

PATENT SPECIFICATION

NO DRAWINGS

940.667

Date of Application and filing Complete Specification: May 7, 1962.

No. 17394/62.

Application made in United States of America (No. 108,310) on May 8, 1961.

Complete Specification Published: Oct. 30, 1963.

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7 Index at acceptance:—Class C5, E(B2F1, B2G1, B2H3).

International Classification:—C 07 c, C 10 g.

COMPLETE SPECIFICATION

Hydrocarbon Combined Reforming-Dealkylation process



5 We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organised under the Laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to a process for the conversion of hydrocarbon charge stocks containing hydrocarbons which boil above the normal gasoline boiling range. More specifically the invention concerns a combination process involving the reforming of charge stocks containing hydrocarbons which boil above the normal gasoline boiling range and dealkylating the polynuclear alkylaromatic hydrocarbons which are recovered from the product of the reforming operation. The reforming step of the invention utilizes a particular catalytic composite, namely a composite comprising a fluoride-free refractory inorganic oxide, a platinum-group metallic component and combined chloride, the latter being the sole halogen component of the catalyst.

30 In the present specification and appended claims, the phrase, "hydrocarbons boiling at a temperature within the normal gasoline boiling range", designates those hydrocarbons and hydrocarbon fractions which have normal boiling points within the range of from about 21° to about 204°C., as determined in accordance with ASTM distillation method D-86 (see "ASTM Standards on Petroleum Products and Lubricants" published 1961 by the American Society for Testing and Materials). The term "hydrocarbons boiling at a temperature above the normal gasoline boiling range", refers therefore, to those hydrocarbons, and fractions having normal boiling points above 204°C. The invention is particularly adapted to the treatment of light naphthas

having an initial boiling point of about 93°C. and an end boiling point of about 232°C., heavy naphthas having an initial boiling point of about 177°C. and an end boiling point of about 246°C. and kerosene fractions having an initial boiling point of about 177°C. and an end boiling point as high as about 274°C. The invention may also be applied to various light and heavy gas oils.

55 Developments in internal combustion engines have steadily increased the demand for motor fuels possessing high octane ratings. This demand has brought about the development of new and improved processes for producing fuels possessing the necessary quality. The greatest development has occurred in the catalytic reforming processes. These reforming processes usually involve numerous hydrocarbon reactions including hydrogenation, cyclization, cracking, dehydrogenation, alkylation, hydrocracking and isomerization. While in particular instances, the catalytic reforming process may be designed to emphasize a single reaction or a combination of two or more of the aforementioned reactions, the process is usually designed for the specific purpose of converting straight-run and cracked gasolines and naphthas, having end boiling points below about 204°C., into hydrocarbon mixtures boiling within the gasoline boiling range and exhibiting a significantly higher octane rating.

80 It is sometimes desirable to supply to the catalytic reforming operation a charge stock boiling at least partly above the gasoline range. This increases the overall supply of high octane gasoline product. In addition to the gasoline formed by reforming these heavier stocks, there is also normally produced a substantial yield of material which is heavier than gasoline. This heavy reformat, like the gasoline reformat, is highly aromatic, but the composition of the heavy reformat has been so varied with respect to compound types as to preclude successful treatment for the re-

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coverly of valuable products. The material contains, for example, polynuclear alkylaromatic hydrocarbons, such as methylnaphthalene, which while not of great value themselves, could, if present in substantial concentration, be converted into corresponding polynuclear aromatics, such as naphthalene.

By means of the present invention a reforming operation wherein a charge stock containing hydrocarbons boiling above the gasoline range is processed over a specially constituted catalyst to produce (besides high octane gasoline) a heavier-than-gasoline reformat containing an unexpectedly high proportion of polynuclear alkylaromatic hydrocarbons, is combined with a separation step for recovering said alkylaromatic hydrocarbons and with a dealkylation operation whereby said alkylaromatic hydrocarbons are converted into valuable polynuclear aromatics. The present invention thus makes possible the treatment of a hydrocarbon charge stock containing hydrocarbons boiling above the normal gasoline boiling range, whereby to produce higher yields of high octane gasoline and at the same time convert the polynuclear alkylaromatic portion of the heavier-than-gasoline product into good yields of hydrocarbons of greatly enhanced value.

Accordingly, the present invention provides a hydrocarbon conversion process which comprises subjecting a normally liquid hydrocarbon charge containing hydrocarbons boiling above the normal gasoline boiling range in a first reaction zone to a reforming reaction in the presence of hydrogen and a fluoride-free catalytic composite containing a refractory inorganic oxide, a platinum group metal in an amount of from 0.01 to 5% by weight, and combined chlorine in an amount of from 0.75 to 1.5% by weight, calculated as elemental chlorine, at superatmospheric pressure, at a temperature substantially in the range of from 454° to 566°C. and at a liquid hourly space velocity in the range of from 0.1 to 10 at which hydrocarbons boiling below the initial boiling point of said hydrocarbon charge and a net volumetric yield of polynuclear alkyl aromatic hydrocarbons boiling above the normal gasoline boiling range are produced, separating a fraction containing said aromatic hydrocarbons from the effluent of said first reaction zone, subjecting the separated aromatic hydrocarbon fraction to hydrodealkylation in a second reaction zone, and recovering the dealkylated aromatic hydrocarbons from the effluent of the second reaction zone.

Desirable conversion conditions in the first reaction zone include a pressure of from about 30 to about 100 atmospheres.

The alkylnaphthalenes separated from the first reaction zone effluent are desirably contacted with a catalytic composite comprising chromia composited on alumina at dealkylation conditions including a temperature within the

range of from about 540° to about 820°C., a pressure in the range of from about 34 to about 41 atmospheres and the presence of hydrogen.

Relatively recent developments in catalytic reforming processes have indicated the advantages of a catalytic composite comprising at least one platinum-group metallic component. Although the prior art abounds in a multitude of such catalytic composites, and the methods employed for the manufacture thereof, the precise mechanism in regard to particular reactions is not fully understood, and the ultimate results of any process which utilizes a specific catalyst are difficult to predict with accuracy. In addition, various manufacturing procedures have been instituted for the purpose of enhancing the degree of activity and stability possessed by the particular catalytic composite, while effecting the reforming of hydrocarbons. It has now been discovered that a fluoride-free catalytic composite containing a platinum-group metal in an amount from 0.01 to 5% by weight, a refractory inorganic oxide and combined chlorine in an amount of from 0.75 to 1.5% by weight, calculated as elemental chlorine, offers unexpected advantages to the processing of hydrocarbon charge stocks containing hydrocarbons boiling above the normal gasoline boiling range whereby the materials found in the product after reforming and which boil in a range in excess of the normal gasoline boiling range contain a relatively high percentage of polynuclear alkylaromatic hydrocarbons. The prior art shows that the use of halogen, in some combined form, with the other components of the catalytic composite imparts a particular acid-acting function to the catalyst which seems to affect the quality and quantity of hydrocracking which results. While it has been said that the various members of the halogen family are equivalent, it had been found that the members of the halogen family are not, in fact, equivalent, and further that there appears to be a degree of criticality attached to the concentration of combined halogen within the catalyst, and that the same unexpectedly affects the processing of those hydrocarbons exhibiting normal boiling points above the normal gasoline boiling range. The known reforming processes utilizing catalytic composites comprising platinum-group metallic components, are rather restrictive in the type of hydrocarbonaceous material which may be processed thereby. The fluoride-free catalytic composite used in the process of the present invention is not restrictive in this manner, but instead permits effective processing of these heavier hydrocarbon components, thereby filling the void between the known catalytic reforming and cracking processes and at the same time providing a greater yield of desired products, namely, a net volumetric yield of hydrocarbons boiling at a temperature below



Hydrocracking

the initial boiling points of the hydrocarbon charge, and a net volumetric yield of polynuclear alkylaromatic hydrocarbons convertible to valuable polynuclear aromatic hydrocarbons.

5 Platinum itself is preferred as the platinum-group metallic component of the catalyst used in the reforming step of the present invention. However, other platinum-group metals such as palladium, rhodium, ruthenium, osmium and
10 iridium may be employed. It is not definitely known in what state the platinum-group metallic component exists within the final catalytic composite. It is believed that this component is at least partly in metallic state, although there is also evidence that it may be
15 present in part as halide, oxihalide, oxide, sulfide, or other combined form, or as mixtures of one or more of these forms. The alternative catalytically active metallic components are not
20 equivalent in effect. While, as stated above, the platinum or other metal from the platinum group will generally comprise from about 0.01% to about 5.0% by weight of the total catalytic composite, it preferably will be present
25 in a concentration of from about 0.1% to about 2.0% by weight.

Suitable refractory inorganic oxide components include alumina, silica, zirconia, magnesia, boria, thoria, titania, strontia, hafnia, and
30 mixtures of two or more, including silica-alumina, alumina-boria silica-magnesia and silica-alumina-zirconia. These refractory inorganic oxides may be manufactured by any well-known convenient method, or they may be
35 naturally occurring substances such as clays, sands or earths, and may be purified or activated by special treatment. Since the present invention is designed to produce high yields of a highly aromatic gasoline boiling range
40 product as well as a net volumetric increase of polynuclear aromatic hydrocarbons boiling above the normal gasoline boiling range, the catalyst preferably utilizes alumina as the carrier material, and avoids those refractory
45 inorganic oxides which tend to promote reactions which lead to the destruction of aromatic hydrocarbons. Thus, the preferred catalytic composite for utilization in the catalytic reforming step of the present combination
50 process will comprise platinum composited with alumina and chlorine as the sole halogen component.

material

The alumina preferably employed as the carrier material for the other catalyst components may be synthetically-prepared or naturally-occurring, and may be of the crystalline or gel type. Commercial alumina known as activated alumina, activated alumina of commerce, porous alumina or alumina gel are
60 highly suitable.

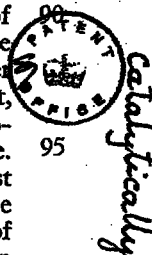
One very effective alumina carrier material may be prepared by adding a suitable alkaline reagent, such as ammonium hydroxide, to a salt of aluminum, such as aluminum
65 chloride or aluminum nitrate, in an amount to

form aluminum hydroxide which, upon drying, may be converted to alumina of any desired shape such as pills, cakes, extrudates, powder, granules, brickettes, etc. A particularly preferred form of alumina is the sphere, which may be manufactured by the well-known oil-drop method which comprises passing droplets of an alumina hydrosol into an oil bath maintained at an elevated temperature, retaining the droplets in said oil bath until they set to form hydrogel spheroids. The latter are usually subjected to aging treatments followed by a drying and calcination sufficient to decrease the volatile matter content of the calcined alumina to a level below about 2.0% by weight.

The chloride may be added to the carrier material in any suitable manner, and either before, or after the addition of the catalytically active metallic components, or simultaneously therewith. The chloride may be added as an aqueous solution of hydrogen chloride, as aluminium chloride, or through the utilization of a volatile salt such as ammonium chloride. Alternatively, at least a portion of the chloride may be composited with the alumina during the impregnation of the latter with the catalytic active metallic component, for example, through the utilization of chloroplatinic acid, chloroplatinous acid or the like. One desirable feature of the reforming catalyst preparation involves the calcination of the carrier material following the deposition of chloride. An excellent catalyst results when the composite is oxidized, or calcined, initially at a temperature within the range of from about 204°C. to about 316°C. for a period of at least one hour, until the volatile matter content thereof is decreased to a level below about 5.0% by weight, and then the calcination temperature is increased to 371° to 540°C. for an additional period of at least about one hour, until the volatile matter content of the final catalytic composite is decreased to a level below about 2.0% by weight. This particular calcination treatment is to render the chlorine component less easily removed from the catalyst.

The incorporation of the platinum-group metal component in the reforming catalyst is readily facilitated by impregnation with water soluble compounds of the platinum-group metals.

A method of manufacturing the catalytic composite for the reforming step of the present invention may be briefly described as follows: The carrier material is preferably alumina. The particularly preferred form of alumina is the sphere, and alumina spheres may be continuously manufactured by the well-known oil-drop method. This method is described in great detail in U.S. Patent No. 2,620,314. Following the formation of the alumina spheres, and the subsequent drying thereof to remove excessive water, the dried



spheres are subjected to high temperature calcination initially at an elevated temperature of from about 454°C. to about 556°C. This initial calcination procedure is effected for a period of at least about one hour, after which the temperature is increased to a level of about 593°C. to about 760°C., and the spherical alumina particles are further calcined until the volatile matter content thereof is decreased to a level below about 2.0% by weight. The calcined spheres are then intimately commingled with an aqueous solution of chloroplatinic acid in an amount producing a final catalytic composite comprising from about 0.01% to about 5.0% by weight of platinum. The impregnated catalyst is dried at a relatively low temperature to remove excessive water therefrom, and the temperature is then increased to 204°C. to 316°C., and the composite is calcined at this temperature for a time sufficient to decrease the volatile matter content thereof below about 5.0% by weight. The calcination temperature is increased to 371°C. to 538°C., and the procedure continued for a time sufficient to further decrease the volatile matter content to a level below about 2.0% by weight. The final catalytic composite will contain combined chloride, calculated as the element, in an amount between 0.75% to 1.5% by weight, which combined chloride is the sole halogen component of the catalytic composite. In addition to possessing an unusual degree of activity while effecting the reforming of hydrocarbons and mixtures of hydrocarbons, particularly those boiling at a temperature above the normal gasoline boiling range, the all-chloride catalyst, prepared as hereinabove set forth, possesses a physical and/or chemical structure such that the greater proportion of the combined chloride tends to remain composited with the catalyst during processing.

The hydrodealkylation step of the present process may be effected either thermally or by catalysis. A suitable dealkylation catalyst may contain a noble metal of Group VIII of the Periodic Table such as platinum, palladium, rhodium, ruthenium, osmium or iridium, composited on a suitable refractory oxide carrier. The catalyst may also contain metal oxides of elements such as vanadium, chromium, manganese, molybdenum and tungsten, composited on a suitable refractory oxide. It is also contemplated that combinations of the latter class of metal oxide components may be utilized by themselves or with a noble metal of Group VIII of the Periodic Table. Suitable refractory oxides which may be used include alumina, particularly aluminas containing a relatively high surface area such as gamma-alumina, eta-alumina and theta-alumina, silica, zirconia, silica-alumina, alumina-boria and silica-zirconia-alumina, A particularly effective dealkylation catalyst

comprises chromia impregnated on high surface area alumina, said chromia being present in an amount of from about 15 to about 20% or more.

The catalyst for the hydrodealkylation reaction may be prepared in any suitable manner. According to one preparation the desired refractory oxide base is first dried in order to reduce the volatile content of said base to a minimum. The dried base is then pilled to a desired crushing strength and calcined at a relatively high temperature of from about 540° to about 700°C. Following this the base is impregnated with a compound of the active metal component, for example by treating the base with a solution of the compound of the metal. The composite is then dried and oxidized at a relatively high temperature of from about 650° to about 760°C. for a period of about three hours.

In carrying out the process of the invention, the hydrodealkylation zone preferably is maintained at a temperature ranging from about 540° to about 820°C. and under an imposed pressure in the range of from about 20 to about 68 atmospheres or more. Especially suitable pressures lie in the range of from about 34 to about 41 atmospheres. Liquid hourly space velocities will desirably lie within the range from about 0.1 to about 10.0 and preferably within a range of from about 0.5 to about 5.0.

The process of the present invention may be effected in any suitable manner and may comprise either a batch or a continuous type operation. For example a charge stock may be continuously charged to a reforming zone containing the desired catalyst and which is maintained at the proper operating conditions, hereinbefore set forth, of temperature and pressure. Following the reforming the resulting catalytically reformed product is passed, in its entirety, into a separation zone wherein a hydrogen-rich gaseous phase is removed and recycled to combine with the original liquid hydrocarbon charge. This gaseous recycle is of an amount such that the mole ratio of hydrogen to hydrocarbons, entering the reaction zone, is within the range of from about 2:1 to about 20:1 or more. The hydrocarbon-rich liquid product is recovered and a fraction boiling at a temperature below the initial boiling point of said hydrocarbon charge and a fraction comprising polynuclear alkylaromatic hydrocarbons boiling at a temperature in excess of the normal gasoline boiling range are separated therefrom. The former is recovered and purified by conventional means while the latter is then passed to a hydrodealkylation zone, where the polynuclear alkylaromatic hydrocarbons are hydrodealkylated in the presence of hydrogen in either a thermal or catalytic process at appropriate conditions of temperature and pressure. The reactor effluent from the dealkylation zone



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about

is withdrawn and passed to a high pressure separator or flash drum which is maintained at a pressure in the range of from about 34 to about 41 atmospheres. In this separator the hydrogen-rich gaseous phase which has a purity in excess of 60% is separated and recycled to the hydrodealkylation zone. The liquid hydrocarbon fraction comprising polynuclear aromatic hydrocarbons and unreacted polynuclear alkylaromatic hydrocarbons along with some light hydrocarbons such as methane, ethane and propane is withdrawn as bottoms and passed to a second separator or flash drum which is maintained at a considerably lower pressure. It is contemplated that the second separator or flash drum may be maintained at a pressure in the range of from about 3.4 to 10.4 atmospheres gauge in the event that a third separator or flash drum is used. However, if only two separators are used, the second separation zone is maintained at approximately atmospheric pressure. In this second separation zone or flash drum the light gaseous hydrocarbons are withdrawn and passed to a gas absorber wherein any desired polynuclear aromatic hydrocarbon or polynuclear alkylaromatic hydrocarbon which has flashed overhead with the light hydrocarbons are absorbed in the absorber oil and passed to a stripper, while the light gaseous hydrocarbons such as methane, ethane and propane are utilized for fuel. The liquid hydrocarbon fraction from the last flash drum is withdrawn, a portion of this fraction going to clay treaters wherein said fraction is treated to remove impurities and from thence to a separator wherein the desired polynuclear aromatic hydrocarbon is withdrawn to storage while any unreacted polynuclear alkylaromatic hydrocarbon is recycled to form a portion of the feed stock. A second portion of the liquid hydrocarbon fraction from the last flash drum is recycled, one portion of this fraction being admixed with the reactor effluent in the dealkylation zone thereby effecting a quench of the reactor effluent, while the other portion of this fraction is admixed with the reactor effluent subsequent to withdrawal from the dealkylation zone and prior to entry into the high pressure separator or flash drum, thereby tending to absorb any light hydrocarbons such as methane, ethane and propane which are present in the reactor effluent and allowing the recovery of the hydrogen in the hydrogen-rich gaseous fraction which is flashed overhead from the high pressure separator in a relatively purer state, said purity of the hydrogen stream being in excess of about 60% (the purity being expressed as the mole ratio of hydrogen to hydrogen plus impurities).

The following examples are given to further illustrate the process of the present invention. The first two examples illustrate the unexpected activity and stability of the reforming

catalyst prescribed for use in accordance with the invention.

EXAMPLE I

A catalyst was prepared utilizing 1/16-inch alumina spheres, manufactured in accordance with U.S. Patent No. 2,620,314 and containing 0.35% by weight of combined chloride. The spheres were intimately commingled with a sufficient quantity of an aqueous solution of hydrogen fluoride to composite therewith about 0.35% by weight of combined fluoride. The spheres were then dried, and subjected to a single calcination procedure at a temperature of about 482°C. The calcined spheres were impregnated with an aqueous solution of chloroplatinic acid in an amount to yield a final catalyst containing 0.75% by weight of platinum, calculated as the element thereof. The impregnated spheres were dried at a temperature of about 150°C., and thereafter calcined, in an atmosphere of air, at a temperature of about 482°C., for a period of about 2 hours until such time as the volatile matter content of the catalyst was below a level of about 2.0% by weight. This catalyst is an example of the present-day, reforming-type catalysts containing platinum and combined halogen. This catalyst was designated as catalyst "A", and was compared with the all-chloride catalyst prepared as set forth below.

A second catalyst, designated as catalyst "B", was also prepared using alumina spheres formed by the oil-drop method. The spheres were dried at 204°C., and calcined in air for one hour at 510°C. The calcination temperature was then increased to 685°C., and the calcination continued for two hours, until the volatile matter content of the alumina spheres had decreased to a level of 1.98% by weight. The calcined spheres were then commingled, in a rotating evaporator, with water, hydrochloric acid, and sufficient chloroplatinic acid to composite 0.375% by weight of platinum therewith. On the basis of about 272 kilograms of the 1.59 mm (average diameter) calcined spheres, 515 liters of water and 15.7 kilograms of a 34.6% by weight of hydrochloric acid were added to the rotating evaporator. The alumina spheres were dried within the rotating evaporator at a steam pressure of about 3.4 atmospheres for a period of six hours. The dried spheres were then subjected to high-temperature calcination, or oxidation, at a temperature of 288°C., for a period of one hour until the volatile matter content was 4.5% by weight. The temperature was then increased to a level of 500°C., and further calcination was effected for a period of two hours, until the volatile matter content had decreased to a level of 1.7% by weight. As indicated in Table I, this catalyst was fluoride-free, and contained 0.375% by weight of platinum and 0.95% by

weight of combined chloride, calculated as elemental chlorine.

- 5 A third catalyst, designated as catalyst "C", was prepared in the same manner as catalyst "B", with the exception that sufficient chloro-platinic acid was employed during the impregnating technique to composite 0.750% by weight of platinum therewith. This catalyst was also fluoride-free, containing 0.95% by weight of combined chloride as the sole halogen component thereof.

10 The three catalyst portions were then subjected, individually, to a reforming activity and stability test which comprises passing a

standard hydrocarbon charge stock, having a boiling range of about 93°C. to about 204°C., through the catalyst at a liquid hourly space velocity of 2.0, in an atmosphere of hydrogen present in a mol ratio of hydrogen to hydrocarbon of 14:1, for a period of 14 hours. The reaction zones were maintained at a temperature of 500°C., and were under an imposed pressure of 34 atmospheres. The liquid product, from each reaction zone, over the entire 14 hour period of the test, was analyzed for its octane rating (F—1 Clear). Results are given in the following Table I:

TABLE I:
Standard Relative Activity Test

Catalyst Designation	A	B	C
Analysis, wt. %			
Platinum	0.750	0.375	0.750
Fluoride	0.350	0	0
Chloride	0.350	0.95	0.95
Total Halogen	0.700	0.95	0.95
Octane Rating of Product, F—1 Clear	94.9	96.4	96.8
Excess Receiver Gas, Liters/Liter	147	153	163
Excess Debutanizer Gas, Liters/Liter	79	82	79
Total Excess Gas, Liters/Liter	227	235	243
Debutanizer Gas Ratio	0.351	0.350	0.326
Activity Ratings			
Debutanizer Overhead			
At same Octane	100	98	93
At same Total Gas	100	98	89
Octane Number — Space Velocity	100	112	119

- 30 For the purpose of obtaining a clear understanding of the data, definitions of the terms employed in Table I are given below:

- 35 1. The excess receiver gas is that quantity of gas in excess of the amount required to maintain the desired pressure within the reaction zone. Analyses have indicated that this gas is, for all practical purposes, substantially pure hydrogen (approximately 90—95 mol % throughout the 14 hour period of the standard activity test).

- 40 2. The excess debutanizer gas is that gaseous product which is composed primarily of

light paraffins, methane, ethane, propane and butane, along with some hydrogen, and results primarily from the hydrocracking reactions being effected within the reaction zone.

3. The debutanizer gas ratio is the ratio of excess debutanizer gas to the total excess gas, on a volume basis, and is indicative of the relative yield of desirable liquid product within the effluent from the reaction zone; it is, to a certain extent, an indication of the relative stability of the catalyst. The lower the debutanizer gas ratio, the more active the catalyst for the purpose of effecting the reforming

of hydrocarbons, and greater is the stability of the catalyst.

4. The activity ratings are employed on a comparative basis with respect to the standard catalyst, namely catalyst "A"; they are first compared at identical octane ratings and total excess gas production, and at equivalent liquid hourly space velocities. In the latter instance, the larger the number, the more active the catalyst; in the former instances, the smaller the number, the greater the yield of high octane product.

The data given in Table I clearly indicates the benefits afforded the catalytic reforming of hydrocarbons through the utilization of the catalyst constituted in accordance with the prescription of the present invention. Both of the fluoride-free, all-chloride catalyst ("B" and "C") resulted in a lesser quantity of excess debutanizer gas than the standard catalyst, when compared at the same octane rating and at the same total excess gas production. Similarly, these catalysts indicated greater than 10% increase in space velocity activity. Upon comparing catalyst "C" with catalyst "A", both of which contain the same quantity of platinum, it is seen that catalyst "C" resulted in 7% less excess debutanizer gas, compared at the same octane rating, and exhibited a significantly lower debutanizer gas ratio, while at the same time producing a liquid product having a significantly greater octane rating. It is further significant that catalyst "C" contained approximately 0.25% by weight additional halogen which, according

to expectations, should have resulted in a greater degree of hydrocracking, in turn resulting in a higher debutanizer gas ratio. Unexpectedly, however, the activity ratings relative to excess debutanizer gas production indicate the contrary.

The same three catalysts were subjected, to a second standard test procedure designed to evaluate the stability of the catalyst over an extended period of time. This secondary evaluation test procedure involves the utilization of a light naphtha having a boiling range from about 71° to about 127°C., and is effected at operating conditions specifically designed to induce a slight instability to the operation. The catalyst is maintained at a pressure of 20.4 atmospheres and the charge is passed therethrough at a liquid hourly space velocity of 1.5, in the presence of hydrogen in an amount to yield a mol ratio of 12:1. The test procedure is effected for a period of approximately 150 hours or more, varying the operating temperature to maintain an octane rating of 100 (F-1 Clear), on the pentanes-and-heavier portion of the product effluent. The various results are plotted against time, and the relative activity and stability is determined by comparing the data to that resulting from the reference catalyst. The relative stability of the catalyst is determined by comparing the slope of the various plots at 100 hours, to the slope of the reference catalyst at 100 hours. The data resulting from the extended stability test are given in the following Table II:

TABLE II:

Extended Stability Test, Stability @ 100 Hours

Catalyst Designation	A	B	C
Block Temperature, °C.	550	538	536
Excess Receiver Gas, Liters/Liter of Charge	198	210	225
Excess Debutanizer, Gas, Liters/Liter of Charge	82	75	64
Total Excess Gas, Liters/Liter of Charge	280	286	289
Debutanizer Gas Ratio	0.293	0.264	0.220
Yield, Pentanes and Heavier Vol. %	57.2	59.1	61.8

Here again, comparing catalyst "A", and "C", the benefits to be afforded the catalytic reforming of hydrocarbons is clearly ascertained. The all-chloride catalyst at the 100-hour comparison, required 14°C. less operating temperature while producing better than 4.0% greater volumetric yield of pentanes and heavier hydrocarbons. Of greater significance,

however, is the lower debutanizer gas ratio exhibited by the all-chloride catalyst, compared to the catalyst containing combined fluoride. The results of the extended stability test are unusual, and totally unexpected from the teachings and results indicated within the prior art.

EXAMPLE II

A second extended stability test procedure was performed, comparing the standard platinum-chloride-fluoride catalyst with a catalyst containing 0.81% of chlorine by weight, as the sole halogen component thereof. This catalyst is designated in the following table as catalyst "D", and differs from catalyst "C" only in the slightly lower concentration of combined chloride. The extended stability operation was carried out for a total period of 185 hours at a liquid hourly space velocity of 1.5, and an operating pressure of 20.4 atmospheres, at a hydrogen to hydrocarbon mol ratio of about 7.5. The charge stock was a light naphtha having a boiling range from

76° to 135°C., and contained 76.0% paraffins, 17.0% naphthenes and 7.0% aromatics, on a volumetric basis. The operating temperature was subjected to change, throughout the total period of 185 hours, for the purpose of maintaining an octane rating, on the debutanized liquid product, of 100.0 (F-1 Clear).

The two catalysts "A" and "D", were compared during the initial portion of the extended stability test, that is, at 41 hours, and at the end of the extended stability test, at 185 hours. The data obtained are presented in the following Table III and indicate the benefits afforded the catalytic reforming of hydrocarbons, utilizing an all-chloride catalyst free from combined fluoride.

TABLE III:

Extended Stability Test — 185 Hours at 100.0 F-1 Clear

Catalyst Designation	A	D	A	D
Period Duration, Hours	41	41	185	185
Block Temperature, °C.	552	549	557	547
Severity Differential, °C./Hr.	—	—	0.065	0.0039
Excess Receiver Gas, Liters/Liter of Charge	229	245	179	215
Excess Debutanizer Gas, Liters/Liter of Charge	72	63	92	76
Total Excess Gas, Liters/Liter of Charge	301	308	271	290
Debutanizer Gas Ratio	.240	.204	.336	.261
Yield, Pentanes and Heavier, Vol. %	60.1	61.8	55.2	59.0
Carbon Deposition, Wt. %	—	—	5.39	3.59

The severity differential was obtained by computing the average slope of the temperature-time plot over the entire period of operation. This differential is indicative of the prospective catalyst life to be expected in terms of the stability of the catalyst.

From the foregoing data, it is seen that the all-chloride catalyst possesses a substantially increased activity and stability. This is indicated by the severity differential of 0.0039°C. per hour for the all-chloride catalyst, as compared to a temperature differential of 0.065°C. per hour. Furthermore, the volumetric yield of pentanes and heavier hydrocarbons decrease to the extent of about 5.0%, and only 2.8% for the all-chloride catalyst. In addition, and of greater significance, is the fact that all the all-chloride catalyst indicated a carbon deposition, as a result of the extended period of operation, of only 3.59% by weight, whereas the stan-

dard catalyst exhibited a carbon deposition of 5.39% by weight. Other comparisons may be made from the data presented in Table III, and these comparisons will indicate the greater degree of stability and activity possessed by the all-chloride catalyst.

EXAMPLE III

The catalyst employed in this example utilized 1.59 mm. alumina spheres, prepared as described in Examples I and II, as the carrier material for 0.750% by weight of platinum and 0.90% by weight of combined chloride, calculated as the element thereof. The hydrocarbon charge stock employed was a heavy naphtha having an initial boiling point of 104°C. and an end boiling point of about 230°C. and containing 89.9% by volume of paraffins and naphthenes. Other properties of this charge stock are given in the following Table IV:

TABLE IV:
Charge Stock Properties

Specific Gravity (15.6° C.)	0.7711
ASTM 100 ML. Distillation (D86)° C.	
Initial Boiling Point	104
5%	117
10%	123
30%	139
50%	154
70%	176
90%	201
95%	211
End Boiling Point	230
Sulfur, Wt. %	0.012
Total Nitrogen, Parts per million	0.14
Hydrocarbon Type Analysis, Vol. %	
Aromatics	9.6
Olefins	0.5
Paraffins Plus Naphthenes	89.9

5 Of the 10.1% aromatics and olefins, boiling at a temperature in excess of the normal gasoline boiling range, 0.26% by volume (based upon the total charge stock) were alkylnaphthalenes. As hereinafter shown, the utilization of the all-chloride catalyst for the reforming of this particular hydrocarbon charge stock, results in a net production of hydrocarbons boiling below the initial boiling point of 104°C., and further reforms the heavier portion of the charge stock to increase the yield of alkylnaphthalenes. The resulting alkylnaphthalenes are separated from

the total reformed product effluent and subjected to hydrodealkylation to produce a substantially pure naphthalene concentrate and the saturated hydrocarbon corresponding to the alkyl group which is removed from the naphthalene molecule.

A total of eight test periods was performed, varying the catalyst bed temperature, the reaction zone pressure and the recycle hydrogen to hydrocarbon mol ratio. The various operating conditions for these eight periods are given in the following Table V:

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20

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TABLE V:
Operating Conditions

Period Designation	1	2	3	4	5	6	7	8
Reactor Block Temperature, °C.	509	518	527	550	533	534	529	529
Average Catalyst Bed Temperature, °C.	—	487	495	517	502	502	502	493
Reactor Pressure, atmospheres, gauge	486	48.6	48.6	48.6	48.6	48.6	48.6	34
Liquid Hourly Space Velocity	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Recycle Gas/Oil Ratio	20.0	20.0	20.0	20.0	20.0	20.0	12.0	12.0
Recycle Gas Hydrogen, Mol. %	—	78.1	76.5	71.1	76.7	76.7	79.2	81.3
Vent Gas Rates, Liters/Liter of Charge								
Separator Gas	128	148	164	189	160	160	153	196
Debutanizer Gas	39	45	50	60	48	52	57	37
Total	167	192	214	249	208	212	210	233
Debutanizer Gas Ratio	.234	.232	.234	.243	.231	.244	.271	.160

It should be noted that the debutanizer gas ratios, previously discussed with respect to Example I, were consistently low throughout the entire period of operation, and compare favourably with the debutanizer gas ratios set forth in the previous examples, notwithstanding that the charge stock contained hydrocarbons boiling at a temperature above the normal gasoline boiling range. This is especially significant in regard to period No. 8, during which the reaction zone pressure was 34 atmospheres, the recycle gas to oil

ratio had been decreased to 12.0, with a resulting lower average catalyst bed temperature of 493°C. The debutanizer gas ratio for this eighth period was only 0.160. The total liquid product effluent was passed into a high-pressure separator, operating at substantially the same pressure as the reaction zone, and at a temperature of about 27°C., for the purpose of removing a hydrogen-rich gaseous phase which was recycled to combine with the original hydrocarbon charge prior to passing the same into the reaction zone.

The normally liquid hydrocarbons from the high-pressure separator were then subjected to precise laboratory distillation in a multi-plate fractionating column, for the purpose of separating a gasoline fraction from the total product at a precise cut point of 200°C. Various product inspections, including the octane rating and hydrocarbon-type analysis of the gasoline fraction, and the naphtha bottoms fraction (boiling at a temperature in excess of 200°C.) are given in the following Table VI:



TABLE VI:

Product Inspections

Period Designation	1	2	3	4	5	6	7	8
Gasoline Fraction, IBP—200° C.								
Specific Gravity	.778	.782	.790	.808	.788	.791	.788	.794
Initial Boiling Point, °C.	60	58	57	47	56	54	54	57
5%	82	74	74	64	72	70	69	76
10%	92	85	83	76	81	80	78	86
30%	113	110	109	109	110	108	104	113
50%	131	129	131	135	131	131	126	134
70%	146	146	148	150	148	148	146	150
90%	166	164	168	170	167	167	166	169
95%	174	171	176	179	176	176	174	176
End Boiling Point	189	191	193	192	183	193	189	187
Reid Vapor Pressure, Atmospheres	0.20	0.22	0.25	0.39	0.26	0.25	0.29	0.22
Octane Rating, F—1 Clear	86.1	90.4	94.6	100.0	94.5	96.0	95.6	95.8
Hydrocarbon Type Analysis, Vol. %								
of C ₆ +								
Aromatics	47.6	52.5	59.7	76.7	57.3	61.8	61.5	61.4
Olefins	—	0.7	0.7	0.5	0.9	0.6	0.7	1.0
Paraffins Plus Naphthenes	52.4	46.8	39.6	22.9	41.8	37.6	37.8	37.6
Naphtha Bottoms Fraction, 200° C.+								
Specific Gravity, (15.6/15.6° C.)	.9245	.9338	.9505	.9920	.9482	.9535	.9552	.9550
Octane Rating, F—1 Clear	111.3	110.5	111.6	—	108.3	116.5	112.9	112.7
Hydrocarbon Type Analysis, Vol. %								
Aromatics	94.3	97.0	100.0	100.0	100.0	100.0	100.0	100.0
Olefins	0.7	0.6	Trace	Trace	Trace	Trace	—	Trace
Paraffins Plus Naphthenes	5.0	2.4	—	—	—	—	—	—

As indicated in Table VI, the naphtha bottoms fraction was virtually 100% aromatic, containing only a trace of olefinic hydrocarbons. In regard to period No. 8, the gasoline fraction, having an octane rating, F-1 Clear, of 95.8 consisted of 61.4% by

volume of aromatic hydrocarbons. When considered in conjunction with the extremely low debutanizer gas ratio set forth in Table V, the production of the gasoline fraction of this nature, as well as a naphtha bottoms fraction consisting of practically 100% aromatic

hydrocarbons, clearly indicates the advantages to be had through the utilization of the process of the present invention. Various liquid and light paraffinic hydrocarbon yields are presented in the following Table VII for these eight test periods.

TABLE VII

Product Yields

Period Designation	1	2	3	4	5	6	7	8
Light Paraffinic Hydrocarbons, Ltrs/Ltr. Charge								
Methane	21	24	29	38	28	28	22	21
Ethane	12	15	18	26	17	17	19	16
Propane	14	17	20	25	21	22	24	17
Total	47	66	67	89	66	67	65	54
Liquid Yields, Gasoline Fraction, Vol. %								
Iso-Butane	1.8	2.3	2.7	3.3	2.8	3.0	3.2	2.5
N-Butane	3.5	4.0	4.5	4.6	4.6	5.0	5.4	3.8
Iso-Pentane	2.9	3.1	3.9	4.5	3.8	4.0	4.6	3.5
N-Pentane	1.9	2.6	2.4	3.2	2.5	2.6	3.0	2.2
Hexanes to 200° C.	73.4	69.3	66.5	61.2	65.0	64.9	64.4	66.0
Pentanes to 200° C.	78.2	75.0	72.8	68.9	71.3	71.5	71.0	71.7
Butanes to 200° C.	83.5	81.3	80.0	76.8	78.7	79.5	80.6	78.0
Liquid Yield, Naphtha Bottoms, Vol. %								
Alkyl-Naphthalenes, Vol. %	7.5	7.9	6.9	5.3	7.8	7.0	7.0	9.4
	2.5	2.9	3.0	3.7	3.2	3.1	3.3	4.6

of iso- and normal butanes which find value either as gasoline blending components or as subsequent charge stock to a unit specifically designated to effect the alkylation thereof.

Similar advantages are realized when the charge stock is considerably heavier. For example, when a "kerosene fraction", having an

initial boiling point of 177°C. and an end boiling point of 274°C. was processed at a temperature of 500°C., a pressure of 68 atmospheres, and a liquid hourly space velocity of about 1.5, 68% of the total liquid product boiled within the gasoline boiling range and the remaining 32% by volume, boiling above

20 Table VII shows particularly good yields for Period No. 8, where there was an increase in alkyl-naphthalenes to 4.6 volume percent (based upon the original charge to the process), a 71.7 volumetric percent yield of gasoline boiling range hydrocarbons having the octane rating of 95.8 and 6.3% by volume

the normal gasoline boiling range, contained over 90.0% by volume of aromatic hydrocarbon.

EXAMPLE IV

- 5 A dealkylation catalyst was prepared by drying alumina powder containing 38.3% volatile matter for a period of four hours at a temperature in the range of from 316° to 343°C. (Volatiles=14.2%). The dried base
10 was lubricated with 5% by weight of polyvinyl alcohol and pilled. The powder was pilled to a crushing strength of between 4.5 and 7.3 kilograms, the size of said pills being of 3.18 mm. diameter. The catalyst base pills
15 were then calcined for a period of 1.5 hours

at 497°C. and three hours at 650°C. The average crushing strength of the calcined pills was 2.6 kilograms and the Apparent Bulk Density was 0.80 gm/ml. The calcined base (20.4 kg.) was impregnated with a chromic acid solution containing 9.3 kilograms of chromic acid and 18.4 liters of water, said impregnating time being 0.5 hours. 56.3% of the solution was absorbed on the base. The resulting composite was dried for a period of three hours at 149°C. following which the dried composite was oxidized in a belt oxidizer for 1.5 hours at 427°C. followed by three hours at 704°C. The finished catalyst had the following characteristics:

Weight % Cr_2O_3	17.6
Volatile Matter at 900° C., Weight %	1.04
Amount Bulk Density, gms./ml.	0.94
Surface Area, $\text{M}^2/\text{gms.}$	1.06
Pore Volume, cc/gms.	0.16
Pore Diameter, Å	60

- The polynuclear alkylaromatic hydrocarbons recovered from the reforming operations set forth in the above examples were separated by fractionation from the other reaction products and charged to a reaction zone containing the above catalyst. The reactor was maintained at a temperature from 621° to 677°C. and a pressure of 41 atmospheres. The polynuclear alkyl-aromatic fraction was charged to the reactor at a liquid hourly space velocity of about 3. Hydrogen is also charged to the reactor at a rate of about 267 liters per liter of charge. The reactor effluent is withdrawn and passed to a high pressure separator (34 atm.) wherein a hydrogen-rich gas fraction is separated and recycled to the reaction zone, the purity of said hydrogen being in excess of 60%. The liquid hydrocarbon fraction from the separator was passed to a low pressure separator (5 atm.) where methane, ethane and propane were removed and passed to a gas absorber. The bottoms from the low pressure separator, comprising naphthalene and alkyl naphthalenes, was withdrawn at a temperature of 60°C. a portion thereof (40%) was passed to a fractionator wherein naphthalene product was separated overhead and passed to storage. The fractionator bottoms stream comprising unreacted alkyl naphthalenes was recycled to the dealkylation zone. A second portion (28%) of the liquid from the low pressure separator was recycled to the reactor, entering the re-

actor near its outlet whereby it served as a quench to lower the temperature of the effluent prior to discharge of the latter from said reaction zone. A third portion (32%) of the low pressure separator liquid was admixed with the reactor effluent after its withdrawal from the reaction zone and prior to entry into said high pressure separator, thereby absorbing a relatively large portion of the light hydrocarbons such as methane, ethane, and propane which are in the reactor effluent.

Analysis of the product showed that the naphthalene recovered amounted to 98% of the theoretical yield based upon the concentration of alkyl naphthalene in the feed.

WHAT WE CLAIM IS:—

1. A hydrocarbon conversion process which comprises subjecting normally liquid hydrocarbon charge containing hydrocarbons boiling above the normal gasoline boiling range in a first reaction zone to a reforming reaction in the presence of hydrogen and a fluoride-free catalytic composite containing a refractory inorganic oxide, a platinum group metal in an amount of from 0.01 to 5% by weight, and combined chloride in an amount of from 0.75 to 1.5% by weight, calculated as elemental chlorine, at superatmospheric pressure, at a temperature substantially in the range of from 454° to 566°C. and at a liquid hourly space velocity in the range of from 0.1 to 10 at which hydrocarbons boiling below the



the normal gasoline boiling range, contained over 90.0% by volume of aromatic hydrocarbon.

EXAMPLE IV

- 5 A dealkylation catalyst was prepared by drying alumina powder containing 38.3% volatile matter for a period of four hours at a temperature in the range of from 316° to 343°C. (Volatiles=14.2%). The dried base
10 was lubricated with 5% by weight of polyvinyl alcohol and pilled. The powder was pilled to a crushing strength of between 4.5 and 7.3 kilograms, the size of said pills being of 3.18 mm. diameter. The catalyst base pills
15 were then calcined for a period of 1.5 hours

at 497°C. and three hours at 650°C. The average crushing strength of the calcined pills was 2.6 kilograms and the Apparent Bulk Density was 0.80 gm/ml. The calcined base (20.4 kg.) was impregnated with a chromic acid solution containing 9.3 kilograms of chromic acid and 18.4 liters of water, said impregnating time being 0.5 hours. 56.3% of the solution was absorbed on the base. The resulting composite was dried for a period of three hours at 149°C. following which the dried composite was oxidized in a belt oxidizer for 1.5 hours at 427°C. followed by three hours at 704°C. The finished catalyst had the following characteristics:

Weight % Cr_2O_3	17.6
Volatile Matter at 900° C., Weight %	1.04
Amount Bulk Density, gms./ml.	0.94
Surface Area, $\text{M}^2/\text{gms.}$	1.06
Pore Volume, cc/gms.	0.16
Pore Diameter, Å	60

- The polynuclear alkylaromatic hydrocarbons recovered from the reforming operations set forth in the above examples were separated by fractionation from the other reaction products and charged to a reaction zone containing the above catalyst. The reactor was maintained at a temperature from 621° to 677°C. and a pressure of 41 atmospheres.
35 The polynuclear alkyl-aromatic fraction was charged to the reactor at a liquid hourly space velocity of about 3. Hydrogen is also charged to the reactor at a rate of about 267 liters per liter of charge. The reactor effluent is withdrawn and passed to a high pressure separator (34 atm.) wherein a hydrogen-rich gas fraction is separated and recycled to the reaction zone, the purity of said hydrogen being in excess of 60%. The liquid hydrocarbon fraction from the separator was passed to a low pressure separator (5 atm.) where methane, ethane and propane were removed and passed to a gas absorber. The bottoms from the low pressure separator, comprising naphthalene and alkyl naphthalenes, was withdrawn at a temperature of 60°C. a portion thereof (40%) was passed to a fractionator wherein naphthalene product was separated overhead and passed to storage.
55 The fractionator bottoms stream comprising unreacted alkyl naphthalenes was recycled to the dealkylation zone. A second portion (28%) of the liquid from the low pressure separator was recycled to the reactor, entering the re-

actor near its outlet whereby it served as a quench to lower the temperature of the effluent prior to discharge of the latter from said reaction zone. A third portion (32%) of the low pressure separator liquid was admixed with the reactor effluent after its withdrawal from the reaction zone and prior to entry into said high pressure separator, thereby absorbing a relatively large portion of the light hydrocarbons such as methane, ethane, and propane which are in the reactor effluent.

Analysis of the product showed that the naphthalene recovered amounted to 98% of the theoretical yield based upon the concentration of alkyl naphthalene in the feed.

WHAT WE CLAIM IS:—

1. A hydrocarbon conversion process which comprises subjecting normally liquid hydrocarbon charge containing hydrocarbons boiling above the normal gasoline boiling range in a first reaction zone to a reforming reaction in the presence of hydrogen and a fluoride-free catalytic composite containing a refractory inorganic oxide, a platinum group metal in an amount of from 0.01 to 5% by weight, and combined chloride in an amount of from 0.75 to 1.5% by weight, calculated as elemental chlorine, at superatmospheric pressure, at a temperature substantially in the range of from 454° to 566°C. and at a liquid hourly space velocity in the range of from 0.1 to 10 at which hydrocarbons boiling below the

initial boiling point of said hydrocarbon charge and a net volumetric yield of polynuclear alkyl aromatic hydrocarbons boiling above the normal gasoline boiling range are produced, separating a fraction containing said aromatic hydrocarbons from the effluent of said first reaction zone, subjecting the separated aromatic hydrocarbon fraction to hydrodealkylation in a second reaction zone, and recovering the dealkylated aromatic hydrocarbons from the effluent of the second reaction zone.

2. Process as claimed in claim 1 wherein the conversion in the first reaction zone is effected at a pressure of from 30 to 100 atmospheres and the hydrodealkylation in the second reaction zone is effected at a temperature in the range of from 540° to 820°C. and a pressure substantially in the range of from 20 to 68 atmospheres.

3. A process as claimed in claim 1 or 2 wherein the conversion in the first reaction zone is effected in the presence of a fluoride-free catalytic composite of alumina, platinum and combined chloride while the hydrodealkylation in the second reaction zone is promoted by a catalyst containing chromia and alumina in the presence of an excess of hydrogen.

4. Process as claimed in any of the claims 1 to 3, further characterized in that the hydrodealkylation reaction is effected at a temperature in the range from 620° to 677°C. at a pressure within the range from 34 to 41 atmospheres and in the presence of an excess of hydrogen supplied to the second reaction

zone in the form of a gas mixture containing at least 60 volume % hydrogen.

5. Process as claimed in any of the claims 1 to 4 wherein the charge to the first reaction zone is a naphtha boiling substantially in the range from about 93°C. to about 232°C.

6. Process as claimed in any of the claims 1 to 4, wherein the charge to the first reaction zone is heavy naphtha boiling substantially in the range from about 177°C. to about 246°C.

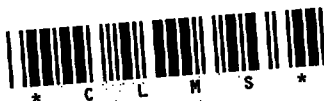
7. Process as claimed in any of the claims 1 to 4 wherein the charge to the first reaction zone is kerosene fraction boiling substantially in the range from about 177°C. to about 274°C.

8. Process as claimed in any of the claims 1 to 7, further characterized by separating from the liquid effluent from the first reaction zone, by fractional distillation, a fraction consisting practically entirely of aromatic hydrocarbons, including alkyl naphthalenes, introducing said fraction into the second reaction zone and therein subjecting said fraction to hydrodealkylation and recovering naphthalene from the resulting reaction mixture.

9. Process for the conversion of a normally liquid hydrocarbon charge containing hydrocarbons boiling above the normal gasoline boiling range, substantially as described.

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Chartered Patent Agents.
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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1963. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.



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