Oct. 30, 1945. A. L. FOSTER 2,387,989

PREPARATION OF CYCLIC HYDROCARBONS

Filed June 12, 1942 2 Sheets-Sheet 1

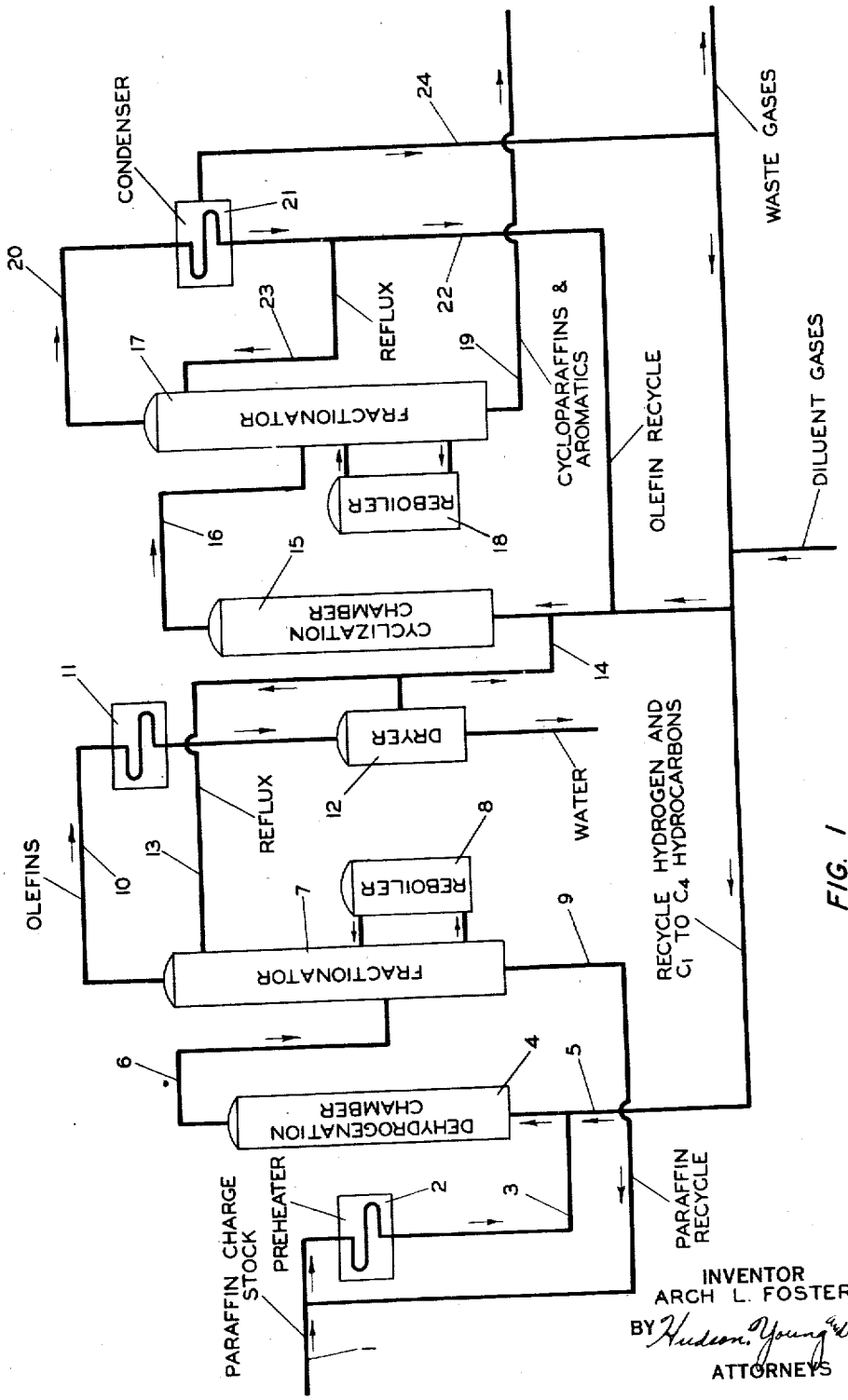


FIG. 1

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PREPARATION OF CYCLIC HYDROCARBONS

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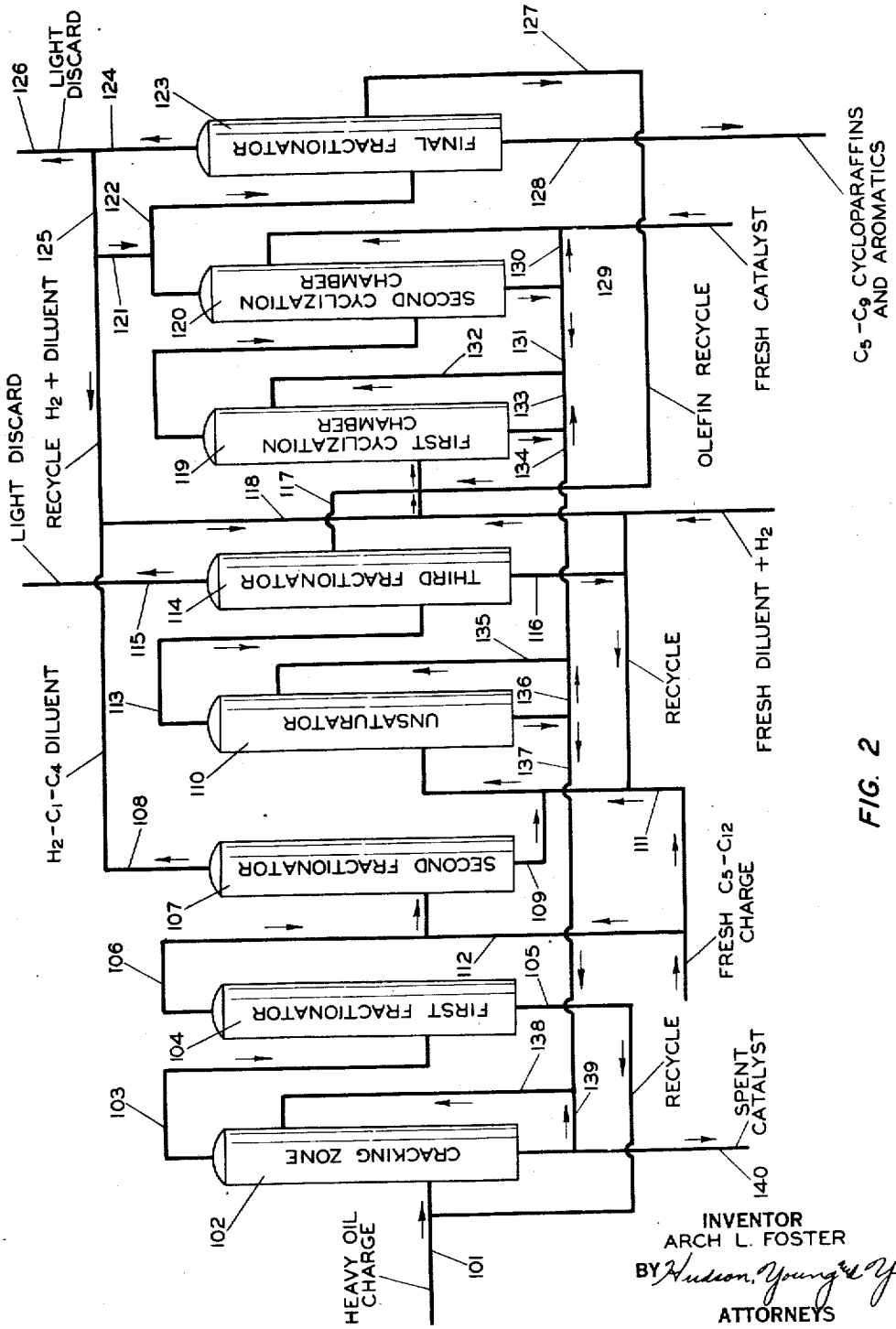


FIG. 2

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Patented Oct. 30, 1945

2,387,989

UNITED STATES PATENT OFFICE

2,387,989

PREPARATION OF CYCLIC HYDROCARBONS

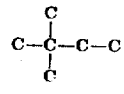
Arch L. Foster, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

Application June 12, 1942, Serial No. 446,752

3 Claims. (Cl. 260—673.5)

This invention pertains generally to the changing of molecular structure of hydrocarbons to produce materials more suitable and efficient for commercial and industrial purposes. It relates more specifically to the cyclization, including aromatization, of light petroleum and natural gas hydrocarbons to obtain hydrocarbons of different boiling ranges and higher anti-knock rating for use in, for example, improved aviation and motor fuels.

It has long been known in the art that differences in molecular structure of fuel hydrocarbons affect remarkably the performance of the hydrocarbons in internal-combustion engines. The rate and nature of combustion of a hydrocarbon of any given molecular weight or carbon-hydrogen composition varies with the structure or molecular configuration of that hydrocarbon. In general, the more complex the molecule, the higher the resistance to detonation when the material is burned under the conditions of elevated temperature and pressure as exist in the cylinder of the internal-combustion engine during the compression and combustion parts of the cycle. The lowest degree of resistance to detonation under these conditions is possessed by straight-chain aliphatic hydrocarbons, such as, for example, normal heptane, having the carbon atoms connected in a straight chain or line, C—C—C—C—C—C—C, in which no tertiary carbon atom is present, that is, no carbon atom is directly connected to more than two other carbon atoms. If this normal paraffin is changed so that one or more carbon atoms are present as side chains, that is, where one or more carbon atoms are tertiary—connected to three other carbon atoms—the resistance to detonation is increased by this change in configuration. As more and more side chains are formed at the expense of the main paraffin chain, the higher becomes the resistance to detonation, that is, the higher the anti-knock quality of the hydrocarbon. To illustrate; normal hexane, C—C—C—C—C—C, has a very low anti-knock rating or octane number on the at present standard A. S. T. M. octane scale as is employed internationally for evaluating relative degrees of tendency to knock under engine operating conditions. The isomeric hexanes, of which there are five, exhibit progressively greater resistance to detonation as the molecule of six carbon atoms becomes more complex, until the isomer neohexane,



rates approximately 95 on the current standard A. S. T. M. scale. Cyclohexane, in which the six carbon atoms are conjoined in a closed ring and which possesses two hydrogen atoms less than the corresponding acyclic or non-cyclic paraffins, is rated at about 75 to 80 on this same scale, making the cycloparaffin a greatly improved ingredient of motor and aviation fuels as compared to the normal, straight-chain hexane structure.

Aromatic hydrocarbons, containing a given number of carbon atoms in a specific and peculiar ring structure, but possessing a smaller number of hydrogen atoms than are found in either the cycloparaffins or the straight-chain or isomeric paraffins, also possess to a remarkable degree the property of resisting detonation in the automotive engine. The typical structure of the aromatic hydrocarbon is that of benzene in which six carbon atoms are arranged in a ring structure, but which contains only six hydrogen atoms, or six less than does cyclohexane with the same number of carbon atoms. This peculiar condition of unsaturation without the existence of olefinic bonds—according to the best accepted theories—imparts to aromatics peculiar properties, especially those of resistance to detonation as a motor fuel, and high reactivity of the hydrogen atoms present in the aromatic nucleus.

Aromatic hydrocarbons are important raw materials for the synthesis of a host of important chemical products, and their preparation from petroleum hydrocarbons is increasing rapidly in importance. An increasingly large proportion of the total aromatic hydrocarbon production is derived from petroleum sources, by synthetic methods. Cycloparaffins, also, are becoming more and more important as starting materials for chemical synthesis and therefore methods for their production or synthesis are increasingly important.

In carbon-hydrogen composition, the cycloparaffin is analogous to the olefin, each possessing two hydrogen atoms less than the corresponding paraffin, which has the generic formula C_nH_{2n+2}, in which n is the number of carbon atoms per molecule. The monoolefin and the cycloparaffin have the formula C_nH_{2n}. The cycloparaffin, however, does not possess the double bond between adjacent carbon atoms which characterizes the olefin and does not show the same properties traceable to this state of unsaturation. The cycloparaffins may be said to possess properties intermediate between olefins and saturated paraffins with some of the advantages of both and less of the disadvantages of each, especially from the viewpoint of motor and aviation-fuel properties.

The cycloparaffin may be prepared from paraffins or from olefins, either by direct dehydrogenation of the paraffin and conjunction of the hydrogen-vacated bonds to close the ring, or by formation of olefinic bonds and later by reallocating these bonds to close the carbon ring. If this dehydrogenation is carried further at the

same time, aromatics may be formed containing the benzene nucleus or multiples of it, with or without substitution of nuclear hydrogen by alkyl or other radicals. It is considered that formation of aromatics takes place in a series of steps, in the case of each molecule so formed. An initial step dehydrogenates the straight-chain paraffin to give two unsaturated bonds on terminal carbons or at least on carbons which, with intermediate carbons in the chain between the carbons sustaining the unsaturation by hydrogen removal, form a six-carbon chain; these unsaturated bonds unite to form a cycloparaffin ring. Further dehydrogenation then removes, apparently preferentially, one of the two hydrogen atoms on each of the ring carbons, producing the peculiar state of unsaturation without olefinic double bonds which characterizes the aromatic molecule.

The preparation of cyclics, i. e., cycloparaffins or aromatics, in accordance with this invention, therefore, is determined not only by the specific conditions and specific catalysts employed, but also by the degree and kind of unsaturation produced. It is possible to employ the same catalysts and the same equipment and cycle of operations for the production of cycloparaffins or aromatics, by varying the severity of the reaction conditions and the time of exposure of the charge stock to the conditions. By employing conditions of operation which promote the formation of cycloparaffins, and by stopping the unsaturating reaction when the degree of unsaturation required for forming cyclic paraffins has been attained, a preponderance of cycloparaffins will be formed at the expense of aromatics formation. In practically any reaction system preparing cycloparaffins some aromatics are formed as byproduct. These aromatics may be isolated from the cycloparaffins and from unreacted charge and purified as such, may be recycled to the dehydrogenation zone for reaction with hydrogen therein to form cycloparaffins therefrom, or may be hydrogenated in a separate zone under any desired conditions to cycloparaffins by the addition of the requisite amount of hydrogen to the aromatic nucleus.

Cyclization of paraffin hydrocarbons, especially aromatization to form the benzene nucleus and its substituted homologues, can be accomplished by heat and pressure alone, in the absence of catalysts, as a number of commercial processes now in operation attest. However, thermal methods alone are non-specific and non-directional and the yield of products other than aromatics and/or cycloparaffins may be large, making the cost of the aromatic and/or cycloparaffinic content excessive. Proper choice of catalysts enables the operator to carry out the process in greater yield, under less severe conditions and with better control over the specific materials produced than can be the case with thermal methods alone.

Analogously, the process may be carried out with one catalyst or a combination of catalysts, one step or two steps, or two catalysts or more may be employed. If, as theorists believe and as is supported by much research data, cyclization is a combination of dehydrogenation of paraffins followed by ring closure of the resulting olefins by juncture of olefinic bonds within the individual molecule and consequently is a two-step reaction, it is of advantage to employ two catalysts and two steps or a single catalyst promoting the two reactions under different reaction conditions, optimum in each case for the reaction desired in each step. This is done in accordance with my invention.

The principal object of my invention is to provide an improved process for the cyclization of paraffins. Another object is to provide for the carrying out of the cyclization in two separately controlled stages, each of which is controlled to give optimum results in the overall process. Another object is to provide such a process capable of ready application to heavy oils of the general type of cracking stock and involving preliminary catalytic cracking to produce an essentially paraffinic cyclization charge. Another object is to provide a process of the foregoing type which utilizes a single catalyst, preferably aluminum chloride or equivalent metal halides, and in a preferred embodiment passes the catalyst countercurrent to the main flow and in such manner that the catalyst encounters increasingly severe or stringent reaction conditions of temperature, pressure and contact time, whereby it is active for each successive conversion. Numerous other objects will more fully hereinafter appear.

Fig. 1 of the accompanying drawings is a diagrammatic representation of one arrangement of apparatus for carrying out one embodiment of the present invention.

Fig. 2 is a similar schematic representation of equipment for carrying out the present invention in another embodiment in which a preliminary cracking step is employed and in which a metal halide, preferably anhydrous aluminum chloride, is used as the catalyst in all zones of the process, being cycled therethrough countercurrently to the flow of hydrocarbons.

In accordance with my invention, in its broadest aspect, the cyclization of C_5 or higher paraffins is conducted in two separately controlled catalytic zones, each operated under different and optimum conditions. In the first zone, which is normally maintained at a higher temperature, the reaction brought about is primarily one of unsaturation or dehydrogenation and conversion to forms which are most readily adapted to ready cyclization to form cycloparaffins and aromatics.

The invention will first be described with reference to the embodiment typified by Fig. 1 and wherein the dehydrogenation catalyst is different from and used under different conditions from that of Fig. 2.

Among the dehydrogenation catalysts which may be mentioned as efficient in carrying out the preliminary step in my cyclization reaction are the normally solid and liquid salts and oxides of the metallic elements in groups IV to VI of the periodic table, which are, in ascending order of their comparative activity in dehydrogenation, as follows: Oxides of elements of Group IV—titanium, zirconium, tin and lead, which show the lowest dehydrogenation activity in these three groups. Oxides of elements in group V—vanadium, columbium, and tantalum, which in general show higher activity than those of group IV. Oxides of elements of group VI—chromium, molybdenum, tungsten and uranium, which are the most effective and strongest dehydrogenating catalysts of the three groups. Other metallic oxides show efficiency under suitable conditions but those mentioned serve to illustrate the invention adequately.

In the cyclization-aromatization reaction, increase of contact time under any given set of conditions increases the likelihood and percentage formation of aromatics at the expense of cycloparaffins. Correspondingly, increased tem-

peratures increase aromatization. Increase of pressure with maintenance of lower temperatures and shortening of contact time tend to form cycloparaffins and isomeric paraffins at the expense of aromatic formation. In operating this process for the preparation of cycloparaffins and isomers thereof it is desirable to control operating conditions to minimize the excessive dehydrogenation which produces aromatics. Increase in the severity of operating conditions enables the operator at will to increase the aromatics output, giving the invention great flexibility to meet commercial demands or to produce a desired material from any variation of charge stock which may be available.

As cyclization catalysts, anhydrous aluminum halides have shown good efficiency under the proper control of operating conditions. For cost reasons the chloride is generally employed and is preferred in this process, especially in the presence of the aids, diluents and/or promoters as mentioned below. Less desirably, other catalysts may be employed, for example, chlorides of other amphoteric metals, such as $ZnCl_2$, $FeCl_3$, $BeCl_2$, $TiCl_4$, $ZrCl_4$, $SnCl_4$, $SbCl_5$, etc. Instead of halides of metals yielding an amphoteric hydroxide, other cyclization catalysts may be used such as zinc oxide, alumina, silica, etc.

Aluminum chloride catalyzes a great variety of reactions involving hydrocarbons and its catalytic activity and the products of its catalysis vary widely, depending on the reaction being carried out and the reaction conditions employed. At higher temperatures, of the order of 375–400° C. (about 700–750° F.) and above, its action becomes non-specific in regard to products formed, and it effects essentially a cracking reaction, decomposing heavier hydrocarbons to form lighter products, along with addition products formed by combination of the chloride molecule with hydrocarbon residues. At the lower temperatures, of the order of 95–150° C. (about 200–300° F.), the temperature depending on the material treated and the pressure employed, paraffin hydrocarbons may be dehydrogenated and cyclized with or without rupture of the molecule to form an intermediate olefin or paraffin of lower molecular weight. For example, nonane is decomposed at 200–230° F. and low pressures to form butane and pentene, which latter cyclizes to form principally cyclopentane. Experiments show that at temperatures within this temperature range, cycloparaffins such as cyclopentane are not reacted on further by aluminum chloride, and therefore cycloparaffins are a desirable end product of the aluminum chloride reaction catalysis in this general temperature range. At still lower temperatures, as from minus 20 to plus 40° C. (minus 4° to plus 104° F.), heavier hydrocarbons are formed from low-molecular-weight olefins; thus, naphthenes, poly-naphthenes and alkyl-substituted naphthenes are formed from butenes and homologues, the products boiling mainly from 500° F. upward. Many other examples might be given of the wide variety of products which may be catalyzed by aluminum chloride when temperatures, pressures, contact times, and composition of charge stocks are controlled satisfactorily, but these specific examples will serve to show the results which may be expected in the process of this invention for the cyclization of paraffins to cycloparaffins and aromatics.

For some reactions so-called "nascent" $AlCl_3$, prepared in situ by introducing into the reaction zone metallic aluminum and anhydrous HCl, appears to give better results than does the anhydrous salt prepared in the usual commercial manner. This is believed to be due to the effect of the nascent hydrogen liberated during the reaction between the metal and anhydrous acid. Largely the same effect may be obtained by the maintenance of the reaction materials under elevated pressure with molecular hydrogen, or a mixture of light hydrocarbons containing appreciable amounts of molecular hydrogen. The presence of the hydrogen doubtless serves to inhibit polymerization of the olefins intermolecularly, to prevent further dehydrogenation and thus to further intramolecular saturation or cyclization. Correspondingly, the presence of appreciable amounts of hydrogen in the reacting materials in the dehydrogenation step aids in controlling the degree of dehydrogenation obtained by approaching more closely, during the reaction period, the equilibrium between olefin and hydrogen content.

I have found that the introduction of an inert gas or vapor as a diluent has a desirable effect on the reactions, both of dehydrogenation and of cyclization. Steam, flue gas or low-molecular-weight hydrocarbons, such as methane and ethane, show this effect to the desired degree, and may be introduced into the charge stock stream prior to its entry into the reaction chambers, along with the hydrogen. A preferable method is to introduce a light hydrocarbon gas rich in hydrogen into the charge stock before the stock enters the preheater where it is heated to reaction temperature before entering the unsaturator, as will be described in connection with the accompanying drawings. Effluent light gases from the final fractionator, containing light hydrocarbons and the hydrogen released from combination during the dehydrogenation step, may be recycled to the latter step, and the quantity may be augmented by hydrogen and/or hydrocarbons from an outside source, if necessary. More commonly excess gases will be discharged to waste from this line and only that portion required to maintain the required equilibrium in the unsaturator and in the cyclization chambers to control the degree of reaction occurring therein will be recycled, since a surplus of free hydrogen and of light gases will be built up gradually in the system.

The essential features of the embodiment of Fig. 1 may be summarized as follows. Charge stock containing one or more hydrocarbons containing from 5 to 12 carbon atoms per molecule is introduced, after preheating to a suitable temperature, into a catalytic dehydrogenation zone. The temperature maintained in this zone will depend upon a number of factors. Mild dehydrogenating catalysts will require higher temperatures than do more active catalysts. Bauxite or oxides of group IV metals may require temperatures as high as 1200° F., to bring about dehydrogenation to simple monoolefins. Temperatures as low as 500° F. may be used under other circumstances. Temperature, dilution and hydrogen content of the entering charge are so adjusted that conversion is restricted to a maximum degree to monoolefin formation. The determination of that combination of conditions giving optimum results with a given stock will be within the skill of workers in the art in the light of the disclosure herein.

More active dehydrogenation catalysts, such as vanadium oxide, chromium oxide, molybdenum oxide and mixtures thereof will require lower

temperatures and shorter contact times. The action of a too active catalyst or one which tends to carry dehydrogenation too far or to induce cracking at the higher temperatures or longer contact times, may be alleviated or reduced by the addition of a retarding or less active material such as aluminum oxide, silica, salts, oxides, or hydroxides of alkali or alkaline-earth metals such as potassium, lithium, sodium, rubidium, beryllium, magnesium, calcium, strontium, barium or other basic oxide of elements in groups II and III of the periodic system. Contact time may also be controlled in such manner as to halt the dehydrogenation reaction at the desired point, namely, upon the formation of alpha and beta monoolefins to the exclusion of diolefins, aromatics, etc.

The pressure in the first step may vary widely but will usually be from about 50 to about 1500 pounds per square inch gauge, depending on the temperature maintained, the catalyst, the charge, etc. In some cases, as when using a catalyst consisting of a halide of an amphoteric metal, it may be as low as atmospheric pressure, ranging therefrom up to 100 pounds per square inch gauge since the temperatures are usually more moderate when using such a catalyst.

After exposure of the charge to the action of the dehydrogenating catalyst for a time which may vary from 0.2 to 30 seconds, depending on the refractoriness of the charge and the conditions employed, the effluent vapors are fractionated to separate the olefins formed as overhead vapors. The unreacted paraffins may be returned to the preheater as recycle. The higher the molecular weight of the paraffin stock the lower its resistance to dehydrogenation and cyclization. Nonanes and decanes, for example, are more reactive than pentane and hexane, and require less severe reaction conditions to obtain the desired conversion.

The olefin fraction thus recovered may be passed through a cooler and, if steam was employed as a diluent in the dehydrogenation zone, through a dryer unit to remove liquid and vapor water, and may be then passed into contact with the cyclization catalyst, which may be either metallic oxides or amphoteric metal halides. Anhydrous aluminum chloride is a preferred catalyst. When it is used, the temperature range is controlled carefully to obtain a maximum of cyclization to the cycloparaffins and to minimize polymerization and aromatization of the olefins. At temperatures of the order of zero °C. and lower, heavy polymers of boiling range corresponding to lubricating oils are formed in preponderant amounts. As temperatures approach 375–400° C. (about 700–750° F.) the reaction minimizes polymerization, and cracking reactions increase along with formation of progressively heavier hydrocarbon-$AlCl_3$ addition products.

Temperature therefore must be controlled within a range which promotes the formation of simple cycloparaffins, minimizing both dehydrogenation to aromatics and multipolymerization to heavy, viscous products. Here the presence of the diluent hydrogen and hydrocarbon or other gases aids also in retarding these undesirable reactions and in furthering cyclization. Temperatures in this reaction are therefore of the order of 200–400° F., the range maintained depending on the hydrocarbons processed and their relative resistance to cyclization, heavier hydrocarbons requiring lower temperatures and shorter contact times than the lighter C_5 and C_6 olefins. The effluent from this step, in which contact times may vary from 0.1 second to 15 seconds or more, is fractionated to recover the unreacted olefins and diluent hydrogen-hydrocarbon gases, and the raw product, including cycloparaffins, aromatics and heavier aromatization and polymerization products, may be refractionated to remove the heavier undesirable materials for recycle. This heavy material may be eliminated from the system or may be cracked or otherwise processed to produce recycle materials as desired. The rectified cycloparaffins and lighter aromatics, the latter formed as by-products, may be sent to storage as finished product except for any desired chemical purification.

The foregoing description may be more fully understood by reference to Fig. 1 of the drawings. Paraffin charge stock, which may consist of essentially one hydrocarbon, as normal hexane, or a mixture of several hydrocarbons, is mixed with recycle material in line 1, enters the preheater 2, is heated to the desired temperature and passes through line 3 to the dehydrogenation chamber, 4, after dilution with hydrogen-hydrocarbon light material, or other diluent from line 5. The effluent vapors from the dehydrogenator are discharged through line 6 to fractionator 7. Bottoms from this tower are stripped of lighter material in reboiler 8 and are returned as recycle through line 9. The overhead olefins pass through line 10 to cooler 11 and dryer 12, where the temperature is reduced to that required in the next step, and water, if present as condensate or for any other reason, is eliminated. Reflux is returned to fractionator 7 through line 13, and the remainder of the olefin charge is blended with olefin recycle and any desired additional hydrogen-hydrocarbon diluent in line 14 and enters the cyclization chamber where it contacts the cyclization catalyst in any desired form. Reaction products are discharged through line 16 to the fractionator 17, where the raw cyclics-aromatics content is condensed, stripped of lighter material in reboiler 18 and is withdrawn through line 19. Unreacted olefins and light diluent material are taken overhead through line 20 to condenser 21, where recycle olefins are condensed and withdrawn through line 22, reflux being drawn off for return to the fractionator 17 through line 23. Uncondensed hydrogen and light hydrocarbon gases (C_1 to C_-) are returned to line 5 and the reaction system.

Pressures as high as 100 atmospheres or about 1500 pounds per square inch may be advantageous in the first or dehydrogenating step; up to 75 atmospheres, or about 1000 pounds per square inch, may be used in the second step, though the pressure in this step may be considerably lower than those indicated when reacting C_5, C_6 and C_7 hydrocarbons.

The essential features of the embodiment of the invention represented in Fig. 2 include catalytically cracking heavier oils, preferably using a metal halide catalyst, provided this step is desired to obtain charge stock for the main part of the process; introducing the C_5—C_{12} aliphatic (chiefly paraffinic) hydrocarbon fraction of the cracking effluent to a catalytic dehydrogenator-isomerizer where the initial rearranging reaction is carried out, preferably in the presence of a metal halide catalyst, whereby compounds, largely olefins, are formed which are adapted to be converted to cyclic compounds; transferring the desired fraction of these reaction products

to a second reaction chamber where they are cyclized in the presence of diluent gases rich in hydrogen, with some aromatization, and frequently with some alkylation as the result of side reactions; fractionating the reaction products from each zone to concentrate the material for the next step, to obtain unreacted material for recycle to the same step, or to obtain the final product. The first reaction is controlled to produce intermediate reaction materials, which may include olefins and partially reacted materials which are optimum charge stock for the next or cyclizing step, and the reactions are arrested before any considerable portion has been either aromatized or saturated to a point which makes it unsatisfactory for the reaction desired in the next step. The reactions taking place involve dehydrogenation of the paraffins to those olefins which are adapted to be cyclized and isomerization of any olefins present to those forms which may be readily and directly cyclized.

In the case where satisfactory charge stock of the required molecular weight, either a single paraffin or isoparaffin hydrocarbon or a mixture of hydrocarbons, is available from refinery or other plane streams or other outside sources in volume sufficient to meet the throughput requirements of the cyclization unit, the first step described above (i. e., the catalytic cracking step) may be omitted. Or, the first step may be used to obtain additional charge stock to augment that available from outside sources. Or, the first or cracking step may be employed to supply the entire charge stock for the unit.

Conditions employed in the cracking step are controlled to produce a maximum of the hydrocarbons desired. The higher the temperature and pressure the lower the molecular weight of the main body of product. The temperature range is between about 650 and about 850° F. If a preponderance of heavier hydrocarbons in the range mentioned is desired the cracking temperature should be maintained in the lower portion of this range, with correspondingly higher pressures; if butanes, pentanes and hexanes are desired in greater percentage a higher temperature and in general lower pressure are employed. Careful control of these conditions, along with simultaneous control of the average time of contact of the charge stock with the catalyst, over a considerable range, is employed in order to control the average molecular weight of the paraffins, isoparaffins and/or aromatics formed from the heavy charge such as gas oil, kerosine, heavy cyclics and so on.

Effluent from the cracking zone is preferably fractionated in two different fractionators, the first to separate the heavier, insufficiently cracked material for recycle, the second stage to separate light gases, i. e. hydrogen and light non-condensable gases, which may be added later as a diluent and hydrogen supplier or may be discarded from the system as the details of operation may make desirable. More frequently this diluent light material will be discarded from the system, although in the embodiment shown in Fig. 2 of the accompanying drawings it is shown as being returned to the system at a later point as diluent, merely as an illustration of one alternative method of operation.

Fresh C_5—C_{12} hydrocarbons from outside sources, in any combination or mixture of these hydrocarbons, may be added at this point, or it may be the beginning of the operation, in case the cracking reaction is not employed to supply part or all of the charge material. The incoming fresh C_5 to C_{12} hydrocarbons may be introduced into a preliminary fractionator if such concentration of the desired hydrocarbons is to be made as a part of this operation, or may be introduced directly in the first reactor chamber, if the charge has the desired composition. This charge, or combined charge materials, in the event the charge is obtained from more than one source, enters a first reactor where several reactions may occur in varying degrees, including olefinic unsaturation, isomerization and apparently formation of unstable complexes including the rupture of heavier molecules to form, for example, a paraffin or isoparaffin and an olefin, unstable cross-linkages between carbons of the same or different molecules, and other probable reactions not well understood. This step and the second or cyclizing or aromatizing step are carried out separately from one another in order that conditions optimum for each reaction and for the furtherance of the final result may be accomplished with greater yields and smaller percentages of byproducts. For the first reaction, temperatures should be maintained approximately within the range 500–600° F., and intermediate pressures of from atmospheric pressure up to 100 pounds per square inch gauge, to effect a re-forming action on the hydrocarbons processed.

The effluent from this first chamber may be fractionated to return recycle to the chamber. The very light hydrocarbons, methane to propane, and preferably to butane, along with free hydrogen may be vented from the system or may be continued as diluent into the second step as the balance of diluent-reaction mixture may be desired. The partially reacted charge, consisting of the C_5 to C_{12} fraction of the effluent from the first chamber, then is introduced into a second chamber, meeting fresh catalyst as outlined later herein and is reacted at lower temperatures and higher pressures, of the order of 50–400° F. and 50–250 pounds per square inch gauge pressure, conditions which promote cyclization of the partially reacted materials from the first step and which minimize but do not necessarily eliminate formation of aromatic hydrocarbons. To increase the contact time and therefore permit employment of lower temperatures but to increase the yield-per-pass, two or more chambers in series may be employed with advantage in carrying out the second step. In a final fraction the main body of reaction products, cyclics and aromatics, including products heavier than those desired from recycle material to this second or to the first step, are separated. Any surplus of very light materials may be vented or returned to steps earlier in the system.

The amount of diluent employed is varied from a few per cent to as much as 50 per cent, depending on the composition of the charge, contact time and temperatures and pressures employed. In general the greater the amount of diluent employed in the cyclizing step of my invention the less the tendency toward polymerization and similar reactions, which form larger molecules and thus defeat the purpose of the invention. However, if diluent and hydrogen percentage present are too high, the tendency is toward a hydrogenation reaction to the exclusion of cyclization and aromatization, which also defeats the purpose of the invention. All operating conditions, therefore, are controlled to carry the reaction desired between the two undesirable ends of oversaturation to form non-cyclic paraffins, on the one

hand, and unsaturation to form high proportions of aromatics and polymeric products, on the other. The high selectivity of the action of the catalyst is taken advantage of to the fullest extent by exact control of operating conditions as outlined herein.

The metal halide, such as aluminum chloride, may be used in the form of a slurry, easily transportable from one vessel to the other, or it may be installed in the chambers in solid form, and by a system of manifolding, the sequence of the flow of charge through the system may be made to follow the countercurrent principle of contact which is shown for illustrative purposes in the drawings. In either case, the catalyst is in countercurrent relationship to the charge, progressing from lower to higher temperatures in the process. Fresh catalyst is introduced into the cyclization step of the process, progresses to the reforming step, and thence, if heavier oils are cracked to supply low-molecular-weight charge stock, the catalyst is employed at the relatively high cracking temperatures as outlined. When spent in this step the catalyst may be discarded or regenerated as desired. In this way the catalyst is used successively under increasingly stringent or severe reaction conditions whereby any spending in the zone from which it comes is overcome.

It must be kept in mind that the principle of this invention is not dependent on nor limited by any theoretical considerations or explanations of what occurs in either the unsaturator step or in the cyclizing step, particularly the nature of the reactions in the unsaturator or reforming step. The intermediate reactions occurring during the action of aluminum chloride and other metal chlorides on hydrocarbons are extremely complex, and not well understood. Arresting these reactions by any practicable means at different stages of the reaction cycle produces a variety of materials or reaction products from any given combination of charge stocks. Experience has shown that separating this part of the operation into two steps, each operated under the optimum set of conditions for effecting the desired result, gives better results and higher yields of the final products desired, and also gives greater flexibility to the process than does an attempt to carry out the complete set of reactions of unsaturating and cyclizing the hydrocarbons in a single step or reaction zone. The reaction mixture transferred from the unsaturator to the cyclization zone may contain a complex mixture of aluminum chloride-hydrocarbon combination products, olefins, paraffins and isoparaffins and other products, the chemistry and the composition of which is not well understood. The invention, therefore, comprises the accomplishment of the series of reactions which give the final products without being limited in any way by any theoretical or scientific explanation or by the lack of such explanation.

Details of this process of the invention may be followed more clearly by reference to Fig. 2 of the accompanying drawings, which illustrates one preferred method for practicing this invention. Heavy oil such as gas oil, kerosine, heavy polymer-cyclate or other similar charge is admitted to the system through line **101** to cracking chamber **102** after admixture with recycle stock from fractionator **104** through line **105**. The charge is cracked in contact with metal halide catalyst, such as anhydrous aluminum chloride, conditions being controlled to produce the hydrocarbons desired, and the entire charge is flashed, through line **103** into fractionator **104**, from which uncracked or insufficiently cracked material is recycled to the cracking zone through line **105**. Cracked vapors are transferred through line **106** to the second fractionator **107** from which very light hydrocarbons and hydrogen are taken overhead through line **108** and rectified distillate (consisting essentially of C_5 to C_{12} paraffins and olefins) is transferred through line **109** to the first reactor chamber **110**. Fresh charge from any outside source is admitted here, either through line **111** directly to the reactor or through line **112** to the second fractionator **107**, in case this charge requires rectification before further processing is undertaken.

After contacting the catalyst in reactor **110** the reaction products may be admitted through line **113** to fractionator **114** if it is desired to eliminate very light products, or this fractionator may be bypassed. Light products may be removed through line **115**, recycle stock may be returned through line **116** to the first reactor **110**, or the entire charge may be passed through line **117** to the first section **119** of the second reactor, after admixing with it diluent containing hydrogen through line **118**. This reactor may be in two or more sections, the reaction products and unreacted material from the first section passing into the second section **120**, and so on, in which fresh catalyst is contacted in countercurrent flow relationship. As a further control means, for stopping the reaction after the charge has passed through the last reactor, cold diluent liquid and/or vapor is added through line **121** to shock-chill the reaction products which pass through line **122** to final fractionator **123** from which diluent is returned for recycle or is discarded, through lines **124** and **125** or **126**, respectively. Insufficiently reacted material is returned for recycle to any section or sections of the second reactor through line **127** while cyclic and other products which require no further processing are withdrawn from the system through line **128**. In the event that heavy material is present in this product, which should be reprocessed, the stream may be further fractionated in equipment not shown in the drawing to remove this heavier material, which may be returned to the cracking zone or used for any other purpose. In case a mixture of hydrocarbon products, mixed with unreacted material, is obtained from the final reactor, multiple fractionation is necessary to yield recycle and finished materials.

The catalyst, in this preferred embodiment of the invention, is introduced into the system through line **129** into the cyclization zone and thereafter passes through the system in countercurrent relationship to the path or flow of the charge stock. If the catalyst is in slurry form it is circulated through the cyclization chamber **120** by means of any convenient pumping arrangement, slurry being returned via line **130** to line **129**, after passing through the reaction chamber. Continuously a predetermined portion of the catalyst stream is withdrawn through line **131** to cycle through the next section or reaction chamber **119** through line **132** and recycle through line **133**. In turn a portion is withdrawn continuously to the unsaturator chamber **110** through line **134**, is recycled in that zone through line **135** downward through the chamber and returned through line **136**. When the activity of the catalyst in this section of the process is reduced to an unsatisfactory level it is withdrawn, a con-

tinuous operation in practice, through line 137 to the cracking section 102 of the unit, is recycled therethrough through line 138, the reaction chamber, and line 139. Spent catalyst is withdrawn to discard or for regeneration through line 140.

For simplicity, preheaters, coolers and other accessory equipment are eliminated from Fig. 2 of the drawings.

The preferred procedure in this embodiment of the invention is to employ anhydrous aluminum chloride. If this catalyst is used, the temperature range in the necessary zones is controlled carefully to obtain a maximum of cyclization and to minimize polymerization. At temperatures of the order of 32° F. (0° C.) and lower, heavy polymers of boiling range corresponding to lubricating oils are formed in preponderant amounts. As temperatures approach 700–750° F. (about 375–400° C.) the reaction minimizes polymerization, and cracking reactions increase along with formation of progressively heavier hydrocarbon-$AlCl_3$ addition products. Temperature therefore must be controlled within a range which promotes the formation of simple cyclics, i. e., cycloparaffins, minimizing both dehydrogenation to aromatics and multipolymerization to heavy, viscous products. Here the presence of the diluent hydrogen and hydrocarbon or other gases aids also in retarding these undesirable reactions and in furthering the desired cyclization. Temperatures in the cyclization reaction are therefore of the order of 200–400° F. (about 90–200° C.), the range maintained depending on the hydrocarbons processed and their relative resistance to cyclization, heavier hydrocarbons requiring lower temperatures and shorter contact times than the lighter C_5 and C_6 olefins. Contact times may vary from 0.1 second to 15 seconds or more. The effluent from this step is fractionated to recover the unreacted olefins and diluent hydrogen-hydrocarbon gases, and the raw product, including cycloparaffins, aromatics and heavier aromatization and polymerization products, may be refractionated to remove the heavier undesirable materials for recycle, which may be either eliminated from the system or may be cracked or otherwise processed to produce recycle materials as desired. The rectified cyclics (cycloparaffins) and lighter aromatics, the latter formed as byproducts, may be sent to storage as finished product except for any desired chemical purification. If desired the cycloparaffins and the aromatics may be separated.

I have found that low pressures and high temperatures, with or without catalysts, tend toward the formation of more aromatic hydrocarbons, increasing the degree of dehydrogenation which accompanies cyclization. The converse of these conditions, combined with the diluent effect of the hydrogen and hydrocarbon vapors, and the displacement of the dehydrogenation-hydrogenation reaction equilibrium in the direction of less severe dehydrogenation because of the excess hydrogen employed, will in general promote the limitation of dehydrogenation to the simpler monoolefin formation and the production of cycloparaffins rather than aromatics, the more highly unsaturated cyclics. Thus higher pressures may be employed preferably in these reactions to the advantage of cycloparaffin production, and correspondingly lower temperatures will suffice for accomplishing the preferred results as indicated.

In cyclizing paraffins or olefins, the greater tendency is to form either five or six-membered rings. For example, when cyclizing hexene-1 either cyclohexane or methylcyclopentane may be formed, with the greater tendency toward the six-carbon ring. If the double bond is broken in the olefin and the bond on the terminal carbon displaces a hydrogen atom on the opposite terminal carbon, a six-carbon ring results, the displaced hydrogen atom satisfying the free bond on the beta-carbon atom. If the broken bond of the beta-carbon unites with the opposite terminal carbon, methylcyclopentane is formed. It is theoretically possible that a dimethyl or trimethyl-substituted ring may be formed by combining the beta-carbon bond with a carbon within the chain, other than the opposite terminal carbon; however, the tendency to form either five or six-carbon rings is strong, to the comparative exclusion of other reactions. Heptanes, octanes and hydrocarbons of higher molecular weight also tend to form alkyl-substituted five and six-carbon rings, with the extra methyl or methylene groups forming first a single straight side chain, which may break down into two or more disubstituted methyl groups. I have found that normal octane, for example, will first form ethylcyclohexane, carbons seven and eight with attached hydrogen atoms forming a single ethyl side chain. Continued exposure to reaction conditions may cause a rupture of this side chain to form two methyl groups, one of which displaces a hydrogen on the nucleus, forming dimethylcyclohexane, with the methyl groups in the ortho, meta or para positions, more frequently the ortho position. Other variations of this formation may occur, by the combination of free methyl or other alkyl groups with the cycloparaffin nuclei formed in the main reaction. The tendency, therefore, in this invention is toward the formation of five and six-membered carbon rings of the generic formula C_nH_{2n}, with or without side-chain substituents, depending on operating conditions and the composition of the charge stock.

This description of my process and invention outlines the principles on which the invention is based, and indicates preferred catalysts and methods for carrying out the invention. The principles of the invention are broad, however, and a large number of variations are permissible in operating the process with good results and within the limits set by these principles and the appended claims.

I claim:

1. A process for the production of cycloparaffin and aromatic hydrocarbons from paraffin hydrocarbons, which comprises subjecting a C_5 to C_{12} paraffin hydrocarbon fraction in a dehydrogenation zone at a dehydrogenation temperature and pressure to the action of an aluminum chloride catalyst to convert it to an intermediate hydrocarbon material adapted for cyclization, recovering a fraction comprising C_5 to C_{12} olefin hydrocarbons from the effluent of the dehydrogenation zone and subjecting said fraction to cyclization in a cyclization zone at a cyclization temperature and pressure in the presence of an aluminum chloride catalyst to effect cyclization of a substantial portion of said olefin-containing fraction, fractionating the effluent from said cyclization zone to recover cyclic hydrocarbons therein, recovering fractions comprising a mixture of hydrogen and light hydrocarbon gases from each of said dehydrogenation and cyclization effluents and passing a portion of at least one of said fractions into each of said dehydrogenation and said

cyclization zones in such amounts as to act as a diluent therein and to prevent polymerization without engendering substantial hydrogenation to the exclusion of cyclization of the olefin hydrocarbons therein, shock-cooling the effluent from said cyclization zone with a further cooled portion of one of said fractions comprising hydrogen and light hydrocarbon gases, introducing fresh aluminum chloride catalyst to said cyclization zone and circulating it therein, withdrawing a portion of the aluminum chloride catalyst from said cyclization zone and introducing and circulating it in said dehydrogenation zone, and withdrawing spent aluminum chloride catalyst from said dehydrogenation zone in an amount substantially equivalent to the amount of fresh catalyst introduced to said cyclization zone.

2. A process for the production of cycloparaffin and aromatic hydrocarbons from paraffin hydrocarbons, which comprises subjecting a C_5 to C_{12} paraffin hydrocarbon fraction in a dehydrogenation zone at a temperature within the range of approximately 500° to approximately 600° F. and a pressure within the range of approximately 0 to approximately 100 pounds per square inch gauge to the action of an aluminum chloride catalyst to convert it to an intermediate hydrocarbon material adapted for cyclization, recovering a fraction comprising C_5 to C_{12} olefin hydrocarbons from the effluent of the dehydrogenation zone and subjecting said fraction to cyclization in a cyclization zone at a temperature within the range of approximately 200° to approximately 400° F. and an elevated pressure within the range of approximately 50 to approximately 250 pounds per square inch gauge in the presence of an aluminum chloride catalyst to effect cyclization of a substantial portion of said olefin-containing fraction, fractionating the effluent from said cyclization zone to recover cyclic hydrocarbons therein, recovering fractions comprising a mixture of hydrogen and light hydrocarbon gases from each of said dehydrogenation and cyclization effluents and passing a portion of at least one of said fractions into each of said dehydrogenation and said cyclization zones in such amounts as to act as a diluent therein and to prevent polymerization without engendering substantial hydrogenation to the exclusion of cyclization of the olefin hydrocarbons therein, shock-cooling the effluent from said cyclization zone with a further cooled portion of one of said fractions comprising hydrogen and light hydrocarbon gases, introducing fresh aluminum chloride catalyst to said cyclization zone and circulating it therein, withdrawing a portion of the aluminum chloride catalyst from said cyclization zone and introducing and circulating it in said dehydrogenation zone, and withdrawing spent aluminum chloride catalyst from said dehydrogenation zone in an amount substantially equivalent to the amount of fresh catalyst introduced to said cyclization zone.

3. A process as defined in claim 2 and further characterized in that the fractions comprising hydrogen and light hydrocarbon gases which are used as diluents in the dehydrogenation and cyclization zones are composed of a mixture consisting essentially of hydrocarbons having from one to four carbon atoms per molecule and containing from approximately 10 to approximately 50 per cent of hydrogen.

ARCH L. FOSTER.

CERTIFICATE OF CORRECTION.

Patent No. 2,387,989. October 30, 1945.

ARCH L. FOSTER.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, second column, line 51, for "(C_1 to C-)" read --(C_1 to C_4)--; line 59, for "those" read --these--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 5th day of February, A. D. 1946.

Leslie Frazer

(Seal) First Assistant Commissioner of Patents.

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