremely desirable because normal paraffins are refractory to hydrocracking and therefore build up in recycle bottoms during recycle operation. A build-up of refractory normal paraffins can effectively prevent the practical use of recycle hydrocracking to produce middle distillates, because prohibitive temperature and pressure increases can be required to crack these refractory compounds; (5) with Catalysts B, C and D the undesirable refractory normal paraffins are selectively cracked and/or are isomerized to valuable isoparaffins, to an extent adequate to permit satisfactory recycle operation.

TABLE III.—COMPARISON OF FIRST STAGE CATALYST OF PRESENT INVENTION WITH CATALYST HAVING SILICA-ALUMINA SUPPORT RE PRODUCTION OF MIDDLE DISTILLATES

The following table further indicates the specificity of the first stage catalyst of the present invention for the production of middle distillates from various hydrocarbon feeds, compared with a catalyst having a silica-alumina support. In this case, the feed is a 650° to 820° F. hydrofined Midway gas oil, containing 3.6 p.p.m. total nitrogen. It is hydrocracked at 0.77 LHSV, 1500 p.s.i.g. and a hydrogen rate of 5000 s.c.f. per barrel of feed, over each of the two catalysts, with the results indicated:

Catalyst	Temp., ° F.	Total conversion to products boiling below 650° F.	Percent of product in 400–650° F. boiling range
NiW on SiO_2–Al_2O_3	650	53.2	41
NiW on SiO_2–MgO	650	53.4	49

TABLE IV.—REGENERABILITY OF FIRST STAGE CATALYST OF PRESENT INVENTION AND REGENERATED CATALYST ACTIVITY

The following table illustrates the regenerability of the preferred nickel-tungsten on silica-magnesia catalyst of the present invention. A catalyst comprising 7.0% nickel and 19.3% tungsten on a silica-magnesia support containing 27.7% magnesia, with an area of 316 m.^{2}/g., was placed in hydrocracking reactor and contacted for 120 hours at 2000 p.s.i.g., 1.0 LHSV, 759° F. average catalyst temperature, and hydrogen rate of 5500 s.c.f. per barrel of feed, with a hydrocarbon feed boiling from 650° to 982° F., said feed having a gravity of 23.5° API, an aniline point of 178.9° F., a pour point of +90 ASTM and a total nitrogen content of 665 p.p.m. The catalyst under these conditions converted 54 weight percent of the feed to products boiling below the 650° F. initial boiling point of the feed, and the gravity of the total products produced was 40.3° API.

After the foregoing on-stream period the catalyst was regenerated in a nitrogen-oxygen stream, at a reactor pressure of 600 p.s.i.g. and a gas rate of 20 cubic feet per hour, for a total period of 20 hours. During this period the temperature was slowly raised from 500° to 900° F., and the oxygen content of the gas was raised from 0.1 to 4.0 volume percent.

The regenerated catalyst, having an area of 237 m.^{2}/g., was then used to hydrocrack the same feed that had been used to hydrocrack prior to regeneration, under the same conditions. The activity of the regenerated catalyst was substantially equal to its original fresh activity, as indicated by its conversion, at an average catalyst temperature of 750° F., of 48 weight percent of the feed to products boiling below the initial boiling point of the feed, the total products produced having a gravity of 38.8° API.

The following summarizes the foregoing results:

Area, m.^{2}/g.	Average cat. temp., ° F.	Whole product gravity	Weight percent conversion to products boiling below 650° F.
Fresh catalyst 316	759	40.3	54
Regenerated catalyst 237	750	38.8	48

TABLE V.—COMPARISON OF FIRST STAGE CATALYST OF PRESENT INVENTION WITH CONVENTIONAL CATALYSTS RE DENITRIFICATION ABILITY, NITROGEN SENSITIVITY AND ABILITY TO CONVERT NITROGEN-CONTAINING FEEDS TO MIDDLE DISTILLATES

The following table indicates results obtainable with the first stage catalyst of the present invention and with a low acidity prior art catalyst, and a high acidity prior art catalyst, respectively, when used to hydrocrack a 650° F. to 1000° F. hydrocarbon feed at the indicated temperatures, and at 1.0 LHSV, 2000 p.s.i.g. and a hydrogen rate of 6500 s.c.f. per barrel, with extinction recycle of unconverted products. The indicated low nitrogen feeds refer to feeds containing from zero to 10 p.p.m. nitrogen and the indicated high nitrogen feeds refer to feeds containing above 10 p.p.m. nitrogen, for example 10 to 1000 p.p.m. nitrogen.

	NiW on SiO_2–MgO 27% MgO	6% Ni+ 22% Mo on Al_2O_3	6% Ni on SiO_2–Al_2O_3, 90% SiO_2
Temperature, in ° F. for 50% conversion with low N feeds	650	850	550
Temperature in ° F. for 50% conversion with high N feeds	740	850	760
Maximum yield of 320–650° F. middle distillate, with high N feed, percent	75–85	75–85	55–65
iC_4/nC_4 product ratio	high	low	high
Pour point of synthetic middle distillate product, ° F	−40	−20	−60
Relative denitrification activity	1.3	1.0	0.1
Sensitivity to S	nil	nil	nil
Sensitivity to N	low	nil	high

From the foregoing it will be seen that the process of the present invention is effective to convert a wide range of hydrocarbon feeds to valuable products, mainly middle distillate, light gasoline and isobutane. It will further be seen that, contrary to many prior art processes for producing middle distillates, no heavy gasoline is produced as a final product.

Although only specific embodiments of the present invention have been described, numerous variations could be made in those embodiments without departing from the spirit of the invention, and all such variations that fall within the scope of the appended claims are intended to be embraced thereby.

I claim:

1. In a process for producing gasoline from a hydrocarbon feed selected from the group consisting of petroleum distillates boiling from 200° to 1100° F. and petroleum residua boiling above 500° F., which comprises contacting said feed and from 1000 to 10,000 s.c.f. of hydrogen per barrel of said feed in a first conversion zone at a temperature from 500° to 950° F., a pressure above 500 p.s.i.g. and an LHSV of 0.1 to 4.0 with a catalyst comprising at least one hydrogenating component selected from the Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from the Group VIII metals and compounds of Group VIII metals intimately associated with a catalyst support comprising silica-magnesia, the improvement which comprises recovering from the effluent from said first conversion zone a light gasoline product boiling below about 180° F., a bottoms product boiling above about 660° F. and a middle distillate product boiling between 300° and 660° F., withdrawing said products from the system, hydrocracking in a second conversion zone in the presence of an active acidic hydrocracking catalyst at a pressure of 500 to 3000 p.s.i.g. and a temperature of 550° to 850° F. a portion of the effluent from said first conversion zone boiling from about 180° to 300° F., and containing light paraffins not converted to isoparaffins in the first conversion zone, to produce a light gasoline product having an increased isoparaffin content, and recovering said light gasoline product from said second conversion zone.

2. A process as in claim 1, wherein said hydrogenating component selected from the Group VI metals and compounds of Group VI metals is present in an amount from 1 to 40 weight percent, based on the total catalyst composite.

3. A process as in claim 1, wherein said hydrogenating component selected from the Group VIII metals and compounds of Group VIII metals is present in an amount from 1 to 20 weight percent, based on the total catalyst composite.

4. A process as in claim 1 wherein said hydrogenating components comprise nickel and tungsten.

5. A process as in claim 1 wherein at least two reactors are used in said first conversion zone, each containing said silica-magnesia supported catalyst, and wherein said reac-

tors are so arranged that they can be switched from parallel, for maximizing middle distillate production, to series, for maximizing gasoline production, whereby the ratio of middle distillate product to gasoline product can be varied.

6. A process as in claim 1 wherein a portion of the effluent from said first conversion zone that boils above about 660° F. is recycled to that zone.

References Cited by the Examiner

UNITED STATES PATENTS

2,428,692	10/47	Voorhies	208—112
2,436,170	2/48	Hill	208—95
2,799,626	7/57	Johnson et al.	208—110
2,932,611	4/60	Scott et al.	208—80
2,945,801	7/60	Ciapetta et al.	208—110
2,952,611	9/60	Haxton et al.	208—65
2,956,002	10/60	Folkus	208—59
3,037,930	6/62	Mason	208—112
3,047,490	7/62	Myers	208—59

ALPHONSO D. SULLIVAN, *Primary Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,180,818 April 27, 1965

William H. Claussen

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

Column 3, line 26, for "with" read -- said --; column 7, line 56, for "or" read -- on --; columns 9 and 10, first table, last column, under the heading "Fouling rate", line 12 thereof, for ".^{3}" read -- High.^{3} --.

Signed and sealed this 28th day of September 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents