PUBLISHED

APRIL 27, 1943.

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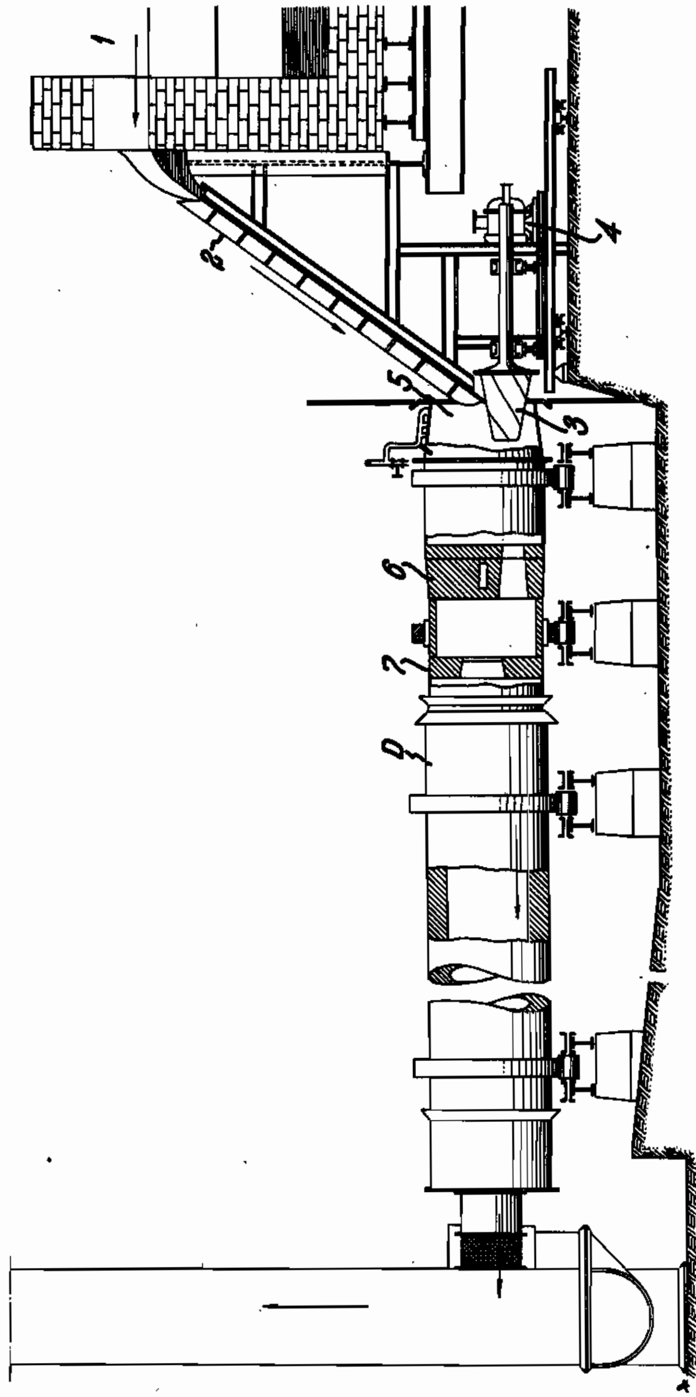
Filed March 14, 1941

Serial No. 383,338



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ALIEN PROPERTY CUSTODIAN

METHOD AND DEVICE FOR PARTIAL OR COMPLETE AZOTIZING OF CALCIUM CARBIDE AND CARBIDE MIXTURES

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Application filed March 14, 1941

In connection with the azotizing of calcium carbide into calcium cyanamide it is a well-known practice to collect fused carbide flowing from a carbide furnace in pans, and, in a given case, for the purpose of partial azotizing, press nitrogen through the walls of such pans and through the fused carbide, respectively; to subsequently finely grind the carbide partially azotized while in complete fusion and then azotize it again. It is furthermore a well-known practice, previous to azotizing to add finished calcium cyanamide to cooled-down carbide. Another well-known method provides the disintegration of carbide by means of an innocuous stream of gas in connection with the rapid cooling of the carbide below the azotizing temperature. These methods involve the disadvantage of heavy wear and tear of the carbide receptacles required for partial azotizing, cumbersome means of transportation, adverse material and energy balances, and difficult adaptability to large-scale industrial operations respectively so that hitherto they could not assert themselves in the field of large-scale technology.

All these disadvantages are eliminated by the new invention which is characterized by the feature that fused carbide flowing from a carbide furnace and having been suitably finely disintegrated, by means of centrifugal forces for instance, is conveyed to a revolving drum in any desired manner, especially by being hurled into such a drum, becoming at the same time, under emission of heat, congealed before reaching, or in, the forward part of the drum in the stream of nitrogen, and subsequently and while in motion azotized by means of nitrogen of higher temperatures and conducted through it. It has been found that azotizing or partial azotizing under temperatures coming from above, such as passed during the cooling-down of carbide fusion, is feasible, surprising as it may seem, but it is feasible under full safety of operation only if the material is continuously kept in rolling motion, without, contrary to other methods, requiring quickest possible cooling-down below azotizing temperature. By the new invention not only the cooling of the carbide in a cooling room and the loss of carbide involved in such cooling is avoided and the damage to the azotizing process, in the form of carbonic acid and water contents of the carbide, reduced, but a return of finished calcium cyanamide, for the purpose of its admixture to carbide filling material, as well as the admixture station of calcium cyanamide proper, are rendered superfluous in an especially advantageous and simple manner. A further remarkable advantage is to be found in the fact that the capacity of any calcium cyanamide plant is considerably increased by the new method, without requiring any increase in the number and size of the azotizing furnaces whatever type they may belong to. Provided, for instance, that the initial nitrogen contents of the carbide filling material be 5 to 7 per cent., then the capacity increase will approximate 25 to 40 per cent. The fact that any return of calcium cyanamide is avoided not only results in shorter and simpler means of conveyance, but also in the elimination of damage due to the absorption of water and carbonic acid, caused by the return, and to hitherto longer means of conveyance, so that by increased yield of azotized carbide further favourable results are attained. A further advantage of the method according to the invention is to be found in the improvement of the energy and material balances of the azotizing process, i. e. in the saving of current required for the operation of mills and furnaces and of energy required for the transportation of material. A special merit is to be found in the fact that all these various advantages and improvements within one and the same apparatus can be effected in an especially simple manner.

Disintegration of the fused carbide flowing from the carbide furnace can be achieved in any desired manner, so for instance by spraying the fluid stream of carbide by means of nitrogen, in which connection, however, during and after disintegration excessive cooling down of the sprayed carbide, caused by excessive extraction of heat, must be avoided. It is especially advantageous to effect disintegration by means of a rotating roller or disc, a centrifuge, or the like, and to convey the so finely disintegrated carbide to a drum in any desired manner, preferably by hurling it directly into the rotating drum, in such a manner that the rotating roller, or the like, represents the means of both disintegration and transportation. If desired, the rotating drum is wholly or partly provided with guide vanes, or with winding guide recesses in its masonry lining, or the like, and/or arranged inclined in front or the rear, so that disintegrated carbide, hurled into it for instance, is made to pass through it. In the forward part, the carbide, if necessary, is made to congeal under emission of heat, whereupon partial azotizing of the disintegrated, congealed carbide—according to the invention coming from higher temperatures—takes place, while in motion, by means of nitrogen which moves in opposite direction (counter-current) to the carbide. However, parallel-current or partly parallel-current and partly counter-current motion may be applied; so for instance in connection with the disintegration of the carbide by spraying it by means of nitrogen. For partial azotizing either pure nitrogen, or residuary nitrogen derived from carbide or calcium cyanamide mills or from azotizing furnaces, or the like, may be used, or vice versa.

It is an astonishing fact that in this manner it is possible during an only short time of stay to fill the carbide with quantities of nitrogen, 3 to 10 per cent. for instance, favourably influencing subsequent final azotizing. It is another astonishing fact that with partial azotizing in the sense of the present invention, while the carbide is in motion, the disintegrated carbide does not agglomerate but passes through the apparatus without sticking, and the like. The carbide which in the form of porous material similar to coking duff results from the use of a spraying roller is especially adapted for partial azotizing, and under temperatures in the sense of the present invention will surprisingly readily and to a large extent absorb nitrogen within a short time, that is to say, more than five per cent. of nitrogen in less than 20 minutes. The absorbed quantities of nitrogen can be smaller or larger, and they depend not only on the time of stay in the azotizing zone, but also on the temperature conditions surrounding partial azotizing, the admixtures or the mixtures added, the size and the composition of the grain, the percentage of the carbide, the conditions under which the carbide is generated, the conditions under which the disintegrated carbide is generated, etc. Partly, these conditions can be regulated, so for instance by the use of a disintegrating device based on the utilization of centrifugal force, by the size and by the speed of rotation of such device, furthermore by the length, the masonry lining, the speed of rotation, the slope, etc., of the drum. Depending on whether a higher or lower degree of nitrogen contents of the partly azotized carbide is required, the different sizes, and measures to be taken, can be regulated in such a manner that the carbide in motion and coming from higher temperatures will absorb the desired quantity of nitrogen.

In the sense of the invention it has proved of advantage for partial azotization at atmospheric pressure to keep the range of temperature between 2912 and 2192° F, and in particular between 2552 and 2282° F. Both below and above this range of temperature the absorption of nitrogen will take place at reduced speed, in the former case because of too low reaction and diffusion speeds respectively, in the latter case because of the influence of the dissociation working in opposition to nitrogen absorption. Nevertheless, temperatures of from 2552 to 2812° F, and in excess thereof, may be used in connection with partial azotizing.

Naturally, the absorption of nitrogen is the quicker and the more uniform the more uniform and finer the splitting up of the calcium carbide stream. It would be erroneous, however, to believe that the process in question be practicable only in connection with difficult measures of disintegration. It has proved a surprising fact that with comparatively coarse and ununiform disintegration favourable degrees of absorption can be obtained too. In one case for instance 40 per cent. of the carbide disintegrated by a rapidly rotating roller had a size of grain of up to 5 millimeters, and 83 per cent. a size of grain of up to 10 millimeters. In the case of admixtures being used, nitrogen contents of 2 per cent. were obtained at a temperature of 2552 to 2372° F in the zone of partial azotizing, and during a time of stay of 5 minutes. During a time of stay of 10 minutes, 5 per cent. of nitrogen were obtained with fluorite, while during 20–25 minutes time of stay, in connection with the use of admixtures, 7.7 and 9.6 per cent. respectively were obtained. An approximately equal admixture of fluorite and calcium cyanamide has also proved advantageous.

After azotizing, the partially azotized carbide is preferably cooled, so for instance by means of enlarging the free cross sectional area of the drum, by external cooling, by free fall through spaces rinsed with protective gas, by cooling coils, or the like. After having cooled down to a temperature commensurable to its further treatment, the azotized carbide can be ground together with or without any admixed material enhancing or rarefying the reaction of azotizing, and then azotized. It also is possible to produce partially azotized carbide of higher nitrogen contents than required, and to add suitable quantities of preliminarily crushed or ground carbide of lower nitrogen contents, or to admix such carbide in a finely divided form after the grinding of the partly azotized carbide. Other admixing materials too must not be admixed until after the partially azotized carbide has been ground.

In the case of a special type of construction embodying the new method, the material, partial azotizing being completed, is further azotized in the rotating drum. Such further azotizing takes place at or below the temperatures applied for partial azotizing. It is of particular advantage to extend the time of stay in the initial zones adjacent to the zone of partial azotizing to such an extent that the material becomes fully azotized, resulting in the direct generation of calcium cyanamide of granular shape or of a shape similar to that of coking duff, which, on the way covered by the carbide while cooling down and coming from higher temperatures, is generated in motion between the tap hole for the carbide and the end of the rotating drum. The material coming out of the higher temperatures of azotizing can be further azotized, at temperatures between 2372 and 1832° F for instance. Without further input of energy, such complete azotizing is possible only by utilization of the heat contents of the glowing carbide being tapped and of the heat of reaction. Excessive heat of reaction can be utilized for any desired purpose, for the generation of steam for instance. However, under certain conditions, especially towards the end of complete azotizing, or in connection with discontinuous operation for instance, it is possible to also apply additional input of energy.

Another advantageous form of application of the new process in connection with partial or continued azotizing is that zones of increased temperatures due to heat of reaction and zones of constant temperature respectively are followed by cooling zones, or vice versa. If partial azotizing takes place at higher temperatures, then the absorbable quantities of nitrogen are physico-chemically limited, while in the case of cooling to lower temperatures, new absorption of nitrogen will start again. It conforms to the sense of the invention for instance that temperature increase and cooling occur several times in succession, or that zones of constant temperature are followed by such of cooled-down temperatures, or that zones of increased temperature and such of constant temperature, interrupted by zones of cooled-down temperature, follow each other alternately as may be desired. In this manner, the present process provides a regulation of the absorption of nitrogen, excluding any and all danger of overheating.

Preferably, admixing substances enhancing azotizing and partial azotizing respectively are added to the carbide by feeding them onto the spraying roller, the disc, or the like, or into the rotating drum. For the purpose of partial azotizing and in order to obtain shorter times of stay of the material in the drum for partial azotizing, preferably such admixing material is used as will result in especially rapid initial absorption of nitrogen. Such admixing substances include for instance chloride and fluorides of alkalies, chlorides of alkaline earths, calcium cyanamide itself, or mixtures composed of such substances or of such substances and other substances. If, however, further azotizing and final azotizing respectively in one and the same drum be simultaneously desired, then admixing substances simultaneously enhancing these two parts of azotizing should be used; fluorite for instance. Fluorite may be used for partial azotizing also. The adding of such substances enhancing further and final azotizing respectively can also be effected by feeding them onto a water-cooled spraying roller, disc, or the like, or into the forward part of the rotating drum, but only after partial azotizing in the cooling zone or prior to the carbide's passing or after its having passed the mills. A suitable form of adding admixing substances or a mixture of admixing substances consists of blowing them in a finely divided condition, by means of a stream of gas—a stream of nitrogen for instance—onto the disintegrating device or into the rotating drum. In doing so, the gas stream carrying the admixing substance can for instance be made to travel in the direction of flow of the material, and the stream of gas supplying the drum, in a direction opposite to the flow of the material, so that the bathing with nitrogen takes place partly according to the parallel-current principle and partly according to the counter-current principle.

Under the present process, the disintegrated material is backed up in the azotizing zone of the drum, by means of baffle plates for instance, and/or the zone of azotizing is narrowed by means of masonry lining, insulation from heat, double walls, or the like, to such an extent that, a favourable time of stay or the most favourable temperatures for partial azotizing provided, the bathing of the azotizing zone with nitrogen is reduced to the lowest possible degree. In this manner, partial azotizing is effected under a minimum consumption of nitrogen and without any restriction of the passage of material.

The invention results in additional advantages, provided, the carbide-furnace tap, the disintegrating device and the head of the rotating drum, or at least the disintegrating device and the rotating drum, are interconnected by means of an easily accessible nitrogen-bathed chamber which, if necessary or desired, is sealed against the rotating parts (rotating drum, drive shaft of the disintegrating device, etc.). With this type of construction, the stream of carbide flows exclusively within the nitrogen-bathed chamber which is tightened against both carbide furnace and rotating drum. In this manner, calcination losses in connection with the discharging or disintegrated carbide are fully excluded, the attendants effectually protected from any and all trouble, and practically a free-from-loss utilization of the nitrogen is attained. Special attention is drawn to the fact that the nitrogen can be used again or pumped off, and, if need be, after its purification conducted again into the rotating drum, the tapping chamber and the mills respectively. The chamber, water-cooled if required or desired, is provided with orifices for burning open the tap hole and for removing pieces of carbide which may have dropped down. Continuous tapping provided, this type of construction represents one single aggregate continuously producing preliminarily azotized, granular carbide and finished granular calcium cyanamide respectively directly from fluid carbide, at highest utilization of the nitrogen, without any loss of carbide and without any additional input of energy.

Another form of application of the new method consists of subdividing the drum into two or more drums, in which case the different drums assume the respective functions of the original drum parts. By doing so, the individual drums serving for azotizing, partial azotizing and cooling respectively, can be regulated in such a manner, as far as speed of rotation, pitch, diameter, etc., are concerned, that at smallest power consumption most favourable effects of azotizing and cooling respectively can be attained, irrespective of how heavily the quantities of material passing through may vary.

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