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PAUL DANCHEWARDT, OF ALHAMBRA, CALIFORNIA

METHOD FOR CONVERTING SOLID CARBON INTO LIQUID HYDROCARBONS

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The object of this invention is to produce hydrocarbons similar to mineral oils from solid carbon, or carbon containing material, such as coal, coke, charcoal, wood, solid bituminous substances, etc., and at the same time, by retreating the heavier hydrocarbons formed, to produce the largest possible proportion of hydrocarbons of low boiling points. The process may also be employed to saturate or hydrogenize hydrocarbons other than those belonging to the paraffin series and change them into paraffin. It is a known fact that carbon combines with hydrogen under great pressure at certain temperatures, though very slowly, also that unsaturated hydrocarbons may be combined with more hydrogen to form saturated hydrocarbons, a process which has been described in United States Letters Patent 1,594,663, granted to me August 3rd, 1926. In that process a mixture of nickel and sodium hydroxide is used to accelerate the reaction, which, without nickel, even with the use of exceedingly high pressure is very slow. The sodium hydroxide was added to the nickel to prevent the latter from getting inactive, or "poisoned", by certain impurities of the raw materials. Ultimately, however, the sodium hydronide will itself become loaded with sulphur, etc., and then it becomes necessary to renew the mixture or regenerate it by submitting it outside to some suitable process of regeneration. The process described in the following specification dispenses of this necessity and permits the use of other raw materials, such as solid carbon, etc., in place of mineral oil.

This process, briefly stated, consists in mixing the raw material, such as coal, wood, or any solid bituminous matter in a finely divided state, with natural oil, or tar, or a fluid hydrocarbon, and forcing the sludge, together with hydrogen and steam under the pressure of one thousand to three thousand pounds through molten sodium hydroxide, or a salt of an alkali metal which can be kept

in a fused state at the temperature used in the process and which ought to be at or somewhat below the cracking temperature of the oil employed, at the same time submitting the hydroxide or salt to electrolysis in such a way that the carbon and hydrogen mixture can come in contact with nickel, preferably in a finely divided state (fine shavings or granules), resting on the bottom of the container and forming a part of the negative pole of the electrolyzer. When the gas pressure in the latter has reached the desired point, hydrogen will readily combine with the solid carbon material forming oil, and with a part of the oil, changing its character from that of a heavy into a lighter oil. In order to prevent the oil thus formed from being oxidized when coming in contact with the positive pole, where oxygen is generated, I introduce there a continuous stream of hydrocarbon gas or a gas containing hydrogen, which becomes oxidized instead of the oil. By this simultaneous use of electrolysis, the nickel and sodium hydroxide are kept in proper shape for continuous catalysis, as will be hereinafter more fully explained. The gas and vapor together with the oil and suspended carbon will escape into a second vessel, called the separator, from where the hydrocarbons of low boiling points are allowed to pass on to a condenser, while all or part of the heavier hydrocarbons and suspended carbon are pumped back to the electrolyzer to be retreated.

In the accompanying drawing an apparatus has been shown in vertical longitudinal section in which the process may be carried on.

In the drawing numeral 1 represents the electrolyzer which is made of heavy steel so as to withstand a pressure of several thousand pounds. It is surrounded by a steam jacket 2, which is provided with an inlet valve 3 and an outlet valve 4 for superheated steam which serves as the heating medium. Through the top of the electrolyzer, the pipe

5 enters the interior. This pipe is electrically insulated from the electrolyzer at point 6 and serves as the positive pole of an electric current. Its lower extremity is perforated, while the outside end is provided with a clamp 7 for connection with a cable carrying current from a dynamo. Through pipe 5, gas may be introduced and discharged through the perforations inside of the apparatus. A small manhole 8 is used for the purpose of introducing the charge. Another pipe 9 extends into and downwardly within the electrolyzer and opens at the lower extremity. Pipe 9 has three branch lines one 10, for the introduction of steam, one 11, for the introduction and circulation of oil and carbon containing material, and one 12, leading to a compressor 13 which supplies the gas. Pipe 9 is provided with a clamp 39 to which the negative pole of the dynamo is connected. In the interior of electrolyzer 1, there is a perforated partition plate 14 and the compartment underneath this plate is filled with nickel in a finely divided state. A pipe 15 connects the electrolyzer with the separator 16 which is also made of strong steel and provided with a removable bottom plate 17 and a valved pipe 18. From the top of the separator 16, a pipe 19 which is provided with a pressure retaining valve 20 leads to the condenser 21 and thence to the receiving tank 22, which latter is provided with a draw-off valve 23 and a gas escape valve 24. Inside of the separator is placed a small pump, consisting of the pump barrel 25, the piston 26, a spring 27 supplying the motive power for the upward stroke of the piston, ball valves 28 and 29 for suction and discharge respectively. The space above the piston is connected by the pipe and union 30 with the line 31 coming from the compressor 13, while a pipe 32 forms the discharge for the gas during the upward stroke of the piston. The pipe coming from the top of the discharge valve 29 is connected to line 11 by a union 40, thus allowing the removal of the pump, if necessary, by disconnecting the bottom plate 17 and the two unions only. The operation of this pump will be hereinafter described. Number 33 represents a rotating valve actuated by a set of gears 34 and 35 and pulleys 36 and 37 connected by means of a belt 38.

In order to carry on the process by means of the above described apparatus, I fill the space below plate 14 of the electrolyzer 1 with nickel shavings or granules, then pour previously fused sodium hydroxide through the manhole 8 until the level reaches almost to the level of the pipe 15. In the meanwhile superheated steam has been admitted into the jacket 2 to keep the hydroxide in a liquid state. I now charge the separator 16 through valve 18 nearly up to the level of pipe 15 with a mixture of finely divided carbon material to be treated and sufficient oil or tar so that

the mixture can be handled by a pump. After the manhole 8 and the valve 18 have been closed, I start the compressor 13, and apply power to the pulley 37, whereby the rotating valve 33 is set in operation. Fixed gas consisting of hydrogen or gas containing hydrogen, such as blue gas, producer gas, decomposed hydrocarbon gas, etc., generally speaking any gas containing a large percentage of hydrogen but no carbon dioxide, or from which the latter has been extracted, is forced by the compressor from an outside source (not shown, but which may be a storage tank) through the rotating valve 33 intermittently into the pump barrel 25 above the piston. If the discharge pipe 32 were of the same size as the inlet pipe 30, there would be no pressure exerted on the piston and it would not move except under the influence of the spring pulling it upwards. In order to produce motion, the outlet opening of pipe 32 must be much smaller than the inlet to the pump. In that case, and as long as the rotating valve is open, which it is during one-half of each revolution, the pressure builds up quickly to the amount required to force the piston downward. The pump then discharges oil and finely divided carbon material through the ball valve 29 and pipe 11 into the mass of nickel and sodium hydroxide contained in the lower part of the electrolyzer. If the valve in line 12 is slightly open all the time and steam is admitted simultaneously through pipe 10, there will be delivered a mixture of oil and carbon, plus a little steam and considerable hydrogen containing gas into the electrolyzer during the downward stroke of the piston. When the rotating valve closes after a half turn, the spring moves the piston back to its top position, forcing the gas slowly out of pipe 32, and causing valve 29 to close and valve 28 to open, thus allowing oil and carbon to enter the part of the pump barrel below the piston. It will be obvious that thus a steady current of gas is discharged from the pipe 32 into the sludge underneath the pump, and on account of this agitation the pump is enabled to deliver sludge of uniform consistency, the carbon being absolutely prevented from settling on account of the agitation. While the rotating valve is closed, the compressor is still delivering gas into the electrolyzer, as the valve in line 12 remains always open, but during that half revolution of the rotating valve, the pump does not deliver any carbon oil sludge to the electrolyzer. I now turn on the electric current and the pressure in the electrolyzer and separator rises gradually to several thousand pounds, which may be observed by the pressure gage placed in line 19 as indicated. It has been found that high pressure favors the reaction though under the influence of the nickel as a catalyzer and with part of the hydrogen in nascent state, the reaction takes place at a

fair rate from one thousand pounds upwards. The valve 20 of pipe 19 is adjusted so that the pressure remains constant at the point found most favorable for the respective mixture under treatment.

5 The current density and the voltage varies somewhat with the size of the apparatus and therefore cannot be specified with exactness. In the small apparatus employed by me for
10 experimental purposes and which holds one and one-half ($1\frac{1}{2}$) gallons of oil sludge I employ 30 amperes at a voltage from 3 to 4 volts. In a larger apparatus this must be increased to some extent but not in direct
15 proportion to the capacity as this is unnecessary due to the fact that the function of the current is to rejuvenate the alkali hydroxide and the catalyzer, which requires only a small amount of current, and not to supply all or
20 even a large part of the hydrogen in the nascent state. If power were very cheap a greater current density might be advantageously employed. If hydrogen in the nascent state could be obtained cheap enough
25 to compete with hydrogen made outside of the apparatus by any of the known methods a large commercial unit would require not more than 60 to 90 amperes which would be an insignificant expense when compared with
30 the advantages obtained by it in the regeneration of the catalyzer and the speeding up of the process.

The reactions involved may be explained as follows: At the negative pole hydrogen
35 and metal are liberated, which latter reacts with steam to reform sodium hydroxide and produce additional hydrogen in nascent state, thus ($\text{Na} + \text{H}_2\text{O} = \text{NaOH} + \text{H}$). This means that the sodium hydroxide is regenerated and
40 hydrogen is set free and this, together with hydrogen brought in by the compressor combines with carbon to form hydrocarbons of varying molecularity. If the temperature employed is near the cracking point of the
45 higher molecules, more hydrocarbons of low boiling points are formed, at a low temperature relatively more hydrocarbons of high molecular weight are formed. If, in place of coal, wood or lignite is used, a good deal
50 of alcohol and other partly oxydized organic compounds and ammonia are formed in addition to the hydrocarbons, some of which form valuable by-products.

At the positive pole oxygen is liberated
55 and the products escaping upwards through the electrolyte are more or less oxidized through the action of this oxygen, if it were not for the hydrogen containing gas introduced through the hollow anode. For oxygen
60 has a greater affinity for hydrogen than for carbon or carbon monoxide, and if enough hydrogen is present, the oxygen will all combine with it and no carbon dioxide will be formed. This formation of carbon dioxide
65 must also be prevented for other reasons. It

may change the hydroxide of sodium into carbonate and the latter would raise the melting point of the hydroxide, eventually to such a degree as to solidify the charge, though the electrolysis is working in an opposite direction, destroying carbonate formed by liberating carbon dioxide at the positive pole. If much carbonate were formed, it would require a considerably greater current for decomposing it, if no hydrogen were introduced at the positive pole. It is therefore
70 better to prevent the formation of carbonate by the introduction of hydrogen at the positive pole. The current is effective also in throwing off other impurities taken up by the sodium hydroxide such as sulphur, arsenic, chlorine, etc., removing the elements in one form or another at the positive pole, while at the negative pole the sodium forms continually fresh hydroxide. It may be remarked that this result is obtained by the
75 expenditure of very little electrical energy, as the electrolyte is constantly reformed.

If, instead of free hydrogen, hydrocarbon gas is used at the positive pole, the oxygen
80 will also combine only with hydrogen as long as there is sufficient hydrogen to satisfy all of it. In this case carbon separates out in the free state and mingles with the oil and carbon and gas moving upwards from the negative pole, in company with which it will pass into the separator. On account of some drop
85 in temperature in the separator, only the hydrocarbons of lowest boiling points will remain uncondensed here and these escape together with the fixed gases to a condenser and are ultimately recovered as liquid in the receiver, while the fixed gas from it may be used
90 over again. Eventually after refining, the heavier hydrocarbons together with the solid carbon are pumped back again to the electrolyzer. But as the carbon is gradually used up, even if at the positive pole, some carbon is produced by the decomposition of fixed hydrocarbon gas, as would be the case
95 if we substitute hydrocarbon gas for other hydrogen containing gas, as above stated, it will soon be necessary to add more solid carbon to the charge. The solid carbon in this process is considered to form the raw material, the oil having been added merely as
100 a carrier for the solid carbon, and while the oil may be altered and the original amount actually be used up during the operation of the process, at the end we will have more
105 heavy oil than originally was added to the charge, besides the light hydrocarbons which have been continuously cut out and removed separately. In other words the addition of oil to the solid carbon is only made to render
110 it possible to make the process a continuous one and to use a pump for the introduction and circulation of the solid materials which can be done easily as long as the solids are finely enough divided to form a proper sludge
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with the oil. Therefore, at intervals we must withdraw a part of the accumulated heavy oil from the separator, which is best done by releasing the pressure temporarily and replacing the oil by a fresh amount of oil carrying more solid carbon. The anode 5 may be made of any suitable conducting material such as nickel, iron or even of carbon and will therefore be referred to in the claims as made of conducting material.

Having described the invention what I claim as new is:

1. The process of hydrogenizing carbon or carbon containing material, which consists in forcing the material together with hydrogen under high pressure, through a body of molten metal hydroxide and subjecting the same to electrolysis with finely divided nickel as the negative pole and an anode consisting of an electrical conductor through or near which latter fixed hydrocarbon gas is injected, allowing the carbon containing material to escape into another vessel, where the light hydrocarbons may be separated from the heavier ones, and returning the latter and the fixed carbon containing material to the electrolyzer to be retreated.

2. The process of producing hydrocarbons similar to natural mineral oil which consists in bringing solid carbon or solid carbon containing material suspended in oil under high pressure and at a high temperature in contact with hydrogen, nickel and an electrolyte, while the latter is subjected to electrolysis, using nickel as a negative pole and a tubular electrical conductor metal as the positive pole, neutralizing the action of oxygen liberated at the positive pole by hydrogen containing gas, allowing the hydrocarbons and carbon to enter a second vessel, from where a part of the hydrocarbons may be withdrawn, while the rest and the solid carbon are used over again.

3. The process of producing hydrocarbons similar to mineral oil from solid carbon and hydrogen, which consists in electrolyzing a metal hydroxide, introducing under high pressure carbon or carbon containing material, together with oil, free hydrogen and steam at the negative pole consisting of nickel, introducing at the positive pole gas containing hydrogen to counteract the oxidizing action of liberated oxygen on the products formed at the negative pole, separating the hydrocarbons formed and returning the carbon and part of the fluid hydrocarbons to the electrolyzer to be used over again.

4. The process of producing hydrocarbons similar to natural mineral oil from solid carbon and hydrogen which consists in bringing the carbon containing material under high pressure in contact with free hydrogen and hydrogen in nascent state, produced by electrolysis of metal hydroxide and the action of

steam on the metal liberated at the negative pole, protecting the products formed from the oxidizing effect of oxygen generated at the positive pole by surrounding the latter with a gaseous atmosphere of hydrogen containing gas, transferring the reaction products to another vessel, where they may be separated and from which the unaffected solid carbon material and oil may be returned to the first vessel and submitted to the further action of hydrogen, while another part of the hydrocarbons formed is withdrawn from the process.

5. The process of producing hydrocarbons from carbon such as coal, coke, wood or any solid carbon containing material, which consists in suspending same in a heavy fluid hydrocarbon and forcing the sludge together with hydrogen and steam through molten metal hydroxide containing nickel, while the hydroxide is subjected to electrolysis at such a rate as to be sufficient to decompose any carbonates, sulphates, sulphides or other salts which might be formed through the interaction of ingredients of the charge with the metal hydroxide, separating the hydrocarbons formed and returning a part of the heavier ones and the unaffected solid carbon material to the process.

6. The process of producing hydrocarbons from solid carbon containing material and hydrogen, which consists in bringing the carbon mixed with oil in the form of a sludge at a pressure of one thousand to three thousand pounds into contact with hydrogen or hydrogen containing gas, such as producer's gas, from which the carbon dioxide has been removed, and a catalyzer consisting of nickel and sodium hydroxide, subjecting the latter to electrolysis so that the gas and carbon react, the nickel forming the negative pole, introducing at the positive pole hydrogen or hydrogen containing gas to neutralize the oxidizing effect of the oxygen created there by electrolysis, on the products formed at the negative pole, separating the hydrocarbons of low boiling points from those of higher boiling points, condensing them and subjecting the heavier hydrocarbons and solid carbon material to further treatment with gas, nickel and sodium hydroxide.

7. The process of producing hydrocarbons from solid carbon containing material and hydrogen, which consists in subjecting sodium hydroxide to electrolysis under pressure and while in contact with solid carbon containing material, oil, hydrogen, steam and nickel, condensing the hydrocarbons formed and returning those of high boiling points and the solid carbon containing material as a sludge to the process for further treatment.

8. The process of producing hydrocarbons from solid carbon containing material and hydrogen, which consists in subjecting sodium hydroxide to electrolysis under high pressure

using a nickel cathode, introducing at the negative pole a sludge consisting of carbon and oil and a mixture of hydrogen and steam, condensing the hydrocarbons formed and separating those of low boiling points from those of high boiling points, and returning the hydrocarbons of high boiling points, together with the part of solid carbon, which has not reacted with hydrogen, into the process.

In testimony whereof I affix my signature.
PAUL DANCKWARDT.

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