

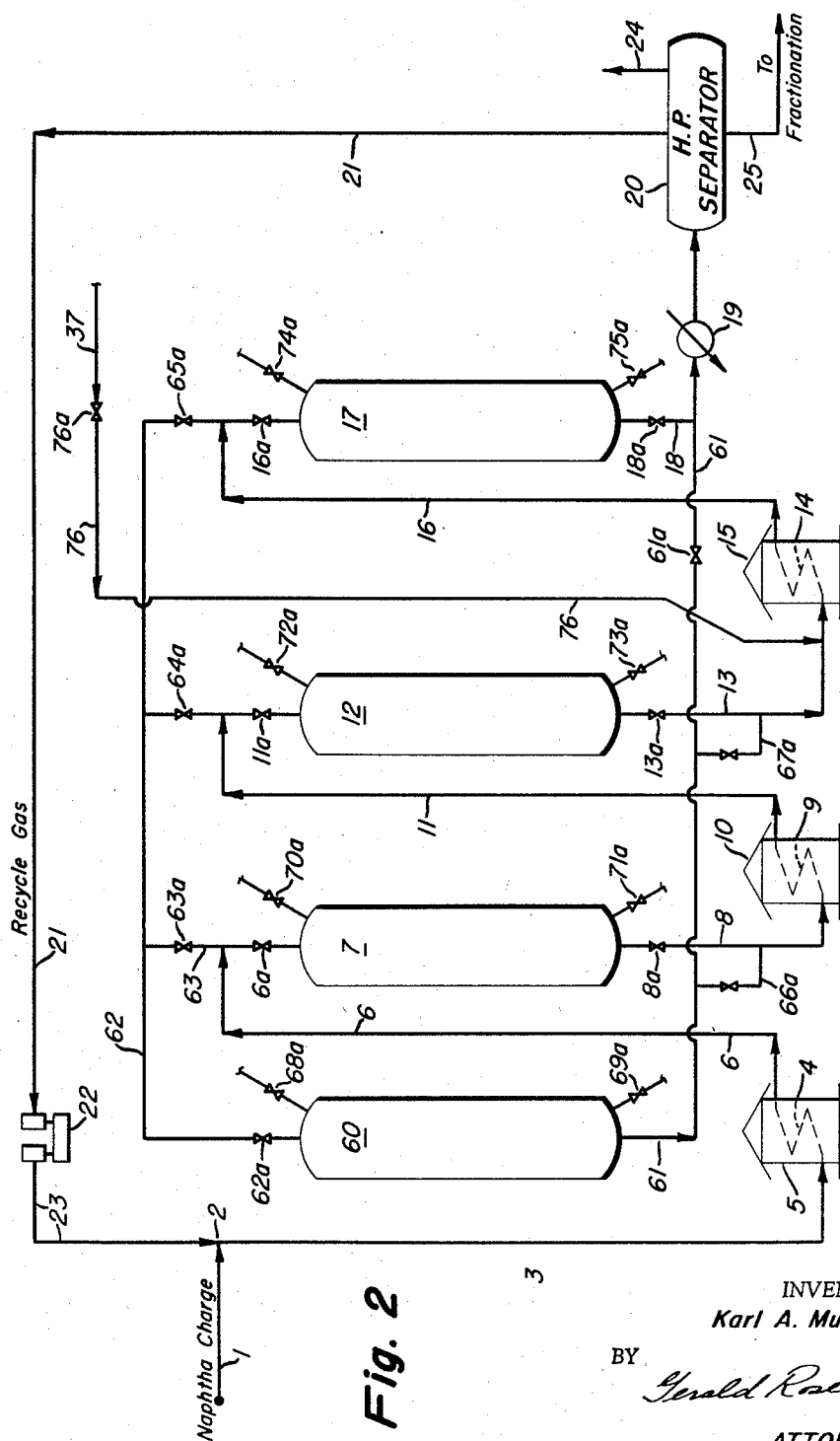
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HYDROCARBON REFORMING SYSTEM

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HYDROCARBON REFORMING SYSTEM

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4 Claims. (Cl. 208—65)

This invention relates to the catalytic hydroforming of petroleum hydrocarbons and more particularly provides improvements in hydroforming processes employing a platinum alumina catalyst for the preparation of extremely high octane number reformates.

Over the past several years the increasing octane number requirements of modern automobiles have presented a major challenge to the petroleum refining industry to provide motor fuels of suitable octane quality. The industry has largely relied on catalytic hydroforming of low octane virgin naphthas as a means for upgrading the refinery pool octane number, and in the early 1950's simple high pressure non-regenerative platinum-alumina catalyzed reforming processes were entirely suitable for the purpose. However as the octane demand reached unprecedented levels it soon became apparent that the incremental cost of attaining higher octane numbers by merely operating non-regenerative reforming units at increasingly high severities was impracticable. The next major processing breakthrough, low pressure regenerative type platinum alumina reforming, made available to the refining industry a process which was economically capable of producing a motor fuel product having a research octane number (CFR-R, or F-1) of 95-105 neat. But even with such processes as the latter, it was recognized that the attainment of each additional octane number was accompanied by a disproportionately higher loss of product due to certain undesirable chemical reactions.

It has long been known that motor fuel products of platinum alumina reforming systems are composed of several classes of compounds, being largely high octane number aromatics but containing rather substantial quantities of paraffins and naphthenes which generally have a considerably lower octane number. These saturates can, at higher severities, be converted to form high octane aromatics by reactions such as paraffin dehydrocyclization and naphthene isomerization and dehydrogenation. However, if the total reformate were to be processed at a high severity to convert these residual saturates, higher boiling aromatic compounds—which are potentially coke formers—would tend to decompose to form wasteful coke or high boiling polymers. In seeking to permit high severity processing of petroleum naphthas or reformates without incurring the destruction of high octane number aromatics already present, it has been proposed to extract aromatics from a reformate with selective solvents such as diethylene glycol or triethylene glycol, and subject the saturates concentrated in the raffinate to further reforming over a platinum alumina catalyst. Extraction however is exceedingly expensive and, except when compelled by extraordinary market demands, unattractive.

It is therefore a primary object of the instant invention to provide an improved hydrocarbon reforming system whereby low octane constituents of a reformate are separated from the balance of the reformate and are subjected to additional reforming in the reforming zone employed for the main hydrocarbon charge stock.

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Another object is to provide an improved hydroforming system whereby low octane components of a reformate are separated by fractionation and returned to the same reforming system for additional reforming, thus eliminating the need for expensive solvent extraction of the reformate. A more particular object is to provide improvements in reforming systems, which improvements may be installed in existing regenerative or non-regenerative hydroforming plants with only minimal additional investment cost. In one aspect, the invention serves to provide a method of attaining from two to six additional octane numbers in reformates without sustaining the disproportionately high product loss associated with prior art reforming systems. Other and more particular objects will become apparent as the description of the invention proceeds.

In conventional platinum alumina catalyzed reforming systems, a preheated stream of charge stock and hydrogen is passed in contact with an initial bed or zone of catalyst and then passed through one or more subsequent reaction zones, under reforming conditions of temperature, pressure, space velocity and hydrogen to hydrocarbon ratio. Conventionally, the reaction mixture from the final subsequent zone is cooled and condensable hydrocarbons are separated from the recycle hydrogen-containing gas, which latter is returned to the initial reforming zone. According to the process of the invention, the condensable hydrocarbons are fractionally distilled to separate a fraction containing most of the C_6 hydrocarbons and heavier hydrocarbons boiling up to about 280° F. A first, preferably major, portion of this fraction is returned to one of the subsequent reaction zones of the process, while a second portion of the C_6 -280° F. boiling range fraction is distilled to separate a low octane C_6 -230° F. and a high octane 230-280° F. fraction. This latter 230-280° F. fraction and the bottoms remaining from the condensable hydrocarbons after removal of the C_6 -280° F. fraction comprise the high octane product of the instant invention.

The above described C_6 -280° F. fraction constitutes the low octane portion of the reformate. Ordinarily this fraction contains the aromatics benzene, toluene, and some of the xylenes-ethylbenzene components, relatively high octane number C_6 and C_7 cyclopentanes, and C_6 - C_9 iso and normal paraffins. The research octane number of this fraction is usually in the class of 70-80 neat, which results from the alkylcyclopentanes which have rather low octane numbers ranging from 31 (n-propyl cyclopentane) to about 91 (methyl cyclopentane). The relatively high octane number cyclohexanes are present in very low concentrations since they are substantially quantitatively converted to aromatics even at low severity reforming conditions. It is the alkyl cyclopentanes and paraffins in the C_6 -280° F. fraction which are reprocessed according to the invention so as to permit an additional pass over the catalyst. It will be observed that the C_6 -280° F. stream, which is largely composed of saturates, is returned to the reforming system downstream of the first reaction zone, and preferably immediately before the last or next to the last reaction zone, and after the preceding two, three or four zones if the system is operated with a plurality of serially connected zones. Thus, the recycle stream which is low in aromatics is returned to a stage in the reforming operation where the main process stream is relatively high in aromatics; and by diluting the concentration of aromatics already present, process conditions favor dehydrocyclization of paraffins and isomerization-dehydrogenation of alkyl cyclopentanes to produce aromatics, reactions which are adversely affected by the mass action law in the presence of large amounts of aromatics.

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The invention will be more fully understood by reference to the accompanying drawings, in which:

Figure 1 is a simplified diagrammatic flow plan illustrating the preferred form of the basic invention as applied to a non-regenerative three-reactor reforming system.

Figure 2 is a diagrammatic flow plan showing the invention as applied to a regenerative platinum alumina catalyzed naphtha reforming system of the type described in U.S. Patent 2,773,014 wherein three conventional reactors and one swing reactor are employed.

In the non-regenerative process shown in Figure 1, a petroleum hydrocarbon charge such as a desulfurized virgin naphtha is pumped in via line 1 where, at connection 2, it joins a recycle stream of hydrogen supplied from line 23. The commingled stream is passed through line 3 to preheater furnace 5 where it is preheated to a temperature of about 850–1000° F., desirably 875–975° F. in coil 4 of furnace 5. The preheated effluent passes through line 6 to reactor 7 which contains a body of platinum alumina reforming catalyst disposed in the form of a fixed bed of pills having about a one-eighth inch diameter and height. Because of the highly endothermic nature of the initially-rapid cyclohexanes dehydrogenation reaction, a substantial temperature drop across reactor 7 occurs, and the effluent leaving reactor 7 through line 8 is reheated by coil 9 of furnace 10 to the usual reforming temperature in the range of about 850–1000° F., advantageously about 900–960° F., and passed via line 11 to reactor 12. An additional bed of platinum alumina catalyst in this reactor further effects hydroforming of the naphtha, again lowering the temperature by endothermic reaction, and the effluent from reactor 12 is passed through line 13 to coil 14 and reheater 15.

Before passage through reheater 15, the recycle stream of C₆–280° F. boiling range material, obtained by fractionation from the reformate in the system to be described hereinafter, is introduced into line 13 via line 37 (or, alternatively, by a line not shown, into line 8). In a new reforming unit specifically designed to employ the invention described herein, reheater 15 may be sized to accommodate the recycle C₆–280° F. stream fed at the temperature from which it is withdrawn from the fractionation system. Where however an existing refinery is modified to employ the invention it may be desirable to provide a separate recycle stream preheater (not shown) in line 37 and supply at least a portion of the necessary feed heat through the preheater.

After reheating in reheater furnace 15, the main process stream is passed through line 16 to final reactor zone 17, and thence through line 18 to product cooler 19, where normally liquid hydrocarbons are condensed and separated from the recycle hydrogen-containing gas in high pressure separator 20. Excess hydrogen gas is vented from separator 20 through line 24, while the major portion of the gas is returned to the reforming system by way of line 21, recycle gas compressor 22, and line 23.

From high pressure separator 20, the liquid hydrocarbons are passed via line 25 to fractionator 26. This fractionator may take any of several forms well known to the art and may be comprised of two separate or superimposed fractionation columns but, for reduced investment cost, is preferably a single fractionator provided with a center well 27 and center well drawoff 29, with a reflux leg 28 around center well 27. In fractionator 26, the liquid hydrocarbon, i.e. unstabilized reformate, is fractionally distilled into pentanes and lighter fraction withdrawn through line 30 (and a conventional reflux system omitted from the drawing for simplicity), while the C₆–280° F. fraction is obtained as a heartcut through center well drawoff 29, and the 280° F.–end point fraction is withdrawn through line 31.

The C₆–280° F. heartcut fraction is separated into two streams, one half or more being pumped via line 37 back to the reforming system, while the minor portion being

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sent through line 38 to a small size fractionating column 39. In column 39 the minor portion of the C₆–280° F. fraction is distilled into a C₆–230° F. fraction of low octane number which is sent through line 36 to the low octane gasoline product line 35, while the highly aromatic 230–280° F. fraction is withdrawn as a bottoms and transmitted through line 31 where it comprises a portion of the high octane gasoline product. Where the reforming unit is operated at less than full capacity, it may be desirable to recycle a portion of the C₆–230° F. fraction from line 36 to line 37.

The pentanes and lighter fraction distilled from fractionator 26 through line 30 are meanwhile conducted to a small size fractionating column 32 where they are depropanized, the light ends being released as off gas through line 33 while the butanes and pentanes are sent via line 34 to low octane gasoline product line 35. It will be understood that the foregoing distillation is conducted for maximum butane retention, and in appropriate cases it may be desired to operate column 32 as a debutanizer and withdraw the butanes, or at least a portion of the butanes, along with the off gas through line 33.

By way of example, a 58.2° API gravity Mid-Continent naphtha having an initial boiling point in ASTM distillation of 120° F., a 10% point of about 175° F., a 90% point of about 340° F. and an end point of about 410° F. comprises the charge. The charge is a virgin naphtha, and contains only 0.02 (or 200 p.p.m.) weight percent sulfur and has a research octane number of 46 neat, and a motor octane number of 45 neat. The charge contains essentially no olefins, about 40% by volume naphthenes, 8% aromatics, and 52% paraffins. Conventionally, the typical range of processing conditions in the reforming system described in Figure 1 includes a pressure range of from 50 to 1000 p.s.i.g., a temperature at the inlet to each of the reactors on the order of 850 to 1000° F., a liquid hourly space velocity of from 1.0 to 3.5 (mass of liquid per hour per unit mass of catalyst), and a molar hydrogen to hydrocarbon ratio of from 4:1 to 10:1. In the specific illustration, the pressure at hydrogen transfer line 23 is about 250 p.s.i.g., the reactor inlet temperatures are each at 925° F., the reactors are loaded to provide an overall space velocity of 1.5, and the hydrogen to hydrocarbon ratio is 8:1. The catalyst is preferably one which has been prepared by contacting an aqueous solution of chloroplatinic acid containing about 3.5 grams of platinum per liter with an ammonium sulfide solubilizing agent for converting the platinum into a solubilized form of platinum sulfide in a stable aqueous solution, then combining this true or colloidal solution with hydrous alumina prepared as taught in U.S. Reissue 22,196, the relative amounts of the two components being such as to produce a final catalyst containing about 0.1 to 1.0 percent or more of platinum by weight on a dry alumina (Al₂O₃) basis, the resulting mixture being then dried and calcined. The alumina may contain up to approximately 1% by weight of fluorine although it is preferably fluorine free. Other methods of preparing the alumina base may be employed but best results are obtained by using the method described above. Since the specific method of preparing the platinum alumina catalyst forms no part of the present invention, variations thereof will not be described in further detail.

The condensible hydrocarbons obtained in high pressure separator 20 have an octane number of about 96 research neat, on a debutanized basis, and in fractionator 26 the 280° F.–E.P. fraction has an octane number of about 101 research neat. The 230–280° F. fraction has an octane number of about 100. The low octane gasoline obtained through line 35 has a research octane number of approximately 75. By blending the 280° F.–E.P. fraction and the 230–280° F. fraction, an extremely high—e.g. 100–105—octane gasoline is obtained from the system.

Referring to Figure 2, the invention is shown as applied

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to a regenerative type platinum alumina reforming system. In Figure 2, the same numbers have been employed to designate the equivalent equipment as used in Figure 1, and since the reformat fractionation is identical in both systems it is not repeated in Figure 2. Where valves appear in a numbered line, the valve is designated with the same number as the line, followed by the letter "a."

Regenerative reforming systems are inherently more efficient than non-regenerative systems since the operation may be conducted at substantially lower pressure, generally on the order of 150–300 p.s.i.g., which minimizes the extent of wasteful hydrocracking and which favors aromatization by naphthene dehydrogenation and paraffin dehydrocyclization. Temperatures, space velocities, and hydrogen to hydrocarbon ratios are the same as employed in non-regenerative systems. At the same time, however, the lower pressure is conducive to somewhat more coke formation and for this reason it is necessary to periodically remove a reactor from the system and regenerate said reactor by controlled burning with an oxygen containing gas. In the system shown in Figure 2, naphtha charge from line 1 and recycle hydrogen gas from transfer line 23 are commingled in line 3, preheated by coil 4 in preheater 5, and transferred via line 6 to reactor 7. The effluent is transferred through valved line 8 into reheater coil 9 of furnace 10, thence through line 11, valve 11a to reactor 12, and from there through valved line 13 to coil 14 in furnace 15 and through transfer line 16 to the final reactor zone 17. The product is withdrawn through valved line 18 and transferred by way of condenser 19 to high pressure separator 20. Liquid unstabilized condensed hydrocarbons are transferred through line 25 to the fractionator system described in Figure 1, while the recycle gas is returned via line 21 to compressor 22.

It will be observed that the system of Figure 2 contains reactor 60, a so-called "swing" reactor. Swing reactor 60 is manifold into the lines connecting reactors 7, 12 and 17 so that it may be substituted for any one of these reactors when one of the latter becomes partially deactivated by coke deposition on the platinum alumina catalyst and it is to be taken offstream and regenerated. Furthermore, swing reactor 60 may be positioned to operate on stream in parallel with any one of the three reactors 7, 12 and 17, and advantageously is maintained in parallel with final stage reactor 17 until needed in the regeneration of one or more of the preceding reactors 7 or 12. When, for example, reactor 7 becomes less active than is desirable, valves 6a and 8a are closed while simultaneously valves 63a and 66a are opened. Thus the preheated naphtha and hydrogen stream from line 6 passes through valved line 63, through line 62 and valve 62a and into swing reactor 60; thence through line 61 and valved line 66a to preheater coil 9 in furnace 10. The feed naphtha and recycle hydrogen may be heated in separate furnaces if desired. The method of catalyst regeneration, with optional high temperature "rejuvenation" at controlled high oxygen partial pressure after the catalyst is regenerated, are fully described in U.S. Patent 2,773,014, and will not be considered here in detail, except to mention that each reactor, typified by swing reactor 60, is provided with valved lines 68a and 69a for the purpose of admitting an oxygen containing gas to burn off carbonaceous deposits from the catalyst.

When swing reactor 60 is employed in parallel with a reactor, say for example final reactor 17, valves 16a, 65a, 61a, 62a and 18a are all opened. Consequently, the effluent from intermediate reactor 12 and passing through line 16 is split, one half going to each of final reactor 17 and swing reactor 60, and thereafter rejoining and entering cooler 19.

In the system shown in Figure 2, the recycle stream of C₆–280° F. reformat is returned to the final reactor(s) via line 37 from which it is distributed to swing reactor 60 and/or to final reactor 17 by way of valved line 76.

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In appropriate circumstances, it may be desirable to introduce the C₆–280° F. stream before reactor 12 rather than prior to reactor 17, but this will depend on particular processing variations obtaining in an individual plant.

From the foregoing description it will be seen that the objects of the invention are fully accomplished in the system described above. While a specific example has been employed to illustrate the preferred embodiment, it should be understood that alternative and additional arrangements, operating procedures, and conditions will be apparent to those skilled in the art. For example, if the original feedstock contains large amounts of sulfur, nitrogen or olefinic materials it may be desirable to remove these constituents by catalytic hydrotreating with, for example, a cobalt molybdate or nickel-tungsten sulfide type catalyst in a reaction zone preceding the systems described above. Where the sulfur content of the naphtha is high but olefins, nitrogen, etc. are at tolerable levels, the naphtha charge may be processed without pretreatment, but to prevent the build up of hydrogen sulfide gas in the recycle hydrogen loop, means may be provided for removing this hydrogen sulfide. For example, a scrubber employing a basic solution such as aqueous caustic or diethanolamine or monoethanolamine may be inserted in line 21, and may be followed by a water scrubber to remove the basic material and, optionally, followed by a liquid desiccant such as ethylene glycol or a solid desiccant such as alumina or molecular sieves to remove water vapors. Also, the naphtha charge to the reforming zone may be given an initial pretreatment in a prefractionator or recycle gas stripper to remove oxygen and water.

The product yield and octane number is, of course, quite dependent on the charge employed and the nature of the catalyst and the severity of the treatment. In general, the process of the invention is particularly applicable to the production of high octane gasoline products having octane numbers in the range of 98–105 but may be used with advantage in operations wherein a lower or higher octane number product is desired. Moreover, while the system has been described with emphasis on production of a motor fuel component, it will be understood that the C₆–280° F. fraction recycle is advantageously used when an aromatic concentrate is desired for any other purpose, such as for solvents, aviation or speciality fuels, or the like.

By way of definition, the various hydrocarbon stocks described above have been described in terms of boiling range. This refers to the true boiling point, or "TBP," boiling range. The exact numerical boiling range of course is rarely attained in practice, there being considerable fractionation slop-over, and day-to-day variations in stream inspections ranging up to 10–20° F. in the boiling range determinations can be expected. Thus it is intended to embrace within the invention defined in the specification and asserted in the claims those compositions of charge stock, distillation fractions, and reformat which boil predominantly within the defined range and which are, composition-wise, substantially the equivalent of fractions having the enumerated TBP boiling points, even though the exact temperatures may depart somewhat from the range described.

Having described the invention, what is claimed is:

1. In the reforming of hydrocarbon charge stocks in the presence of a platinum alumina catalyst and hydrogen, wherein the catalyst is disposed in an initial reaction zone and at least one subsequent reaction zone, the process which comprises: passing the preheated hydrocarbon charge and hydrogen through said initial and said subsequent reaction zones under reforming conditions of temperature, pressure, space velocity and hydrogen to hydrocarbon ratio; separating condensable hydrocarbons from the subsequent reaction zone effluent and recycling the hydrogen to the initial reaction zone; fractionally distilling an approximately C₆–280° F. boiling range fraction from the condensable hydrocarbons, cycling a

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first portion of the C_6-280° F. fraction to the at least one subsequent reaction zone, fractionating a second portion of the C_6-280° F. fraction into a low octane number approximately C_6-230° F. fraction and a high octane number approximately $230-280^\circ$ F. fraction; and recovering the latter high octane number $230-280^\circ$ F. fraction as a first produce, and recovering a high octane number 280° F.-E.P. fraction as a second product from the condensable hydrocarbons remaining after the C_6-280° F. fraction removal.

2. Process of claim 1 in which the first portion of the C_6-280° F. fraction is at least one half of said fraction.

3. Process of claim 1 in which the reaction zones are operated non-regeneratively, at least two serially-connected subsequent reaction zones being employed, and

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the first portion of the C_6-280° F. fraction is conducted to the final of said subsequent reaction zones.

4. Process of claim 1 in which the at least one reaction zone is operated regeneratively, and the first portion of the C_6-280° F. fraction is conducted to the final of said subsequent reaction zones.

References Cited in the file of this patent

UNITED STATES PATENTS

2,644,785	Harding et al.	July 7, 1953
2,730,557	Max et al.	Jan. 10, 1956
2,737,474	Kimberlin et al.	Mar. 6, 1956
2,773,014	Snuggs et al.	Dec. 4, 1956

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,909,477

October 20, 1959

Karl A. Muller, Jr.

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

Column 3, line 67, after "into" insert -- a --; column 7, line 7, for "produce" read -- product --; column 8, line 3, after "one" insert -- subsequent --.

Signed and sealed this 19th day of April 1960.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON

Commissioner of Patents