

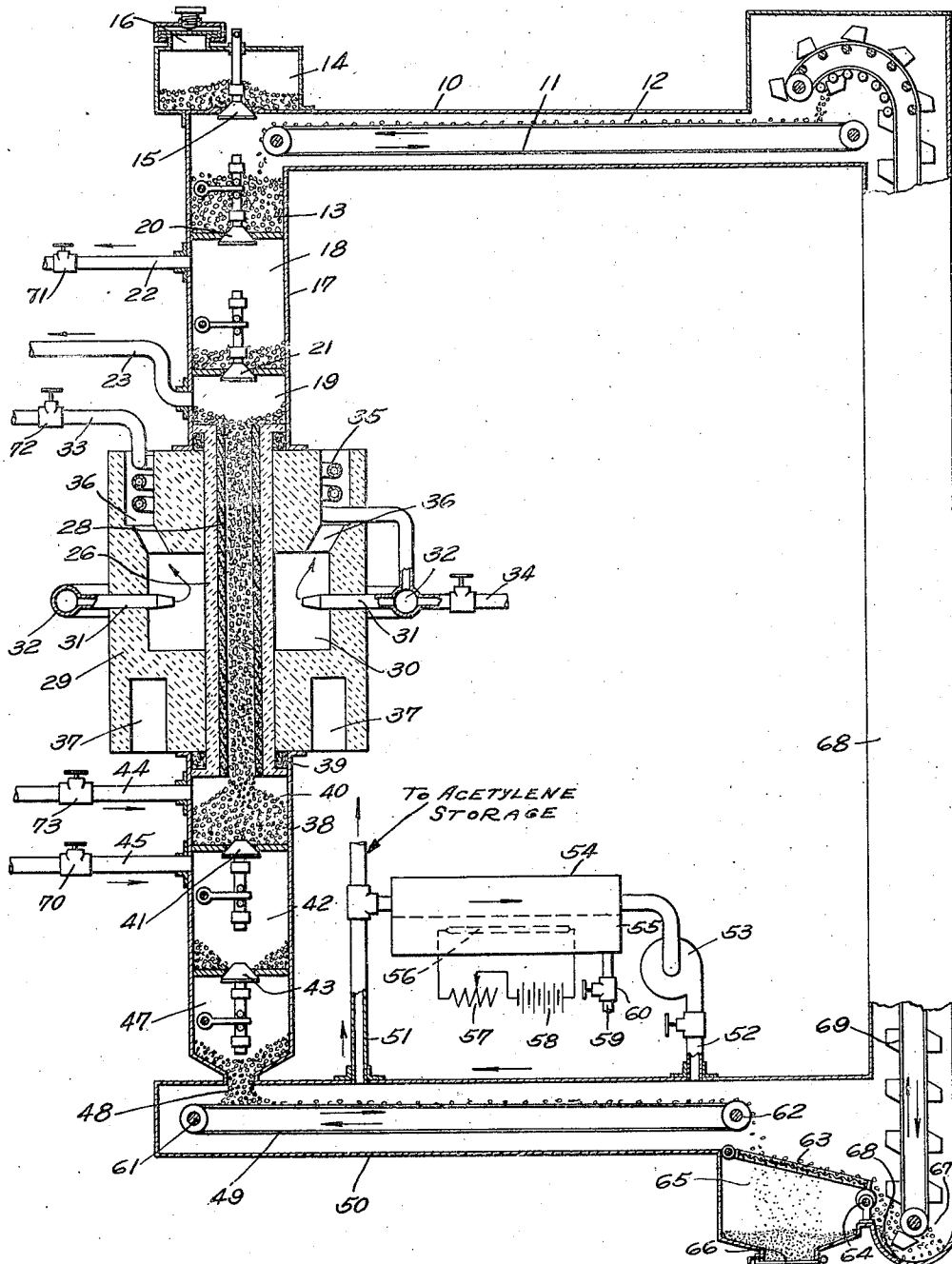
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PROCESS OF PRODUCING CARBIDES AND MAKING ACETYLENE THEREFROM

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PROCESS OF PRODUCING CARBIDES AND
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The present invention concerns a process of making alkali- or alkali-earth metal carbides and for producing acetylene therefrom. The process has for its object the manufacture of such carbides and acetylene continuously and without the aid of electric heat, although the latter may be used if sufficiently cheap. A further object of the invention is to expedite carbide formation and acetylene formation by continuous removal of carbon monoxide from the sphere of the reaction, which it has been determined exerts a retarding effect upon the desired reactions if allowed to remain.

In my study of the ordinary process of making calcium carbide, I came to the conclusion that the reason for the high temperature required was that the reaction was so conducted as to demand that temperature for the reduction of lime rather than for the formation of carbide. A further conclusion was that alkali forming metals and alkali-earth metals other than calcium were more suitable for the easy formation of carbides at comparatively low temperatures.

In the process which has been worked out and which is susceptible of numerous modifications, the result aimed at has not been the production of a high grade of carbide, but rather the efficient production of acetylene from superficially carbide-coated or carbide-impregnated metal oxides or carriers therefor.

Briefly stated, my process comprises circulating rather coarse fragments of alkali or alkaline earth oxide or hydroxide or coke impregnated with such oxide or hydroxide through a vertical gas-fired furnace through which hydrocarbon or hydrogen gas or a mixture of these is blown in counter-current to furnish carbon, if necessary, and remove carbon monoxide, continuously decomposing the carbide layer so formed on the fragments by means of a water-vapor-containing atmosphere and then continuously returning the denuded fragments to the furnace for reuse.

In the drawing is shown an apparatus preferred for carrying out the just described process, although other apparatus will also be suitable.

The particular apparatus to be described has been invented with the particular objects of being able to produce an uncontaminated product quickly, continuously, safely, and efficiently.

In the drawing 10 indicates a housing in which runs a belt conveyor 11 upon which the oxide material 12 to be treated is returned from previous use to a furnace supply magazine 13.

Above the magazine is superposed a new material feed chamber 14 from which a supply of oxide may be added through conical valve 15 to the supply of oxide already in the system. A manhole 16 in the top of chamber 14 admits of filling the latter chamber. The shell 17 which encloses chamber or magazine 13 also encloses two other chambers 18 and 19 located in the order named below chamber 13. The floors of chambers 13 and 18 are each provided with a conical valve 20 and 21 respectively. Both chambers 18 and 19 have entering them respective exhaust pipes 22 and 23. A vacuum pump or exhauster and gasometer (not shown) is connected to pipe 22.

Below chamber 19 there is a vertical refractory tube 26 which may be made of carborundum, sillimanite, or porcelain. The carborundum or like tube encloses an inner one 28 which is made of graphite. Both tubes are cemented or otherwise fastened into shell 17 in a gas-tight manner and both are encircled by a refractory furnace wall 29 about their middle section.

The wall 29 is of special construction; it encloses a comparatively large heating space 30 into which two or more burners 31 project. The burners are supplied with air and fuel through an annular manifold 32 which in turn may be supplied with air from pipe 33 and fuel from pipe 34. The purpose of the two pipes is to make the preheating of air possible since pipe 33 connects with the manifold 32 through a preheating coil 35 which encircles the furnace tubes 26 and 28 and which is heated by combustion products escaping through flue vents 36. An annular void 37 may be provided to lighten the weight of the furnace wall.

Below the furnace there is another metallic shell 38 very similar to shell 17 except that it occupies a vertically reversed position. The carborundum and graphite tubes are fitted into shell 38 in the same manner as into shell 17. Immediately below the point 39 at which such fitting occurs, there is a chamber 40, in the bottom of which is a conical valve 41.

Below chamber 40 is a chamber 42 containing in its floor the conical valve 43. Entering chambers 40 and 42 from the side and near the tops thereof are pipes 44 and 45 respectively. Pipe 44 delivers methane, artificial or natural gas, or hydrogen to the apparatus while pipe 45 is connected to a vacuum pump through the valve 70 for causing a vacuum in chamber 42.

A third chamber 47 is situated in the shell 38 below chamber 42; its floor is conical and has a valve-

less opening 48 through which oxide-carbide material may be dropped upon a traveling belt 49 which is enclosed in a housing 50. From the top of the housing there extend vertically upward
 5 pipes 51 and 52. Pipes 52, into which is connected a blower 53, is arranged to deliver gas derived from the interior of housing 50 into pipe 51. Gas from pipe 51 traverses a chamber 54, however, before being delivered into pipe 52. The chamber
 10 54 is a humidifying box containing water 55 in which there is submerged an electric heater 56 connected through a suitable rheostat 57 to a source of electrical energy 58. A pipe 59, in which there is a valve 60, is arranged to deliver
 15 water to the bottom of the box. Pipe 51, the purpose of which is to dispose of excess acetylene generated within the housings, is connected with a storage gasometer (not shown) for the finished acetylene.

20 Belt 49 passes over left and right pulleys 61 and 62 respectively. Below pulley 62 is an inclined screen 63, the meshes of which are of a size that will retain particles of the size chosen for the oxide, but which will pass particles which have had
 25 their size materially reduced through wear or disintegration. The screen is arranged to be vibrated by the action of a cam 64 which is revolved rapidly by any suitable means. Below the screen is a reservoir space 65, at the bottom of which is a
 30 discharge hopper 66.

The point of discharge of the retained material from screen 63 is so arranged that the coarse material falls into a pocket 67 of a housing 68 which encloses a vertically arranged bucket type conveyor
 35 69. The latter is arranged to discharge lifted oxide onto belt 11, previously mentioned. All operations are conducted within housings of a gas-tight nature.

When using the above described apparatus to
 40 carry out my process, the sequence of operations occurs as follows:

All valves shown are closed, and manhole 16 opened to charge oxide or hydrated oxide particles or coke particles impregnated with such material.
 45 Particles in any event are of about one-half inch size. Valves 15, 20, and 21 are opened to permit all this material to fill the chamber 40, the tube 28, and the chambers 19, 18, 13, and 14. Manhole 16 is then tightly covered again. Fuel is turned
 50 on through the pipe 34 and air through the valve 72, the mixture being lighted in the fire-box 30. At the same time flushing gas is turned on through the valve 73, which enters the chamber 40, passes up through the charge in the tube 28, enters the
 55 chamber 19, and makes exit through the pipe 23 to a receiver, not shown. This gas is hydrogen if no carbon is necessary to the charge being treated other than said charge already contains, as for instance when impregnated coke is used. The
 60 gas may contain hydrocarbons such as the lighter paraffin hydrocarbons, if additional carbon is needed. It may even be pure methane, and the speed of its passage adjusted to the temperature therein so that only the proportion desired has
 65 time to decompose and form carbon for the reaction of forming carbide. For purposes of flexibility there may be added to this methane a minor proportion of higher paraffins, preferably ethane.

As soon as sufficient time has been allowed for
 70 the furnace and its charge to reach an operating temperature, chamber 42 is evacuated through the valve 70, which is then shut again. Valve 41 is then opened to allow for the filling of the chamber 42 with treated material. At the same time
 75 the void space in said chamber is filled with gas

from the chamber 40. Valve 41 is again closed, and the gas in the void space of chamber 42 withdrawn by evacuation as before. Valve 43 is then opened to let chamber 47 be filled from chamber 42. This now admits gas from chamber 47 to
 5 chamber 42, which must be withdrawn before chamber 42 is again filled with a charge.

Each time material is dropped from chamber 40 into chamber 42, the heated charge in the tube 28, being loose slides down accordingly, and chamber 19 in this way is substantially emptied.
 10 Thus each time the chamber 19 is emptied there must be a refilling sequence of operations on the connected chambers 18 and 13. Chamber 18 is first evacuated through valve 71, and said
 15 valve again closed. Valve 21 is then opened and chamber 18 emptied into chamber 19. With this operation gas fills the void space in chamber 18 from the chamber 19. This gas is evacuated
 20 from the chamber 18 as before, after closing valve 21. Chamber 18 may then again be filled by opening valve 20. This operation admits gas from chamber 13 into the chamber 18, which gas is again evacuated after closing valve 20.

The rate of passage of material through the
 25 tube 28 will be dependent on the design of the furnace used, the nature of the charge used, and the temperature employed. It is safe to say, however, that the desirable thing is the formation of a superficial coating of carbide-impreg-
 30 nated particles, of from 1/64th to 1/8th inch in thickness. The movement of particles or charge through the furnace is seen to be intermittent, but the size of the chambers feeding and with-
 35 drawing material is made small enough to be continuous, for practical purposes. It is also advisable to have the proportion of chambers below the tube 28 such that chamber 47 is never entirely empty, but is continually feeding material
 40 onto the conveyor belt 49. These chambers must also be properly proportioned to the chambers above tube 28 so that the tube 28 is at all times full of material for treatment.

The purpose of the multiplicity of chambers 17 and 38 is to provide against contamination of the
 45 acetylene generated by the flushing gas. Chambers 47 and 13 are at all times full of pure acetylene, and when communication from these chambers to the chambers 42 and 18 respectively is made, said latter chambers must first be evacuated.
 50

One of the particular advantages of my process resides in the fact that the upward sweeping current of methane, etc., carries away and dilutes the carbon monoxide formed in furnace tube 28
 55 and thereby acts to remove a hindrance to the progress of the carbide-forming reaction. The contaminated flushing gas may be freed from carbon monoxide by any suitable known means and used over again in the process, although I
 60 prefer to convert the CO into methane and water in the known manner by adding the quantitatively necessary amount of hydrogen and then passing the mixture over a heated nickel catalyst. The gas is then preferably dried before reuse.
 65

Carbide-coated granules which have passed chamber 42 automatically drop onto belt 49 and are there exposed to the damp atmosphere generated by humidifying box 54, in which the water is kept vaporizing through being continuously
 70 electrically heated. Evolution of acetylene from the carbide coating takes place, filling housings 50, 68, and 10 with acetylene, which is continuously circulated through box 54 by blower 53 in a left to right direction. This movement will bring
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volumes of wet gas into counter-current contact with the carbide-coated particles on belt 49, which will result in the drying of the acetylene and the generation of more acetylene. In time such an excess of acetylene will be generated that it will be forced to seek its exit through pipe 51 to the acetylene storage gasometer, not shown.

The vibrating screen 63 operates to separate all fines from the oxide particles and to dump the denuded large granules of oxide into conveyor pocket 67. Such fines as drop through the screen may be collected from hopper 66, and calcined to convert all hydroxide into oxide and then be re-granulated and recharged into the apparatus. The granules reaching pocket 67 are lifted by conveyor 69 and dumped upon belt 11, which again drops them into chamber 13.

While the above matter sufficiently describes the mechanical and thermal arrangements, some additional remarks upon chemical considerations may aid in understanding the breadth of those aspects of the invention.

Barium oxide is the preferred basic oxide, but strontium, sodium, and calcium oxides may also be used, and these may at times be in the hydrated state, as for instance after leaving the acetylene generating chamber 50.

The oxide chosen may be pelleted to suitable size with a carbonizing binder such as dry pitch or molasses. As an alternative, coke may be brought to the proper mesh, and impregnated at high temperature with the molten basic oxide or hydroxide used. It may be seen also that from the similarity of the different basic materials mentioned, they may be used in admixture to get desired intermediate properties such as modified alkalinity. The description of such materials as a metal compound selected from the group comprising the alkali forming metal oxides and hydroxides and the alkali earth metal oxides and hydroxides means, therefore, one of such compounds alone, or a mixture of any two or more of such compounds. Likewise, the description of such materials as an oxide or hydroxide selected from such group means any oxide or hydroxide from such group, alone, and any oxide or hydroxide from such group together with any one or more of the oxides or hydroxides from such group.

It is to be observed that where bonded oxide material is fed into the furnace, there will be carbon added superficially to the charge in the hottest portion of the furnace by the addition of methane or other cheap hydrocarbon to the flushing gas. Flexibility is at hand in the choice between methane and ethane, which show great difference in the ease with which they decompose under heat to yield carbon. The ratio of these can be adjusted, so that with suitable rate of flow of flushing gas, there will be just enough carbon liberated on the surface of the charge. The description of the employment of a suitable hydrocarbon in the process, therefore, means the employment of methane, ethane or other suitable hydrocarbon alone or in any combination with each other. In any case the flushing gas has the function of removing carbon monoxide, by-product of the carbide-forming reaction which otherwise retards carbide formation.

The source of flushing gas is immaterial, as long as it does not contain carbon monoxide in appreciable amounts. Such flushing gas may be made from oil by a separate furnace in which the same may be cracked. This will furnish a mixture of hydrogen and varying amounts of

methane and ethane according to the treatment. Heavier constituents such as propane and light gasolines may be removed by known means. These heavier constituents are not desirable in large quantities in the flushing gas because they decompose too easily under heat.

Flushing gas making exit from the furnace can be used to any extent required for fuel in the burners 31, and if there is any excess, it may be treated by any known means to remove the carbon monoxide so as to make it usable for flushing gas again.

Depending upon the metal oxide or hydroxide used, the maximum temperature attained by the charge, which is the carbide formation zone, will vary from anywhere between 900 to 2800° F., being lowest for sodium oxide and highest for calcium oxide. Barium oxide will require a temperature of from 1400 to 1800° F.

In the formation of carbides by this process a temperature for the particular metal oxide has to be reached where said oxide will materially reduce to metal and carbon monoxide. At the same time the temperature must not be high enough to prevent formation of carbide from the metal and carbon, or to decompose any such carbide formed.

Chemical considerations also enable the showing of my essential process in a modified form which is, however, not recognizable mechanically as having much relationship with the process just described. The modified method is to melt NaOH or KOH in a deep iron crucible and then to bubble methane or natural gas therethrough. If finely divided carbon were suspended in the melt, hydrogen may be the gas bubbled through. In any case there will occur carbide formation under conditions favoring the continuous removal of CO by a flushing gas (methane and liberated hydrogen). This form of my invention avoids the feature in the form first described of forming carbide through a progressively thicker and thicker shell of already formed carbide. The action of removing carbon monoxide from under this shell becomes more difficult as the shell gets thicker. In the case of the second form, we are working with a liquid material in which the carbon monoxide will always be easily removed, suffering dilution immediately upon forming. This effect, however, can be secured with the impregnated coke, if said coke in the tube 28 is held at a sufficiently high temperature for the basic oxide to be in a molten condition, held in place by capillarity.

I claim as my invention:

1. A cyclical process of forming acetylene which consists in: contacting particles of an oxide or hydroxide selected from the group comprising the alkali-earth metal oxides and the alkali-forming metal oxides and hydroxides with a gas rich in methane at carbide-forming temperatures, said temperatures being obtained by burning a combustible mixture, contacting the carbide-bearing particles with a moist atmosphere, thereby obtaining acetylene and the original particles, and recycling said original particles.

2. A cyclical process of forming acetylene which consists in: countercurrently contacting particles of an oxide or hydroxide selected from the group comprising the alkali-earth metal oxides and the alkali-forming metal oxides and hydroxides with a gas rich in methane at carbide-forming temperatures, said temperatures being obtained by burning a combustible mixture, contacting the carbide-bearing particles with a

moist atmosphere, thereby obtaining acetylene and the original particles, and recycling said original particles.

3. A cyclical process of forming acetylene which consists in: contacting particles of an oxide or hydroxide selected from the group comprising the alkali-earth metal oxides and the alkali-forming metal oxides and hydroxides with a gas rich in methane at carbide-forming temperatures, said temperatures being obtained by burning a combustible mixture, said gas being supplied under such conditions as to continuously remove carbon monoxide at substantially the same rate at which it is formed, contacting the carbide-bearing particles with a moist atmosphere, thereby obtaining acetylene and the original particles, and recycling said original particles.

4. A cyclical process of forming acetylene which consists in: contacting particles having a surface of a metal compound selected from the group comprising the alkali-earth metal oxides and the alkali-forming metal oxides and hydroxides with a gas rich in methane at carbide-forming temperatures, said temperatures being obtained by burning a combustible mixture, contacting the carbide-bearing particles with a moist atmosphere, thereby obtaining acetylene and the original particles, and recycling said original particles.

5. A cyclical process of forming acetylene which consists in: contacting particles of coke impregnated with a metal compound selected from the group comprising the alkali-earth metal oxides and the alkali-forming metal oxides and hydroxides with a hydrogen containing gas at carbide-forming temperatures, contacting the carbide-bearing particles with a moist atmosphere, thereby obtaining acetylene and the original particles, and recycling said original particles.

6. A cyclical process of forming acetylene which consists in: contacting particles of coke impregnated with a metal compound selected from the group comprising the alkali-earth metal oxides and the alkali-forming metal oxides and hydroxides with a hydrogen containing gas at carbide-forming temperatures, said gas being supplied under such conditions as to continuously remove carbon monoxide at substantially the same rate at which it is formed, contacting the carbide-bearing particles with a moist atmosphere, thereby obtaining acetylene and the original particles, and recycling said original particles.

7. A process of producing acetylene which consists in: countercurrently contacting particles of one or more metal compounds selected from the group comprising the alkali-forming metal oxides and hydroxides and the alkali-earth metal oxides and hydroxides with one or more suitable hydrocarbons at carbide-forming temperatures so that the hydrocarbon reacts with the particles to form

carbide; treating the particles to form acetylene from said carbide; and utilizing the particles after the acetylene has been so produced in the formation of additional carbide.

8. A process of producing acetylene which comprises: forming a carbide by subjecting a suitable hydrocarbon to the action of heat in the presence of particles of a metal compound selected from the group comprising the alkali-forming metal oxides and hydroxides and the alkali-earth metal oxides and hydroxides so that the hydrocarbon reacts with the outer surface of the particles to form a carbide; treating the particles to form acetylene from said carbide; and utilizing the particles after the acetylene has been so produced in the formation of additional carbide.

9. A process of producing acetylene which comprises: heating a hydrocarbon to a temperature in excess of 1400° F. in the presence of particles of a metal compound selected from the group comprising the alkali-forming metal oxides and hydroxides and the alkali-earth metal oxides and hydroxides so that the hydrocarbon reacts with the outer surface of the particles to form a carbide; treating the particles to form acetylene from said carbide; and utilizing the particles after the acetylene has been so produced in the formation of additional carbide.

10. A process of producing acetylene which comprises: subjecting a suitable hydrocarbon to the action of heat in the presence of particles of a metal compound selected from the group comprising the alkali-forming metal oxides and hydroxides and the alkali-earth metal oxides and hydroxides so that the hydrocarbon reacts with the outer surface of the particles to form a carbide, the hydrocarbon being passed through the reaction zone in gaseous form in sufficient quantities to rapidly remove from that zone any carbon monoxide formed therein; treating the particles to form acetylene from said carbide; and utilizing the particles after the acetylene has been so produced in the formation of additional carbide.

11. A process of producing acetylene which comprises: forming acetylene by heating a hydrocarbon to a temperature in excess of 1400° F. in the presence of particles of a metal compound selected from the group comprising the alkali-forming metal oxides and hydroxides and the alkali-earth metal oxides and hydroxides so that the hydrocarbon reacts with the outer surface of the particles to form a carbide, the hydrocarbon being passed through the reaction zone in gaseous form in sufficient quantities to rapidly remove from that zone any carbon monoxide formed therein; treating the particles to form acetylene from said carbide; and utilizing the particles after the acetylene has been so produced in the formation of additional carbide.

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