

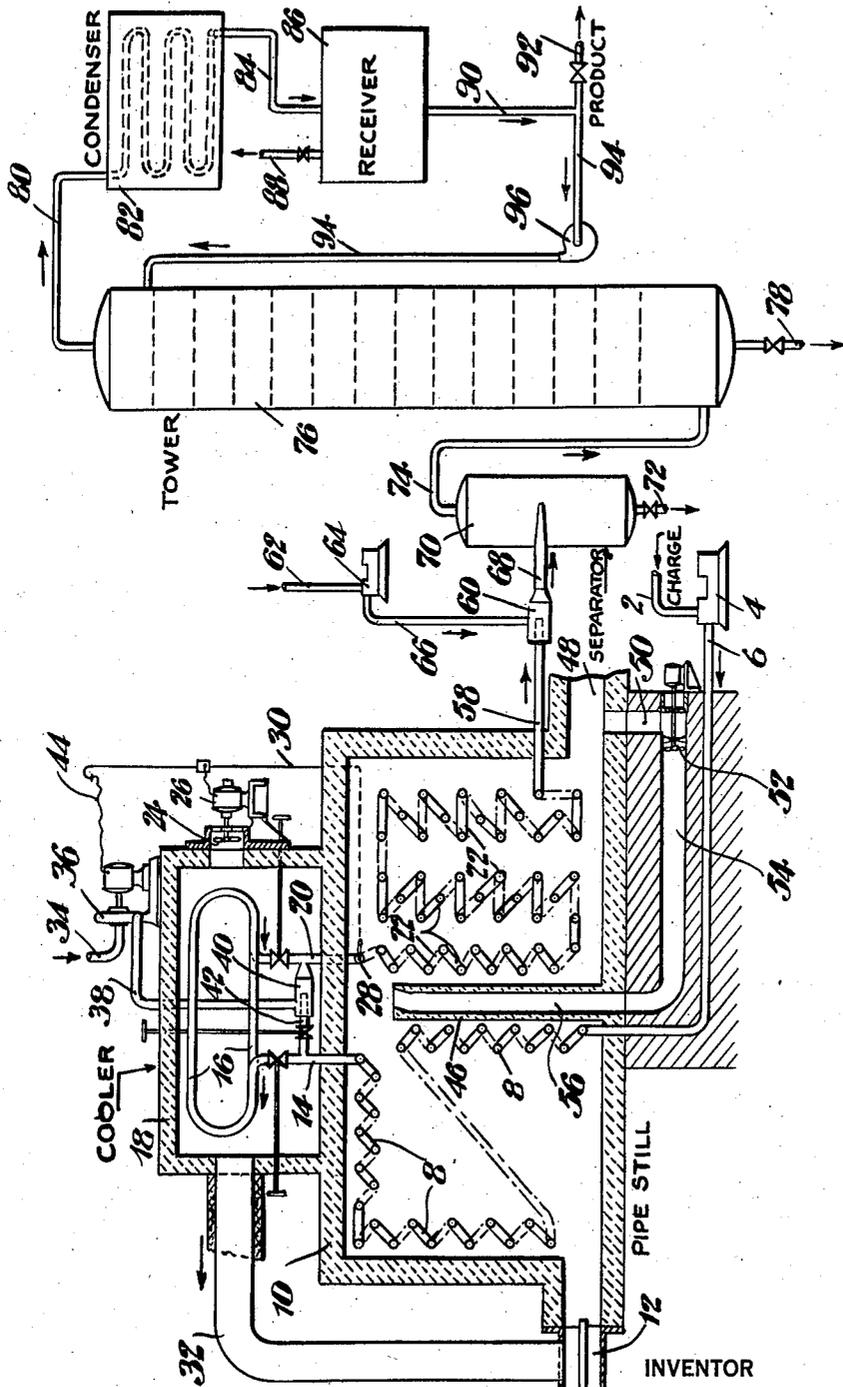
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PROCESS FOR CRACKING HYDROCARBONS

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# UNITED STATES PATENT OFFICE

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## PROCESS FOR CRACKING HYDROCARBONS

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This invention relates to a process for cracking mineral oils for the production of aromatic and/or cyclic hydrocarbons, and more particularly to such a process for producing a high compression motor fuel consisting mainly of cyclic and aromatic hydrocarbons.

The process of the present invention includes certain improvements in high temperature coil cracking operations. Some high temperature coil cracking operations are now being carried on in which the oil stock such as gas oil is heated to a temperature of approximately 1000° F. and then maintained at that temperature or slightly higher for the desired length of time for completing the cracking reaction. Motor fuel products containing substantial amounts of aromatic hydrocarbons have been obtained from such cracking operations but very little has been done toward controlling the formation of aromatic hydrocarbons in such processes.

The primary object of the present invention is therefore to provide a cracking process in which the formation of aromatic and cyclic hydrocarbons is more accurately controlled than has been the case in the past.

Another object of the present invention is to provide a process in which the cracking operation is controlled in such a way as to influence the production of side chain cyclic and aromatic compounds which have a higher anti-knock value than the normal cyclic and aromatic compounds such as cyclopentane and benzol.

In accordance with the features and objects of the present invention, the cracking reaction or certain of the reactions which occur during a particular type of cracking is controlled by accurately correlating the temperature, pressure and time elements of the improved cracking process. In carrying out the improved process, the oil charging stock which may be a gas oil, kerosene or straight run gasoline is passed through an initial heating coil under a pressure of from 200 to 500 pounds per square inch and quickly raised to a temperature at the outlet of the coil of from 1100 to 1300° F. The heating of the oil in this coil is carried out rapidly for the purpose of converting as much as possible of the oil into products of the type of hexylene, heptylene and styrol, which are all olefin hydrocarbons having the general formula  $C_nH_{2n}$ . The resulting mixture of olefin hydrocarbons is quickly cooled to a substantially lower temperature of approximately 1000° F., after which it is passed through a further heating coil where the temperature of approximately 1000° F. is maintained

without permitting any substantial rise or decrease in the temperature. This second coil should be sufficiently long to give the desired time reaction within which to permit the polymerization of the olefin type hydrocarbons into cyclic and aromatic side chain compounds. Some of the polymerizing reactions are exothermic and therefore considerable heat is developed during the time reaction in the second coil which will greatly minimize the amount of external heat necessary to maintain the desired temperature.

After completing the cracking reaction in the second coil the cracked constituents are brought in intimate contact with a cooling medium such as water or a hydrocarbon cooling fluid in sufficient amount to reduce the temperature below that of active cracking or polymerization. The vapors are thereafter fractionated to recover the highly aromatic motor fuel product.

Other features and advantages of the improved process of the present invention will be apparent from the following detailed description taken in connection with the accompanying drawings which form a part of this application.

In the single sheet of drawings;

The figure is a diagrammatic view partly in elevated section of an apparatus adapted to carry out the process of the present invention.

Referring to the drawing, the oil to be cracked and converted into aromatic hydrocarbons is introduced into the apparatus through a line 2 and forced by means of a pump 4 at a high super-atmospheric pressure through a line 6, into a plurality of radiant tube banks 8, through which the oil is passed in series. The tube banks 8 are mounted as shown in a radiant heating chamber of a pipe still furnace 10 which is provided with a burner or burners 12. The oil being treated is forced at high velocity through the tube banks 8 and therein rapidly heated to a temperature of from 1100 to 1300° F. so that the major portion of the oil is decomposed or cracked into unsaturated cyclic and olefinic hydrocarbons of a more or less unstable nature.

The highly heated decomposition products of the oil are discharged from the last tube bank 8 through a transfer line 14 and then quickly cooled by direct or indirect cooling to a temperature of from 930° to 1050° F. The indirect cooling of the decomposition products may be accomplished by passing them from line 14 through a cooling coil 16 which is mounted in an air cooling chamber 18. The cooled products from the coil 16 are conducted through a valved line 20 into and through a reaction zone com-

prising a series of tube banks 22 which are mounted in a convection chamber of the furnace 10 as shown. The requisite amount of cooling may be effected in the chamber 10 by regulating the amount of air passed over the cooling coil 16. Air is conducted into the chamber 10 by means of a fan 24 which is operated by a thermostatically controlled motor 26. A thermostat 28 for controlling the speed of motor 26 is placed in the line 20 and connected to the motor through a suitable connecting line or lines 30. The air heated in chamber 10 by the cooling of the oil products in coil 16 is conducted through an insulated conduit 32 to the burners 12 and used to supply at least in part the air for combustion in furnace 10.

The decomposition products of the oil discharged through the line 14 may be cooled to the desired reaction temperature by contacting them with a cooler fluid such as oil, water, steam or other suitable cooling medium which is introduced through a line 34 and forced by means of a pump 36 and a connecting line 38 into a mixing nozzle 40. The oil products from the line 14 are introduced into the nozzle 40 through a valved line 42 and therein cooled by direct contact and mixing with the cooler fluid from the line 38. The resulting mixture at the desired temperature is discharged into the line 20 from which it is conducted through the reaction tube banks 22. The amount of cooling fluid introduced through the line 38 may be accurately controlled by thermostatically controlling the speed of pump 36. This is accomplished by means of thermostat 28, line 30 and a connecting line 44 which connects the thermostat 28 with the motor for pump 36. By properly setting the valves in pipes 14, 42 and 20, the decomposition products of the oil discharged through the line 14 may be cooled by direct or indirect cooling, and if desired both methods of cooling may be used simultaneously.

The radiant and convection chambers of the furnace 10 are separated by a bridge wall 46 so that the furnace may be fired in such a manner as to give an extremely rapid heating of the oil constituents passing through the tube banks 8. The products of combustion from the radiant heating chamber are conducted over the bridge wall 46, around the tubes of the tube banks 22 and discharged through a flue 48. In order to maintain a substantially constant relatively low temperature around the tubes of banks 22, a portion of the flue gas is withdrawn from flue 48 through a conduit 50 and forced by means of a blower 52 through a conduit 54 into vertical distributing passages 56 in the bridge wall 46. The relatively cool flue gas withdrawn through the conduit 50 is therefore mixed with the hot flue gas passing over the top of the bridge wall 46, before it is brought in contact with the tube banks 22. This recirculation of flue gas provides a convenient means for maintaining a controlled temperature in the convection chamber of the furnace.

In accordance with the features of the present invention, the decomposition products passed through the tube banks 22 are maintained at a substantially constant temperature for a time sufficient to bring about a condensation or polymerization of the various oil constituents, into side chain cyclic and aromatic hydrocarbons. It is an object of the invention to bring about as great as possible a decomposition of the oil in the tube banks 8 without converting any substantial proportion of the oil constituents into gas. The

decomposition products are thereupon quickly reduced in temperature to the desired reaction temperature for causing the formation of side chain cyclic and aromatic hydrocarbons.

The polymerizing, condensing and other reactions such as hydrogenation which occur in the tube banks 22 are primarily exothermic reactions which produce very substantial amounts of heat. These reactions are favored by the maintenance of high superatmospheric pressures of the order of from 300 to 500 pounds per square inch in the tube banks 22. It is apparent therefore that very little heat will be required for heating the convection banks 22 and that the high flue gas recirculating rate may be necessary to keep the temperature in the tubes from rising.

The final reaction products produced by the reaction in tube banks 22 are withdrawn through a transfer line 58 and immediately cooled to a temperature below about 700° F. by mixing them with a cooling fluid in a mixing nozzle 60. The cooling fluid may comprise water, steam, oil or other suitable cooling material which is introduced through a line 62 and forced by means of a pump 64 and a line 66 into the mixing nozzle 60. The resulting mixture of cooled products and cooling fluid are discharged through a line 68 into a separator 70 in which vapors are separated from liquids or carbon present in the mixture. The liquid or carbon or both may be withdrawn from the chamber 70 through a valved line 72 while the vapors are withdrawn through a line 74 and conducted into the base of a fractionating tower 76. The cooling of the oil products discharged through the transfer line 58 stops the reactions, and particularly prevents the formation of coke deposits which usually occur at temperatures below 950° F.

The vapors introduced into tower 76 through the line 74 are fractionated to eliminate the higher boiling constituents which are unsuited for use in motor fuels. These constituents are withdrawn as condensate through a valved line 78, and with some forms of charging stocks may be returned to the pipe 2 for cracking. The constituents comprising the desired products and containing very substantial proportions of side chain cyclic and aromatic hydrocarbons are conducted as vapor through a line 80 and condensed in a condenser 82. The resulting mixture of condensate and uncondensed gases are conducted through a line 84 into a separator and receiver 86 from which relatively dry gases are withdrawn through a valved line 88. The condensate product is withdrawn from receiver 86 through lines 90 and 92. A portion of the product is preferably used for controlling the fractionation of the vapors in tower 76 and such portion may be introduced into the top of the tower through a line 94 in which is mounted a pump 96. The operation of pump 96 may be thermostatically controlled by means of a thermostat placed in the upper part of tower 76.

The tube banks 8 mounted in the radiant section of the furnace 10 are preferably made up of three or four inch inside diameter tubes adapted to withstand high pressures and severe temperature conditions. The tube banks 22 may comprise tubes of similar diameter or they may be of larger diameter up to approximately six inches. The tubes of banks 22 are not so important from the standpoint of heat transfer except for temperature control because of the exothermic reactions which occur therein. The

tube banks 22 therefor may be of larger diameter than those of banks 8.

In carrying out the cracking operation as described above the products discharged through the line 14 are preferably cooled by indirect heat exchange as in coil 16 unless some inert or a reactive material is available as a cooling medium to be introduced through the line 38. Steam is a suitable inert cooling medium. A reactive medium would preferably comprise unsaturated olefinic materials of the type being discharged through the line 14. Other more or less reactive materials may comprise the gas withdrawn through the line 38 which may be introduced through the line 34 and used as a cooling medium. Likewise a regulated proportion of hydrogen or hydrogen containing gas may be introduced through the line 34. In any case it is the object to avoid adversely influencing the equilibrium of the decomposition products discharged through the line 14. For example, large proportions of steam introduced through the line 38 as a cooling medium may decrease the proportion of cyclic and aromatic hydrocarbons produced in the tube banks 22 because the steam tends to disperse the reactive oil constituents.

In some cases it may be advisable to introduce a small proportion of reactive material through the line 38, even though the primary cooling is accomplished in the cooling coil 16. The reactive constituents introduced through the line 38 are preferably highly unsaturated olefinic or cyclic materials. Only a relatively low partial pressure of hydrogen should be maintained in the tube banks 22, otherwise the olefins and unsaturated constituents will be saturated before they have an opportunity to condense and polymerize to form aromatic and cyclic compounds. If any substantial amount of hydrogen is to be introduced, it should be introduced at a point in the later portion of the coil comprising tube banks 22.

The high boiling material withdrawn through the line 78 may be reintroduced into the system through the line 2, but this material is usually too valuable for use as recycle stock because it contains valuable polycyclic aromatic compounds which may be readily separated from the mixture by fractionation.

The low boiling product withdrawn through the line 92 comprises a very high gravity material which may be effectively used for blending purposes in the manufacture of motor fuels. It may be used directly as a motor fuel, but for ordinary use it is too valuable for this purpose, since as a blending agent it may be used to increase the anti-knock properties of straight run and other gasoline. Instead of using the low boiling product withdrawn from line 92 as a motor fuel, it may be fractionated into its various constituents for the recovery of individual aromatic compounds since the product contains on the average about 75% of aromatic constituents.

These aromatic compounds are for the most part side chain compounds in which the side chains range from 2 to 8 carbon atoms. These compounds are more effective anti-knock agents than the normal compounds.

The process of the present invention has been described in substantial detail in connection with one form of apparatus, but it is to be understood that various modifications may be made in the process and that it may be carried out in other types of apparatus without departing from the spirit and scope of the invention.

The separator 70, tower 76 and oil lines such as 2, 6, 66 and 68 preferably are insulated for proper control of temperatures.

With the apparatus illustrated in the drawings, the charging stock should preferably be a clean petroleum distillate. In case a product such as a topped crude oil or a residuum oil is available as a charging stock this material may be used in the first stage heating but it is necessary in such case to provide a separator in the line 14 whereby the heavy tarry products may be separated from the vapor so that such products will not pass through the coil 16 and coils 22. With such a separator interposed in the lines 14 or 20 the oil passing through the subsequent coils will be in the vapor state.

An illustrative example of an operation carried out in accordance with the features of the present invention comprises the use of a gas oil charging stock having a gravity of 38.7 A. P. I. which is heated to an outlet temperature of 1160° F. in the tubes 8. The resulting products are quickly cooled to a temperature of about 1020° F. and then passed on through the tubes 22 in which the temperature is maintained approximately at this point. The outlet pressure in the line 58 is 245 lbs. per square inch. The conversion products discharged through the line 58 are suddenly cooled to a temperature of about 690° F. and the gasoline boiling range material fractionated out in the usual manner. In the tubes 8 the oil is subjected to heating between the temperatures of about 1050° and 1160° F. for only about forty seconds, whereas the oil is subjected to heating in the coils 22 for a period of about seven minutes.

Having thus described the invention in its preferred form, what is claimed as new is:

1. The process of manufacturing side chain cyclic and aromatic hydrocarbons from normally liquid petroleum distillates, which comprises passing the oil distillate at a pressure of from 300 to 500 pounds per square inch through a heating zone in a rapidly flowing stream of restricted cross section, rapidly heating the oil passing through said zone to a temperature of from 1100° to 1300° F. to thereby decompose a major portion of the oil constituents into unsaturated olefin type hydrocarbons, continuing the passage of the resulting products from said heating zone as a rapidly flowing stream and quickly and rapidly cooling the same only to a temperature of from 980° to 1050° F., passing the cooled flowing stream of said products at the latter temperature through a reaction zone in which the said products are heated and the said latter temperature is maintained for a time sufficient to cause a substantial exothermic reaction resulting in the recombination of the decomposition products to produce side chain cyclic and aromatic hydrocarbons, discharging the resulting products from the reaction zone and immediately reducing their temperature below approximately 700° F. whereby further reaction is prevented, and fractionating the cooled products to recover the desired cyclic and aromatic hydrocarbons.

2. The process of manufacturing cyclic and aromatic hydrocarbons from normally liquid petroleum oil distillates in a series of directly succeeding steps, which comprises rapidly heating the oil in a confined stream of restricted cross section to a temperature above 1100° F. to decompose a substantial portion of the oil into unsaturated hydrocarbons of the olefin type, rapidly cooling the stream of resulting products of de-

composition to a predetermined lower temperature not below about 980° F. and not above 1050° F. which is particularly adapted to effect polymerization of the products of the heating, heating and maintaining the resulting cooled products in a rapidly flowing stream of restricted cross-section in a reaction zone at approximately said predetermined temperature for a time sufficient to cause substantial conversion thereof to side chain cyclic and aromatic hydrocarbons, automatically regulating the cooling of the oil products in said cooling operation in accordance with the temperature of the resulting cooled products entering the reaction zone to obtain said predetermined lower temperature, maintaining a substantial superatmospheric pressure on the products being treated in the process, and fractionating the resulting conversion products to obtain the desired side chain cyclic and aromatic hydrocarbons.

3. The process of manufacturing a high anti-knock motor fuel containing substantial proportions of side chain aromatic hydrocarbons from normally liquid petroleum distillates, which comprises rapidly heating the petroleum distillate to be treated to a temperature of from 1100° to 1300° F. while passing it in a rapidly flowing stream through a heating zone thereby breaking up the constituents of the distillate into unsaturated hydrocarbons of the olefinic type, continuing the passage of the resulting highly heated products from the heating zone as a rapidly flowing stream and quickly cooling them to a substantially lower temperature of only from 980° to 1050° F., thereby preventing substantial conversion of said distillate into uncondensable gases, immediately heating all of the cooled products in a reaction zone at a pressure of from 200 to 500 lbs. per square inch wherein said products are maintained at substantially said last named temperature for a sufficient time to cause substantial polymerization and conversion of the olefin constituents to side chain aromatic hydrocarbons, thereafter immediately cooling the resulting products to a temperature of approximately 700° F., and fractionating the cooled vapor products to obtain the desired high anti-knock motor fuel product.

4. The process defined by claim 3 in which the quick cooling of the products heated in the first heating zone is effected by intimately mingling therewith a substantially cooler fluid containing constituents of the type formed in the first heating zone.

5. The process defined by claim 3 in which the products heated in the first heating zone are quickly cooled by intimately mingling therewith a cooler fluid which will not adversely influence the subsequent polymerizing reaction.

6. A continuous process of cracking liquid paraffin hydrocarbon oil distillates for the production of a high anti-knock motor fuel, which comprises rapidly heating the distillate in a rapidly flowing stream of restricted cross-section to a temperature sufficient to cause a substantial decomposition of its constituents into unsaturated hydrocarbons and holding the heated distillate under such temperature conditions for a comparatively short period of time, quickly cooling the resulting products to a substantially lower temperature below 1050° F. but not substantially below 1000° F. thereby avoiding the formation of excess proportions of uncondensable gases and the separation of condensable constituents, continuing the heating of the stream of cooled products in a reaction zone in which they are maintained at a

temperature below about 1050° F. but not substantially below 980° F. for a comparatively long period of time whereby cyclic and aromatic hydrocarbons are synthesized from the unsaturated hydrocarbons produced in the first heating step, and thereafter fractionating the resulting products to obtain the desired antiknock motor fuel.

7. A continuous process for cracking liquid hydrocarbon oils for the production of high anti-knock motor fuel, which comprises rapidly heating the oil in a confined stream to a temperature of from 1100° to 1300° F. which is sufficient to cause a high percentage conversion of the oil constituents into unsaturated hydrocarbons, quickly cooling the resulting stream of products to a temperature of approximately 1000° F. to substantially prevent the formation of excess portions of condensable gases and carbon, continuing the flow of all of the products of said stream from said cooling operation in a confined stream in a reaction zone in which the products are heated and maintained at a temperature below about 1050° F. and not substantially below about 980° F. for a sufficient period of time to give a preponderant formation of cyclic and aromatic hydrocarbons in the product and continuing the polymerizing reaction to the commencement of carbon formation in the stream of products, thereafter quickly quenching the products to a temperature below the cracking temperature, and thereafter fractionating the resulting quenched products to obtain the anti-knock motor fuel.

8. The process of manufacturing cyclic and aromatic hydrocarbons from normally liquid petroleum oil distillates which comprises rapidly heating a high boiling point distillate under a pressure of 200 to 300 pounds to a temperature above 1100° F. to form unsaturated hydrocarbons of the olefinic type, immediately cooling the cracked vapors and gases upon reaching such temperature and while under said pressure to a temperature of 980° to 1050° F. to check the decomposing reaction, then passing said gas and vapors in a stream while under all of said pressure and at said temperature with controlled heating conditions to maintain the temperature of 980° to 1050° F. for a sufficient period of time to promote the polymerization of the vapors to a point of carbon formation, then quickly quenching the polymerized products to a temperature sufficiently low to prevent coke formation and deposition during the cooling of the vapors, and fractionating the resulting products.

9. The process of manufacturing cyclic and aromatic hydrocarbons from normally liquid petroleum oil distillates, which comprises passing the distillate in a confined stream of restricted cross-section continuously and in succession through a first heating zone, a cooling zone and a second heating zone, rapidly heating the distillate oil being treated in the first heating zone to a temperature of from 1100° to 1300° F. to form unsaturated hydrocarbons of the olefinic type, quickly cooling the highly heated oil products as they leave said first heating zone in the cooling zone to a temperature of from 980° to 1050° F. thereby checking the rapid decomposition reactions initiated in said first heating zone, heating the products passing through said second heating zone to substantially maintain them at said temperature of from 980° to 1050° F. for a relatively long period of time thereby converting substantial proportions of the oil products into cyclic and aromatic hydrocarbons, discharging the resulting converted products from the second heat-

ing zone and quickly cooling the same to a temperature below that at which further decomposition or carbon formation occurs, maintaining a superatmospheric pressure of from 200 to 500 lbs. per square inch on the oil constituents passing through said zones, and fractionating the resulting cooled products.

10. The process defined by claim 9 in which the cooling of the oil products in the cooling zone is regulated automatically in accordance with the temperature of the resulting cooled products entering the second heating zone.

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CERTIFICATE OF CORRECTION.

Patent No. 2,147,399.

February 14, 1939.

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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 44, claim 8, strike out the words "all of" and insert the same after "passing" in line 43, same claim; line 51, same claim 8, for "cope" read coke; 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 7th day of November, A. D. 1939.

(Seal)

Henry Van Arsdale,  
Acting Commissioner of Patents.