

UNITED STATES PATENT OFFICE.

CARL FREDRIK JAKOB FORSELL, OF CLEVELAND, OHIO, ASSIGNOR TO NATIONAL CARBON COMPANY, OF CLEVELAND, OHIO, A CORPORATION OF NEW JERSEY.

METHOD OF GRAPHITIZING.

983,888.

Specification of Letters Patent.

Patented Feb. 14, 1911.

No Drawing.

Application filed April 29, 1907. Serial No. 370,803.

To all whom it may concern:

Be it known that I, CARL FREDRIK JAKOB FORSELL, a subject of the King of Sweden, residing at Cleveland, in the county of Cuyahoga and State of Ohio, have invented a certain new and useful Improvement in Methods of Graphitizing, of which the following is a full, clear, and exact description.

The object of the present invention is to provide a new method of graphitizing particularly adapted to converting amorphous carbon into the graphitic form.

The methods of graphitizing previously known are few in number, particularly such methods as are capable of use commercially. These methods are conducted within certain lines of procedure, which lines are determined by very scanty general laws on the subject, and a certain amount of empirical knowledge. Recognizing the insufficiency of the known facts, the generalizations based thereon have not been regarded as of much value, except as they may relate to the specific processes growing out of such empirical knowledge.

I have discovered a method of procedure which is founded fundamentally upon the discovery, that when carbon is subjected to heat, together with a compound, with a part of the constituent elements of which compound the carbon will combine to form a gas, which gas is, under the conditions maintained, capable of being reduced, it is possible, by disturbing in certain ways the equilibrium of the vapors there present, to cause the carbon-containing gas to deposit the carbon in the form of graphite.

My invention relates to this method of procedure, and, in view of the value of generalizations in this art as set forth above, I do not seek to have the invention construed to be of any greater scope, as the general rule, based upon the specific procedure which I prefer to follow, is all that I desire to claim as my own invention.

In conformance with the general principles of my process, as above stated, a limited number of substances may be used for effecting the graphitization of carbon and carbon articles,—such substances as, for exam-

ple, sodium carbonate and its equivalents, which equivalents should be, of course, true equivalents for the purpose of accomplishing the same functions in the process as set forth in the general statement given above.

In practicing the invention, the sodium carbonate should be preferably mixed in the carbons, though it is possible to obtain partial graphitization and effective results by packing the carbons in sodium carbonate. I will below describe a process of graphitizing carbon articles in which the sodium carbonate is in the mix.

The carbons themselves are ordinarily petroleum coke carbons containing only such impurities as accompany the raw materials and as are accumulated during the course of manufacture. The total percentage of ash in the carbons, baked preliminarily, amounts to 1 to 2 per cent. and sometimes less. These carbons are packed in an electric furnace of suitable type having resisters of proper form and construction, it being understood that they have been previously baked, by preference, as there are certain practical difficulties in baking them in the electric furnace, though this could be done if necessary. The carbons are packed in compartments between the resisters, and powdered charcoal is used as a packing material. The carbons are not allowed to touch the resistor walls for fear of short-circuiting the current across the compartments and therefore a layer of charcoal one-fourth of an inch thick is packed between the carbons and the resistor walls. When the compartments are filled a course of carborundum fire-sand brick is placed on the top and then a layer of refractory material 4 to 5 inches deep spread over the furnace. The furnace is then covered with movable arched fire-brick covers and the gas fire started. In this way the furnace is pre-heated by means of gas firing up to a temperature of about 900°. This heating lasts from four to five days. While the gas is still burning all the time to keep the outside hot, thus diminishing losses of the heat generated inside, the electric current is now turned on.

In figuring the total energy required for

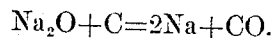
the furnace, it has been found suitable to suppose that double the amount of heat per square inch passes through the top of the resister as through the sides and bottom. 5 The losses through top and bottom thus derived are added to the energy distributed into the compartments. To this sum is further added the energy consumed in heating the resisters proper. Assuming the temperature rise in them to be 1000° C. (900–1900), 10 this total sum gives the energy needed for the electric bake, this bake lasting for about 18 hours. It will run with voltage varying from 75 at the start to about 45 at the end of the run. After the electric run, 15 the gas fire is left burning for about six hours in order to maintain the high internal temperature and promote the process. From conditions obtaining I compute the average 20 temperature in the compartments not to be above 1700° C. and probably to lie between 1600° to 1700°. The extent of graphitization will depend upon the length of time the furnace is allowed to run and the temperature. The above is an example of a 25 process used to accomplish partial graphitization. By thus incorporating the sodium carbonate in the carbons and using a sufficiently refractory packing material it is possible to 30 reach a higher temperature in order to graphitize completely if this should be thought preferable. In this latter case the energy consumption will probably be higher than the figures given. These figures therefore 35 should be looked upon only as applying to a special case.

It will be immediately noted, of course, that the utilization of sodium carbonate to effect graphitization is radically different 40 from the present known methods of graphitizing, the principal one of which is based upon the selection of such elemental substances as, in their elemental state or in compounds, are capable of reacting or combining 45 with carbon to form a compound therewith at the temperature of the electric furnace, in which the process is carried out, which compound is decomposed, the carbon being thrown out in graphitic form. This 50 prior process and the fundamental facts known about the same may be summed up in their broadest statement in the language just given and the materials used in this process are selected along these lines, such materials 55 being used, for example, as silica or iron oxid, the bases of which compounds, the silicon and iron, are capable of combining with the carbon to form a compound (commonly called a carbid) which is decomposed 60 upon continued heating and sufficient rise in temperature so that the carbon is thrown out in a graphitic form and the silicon or iron released for further reaction. A process limited in the selection of its material by the

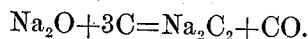
principle which I have just outlined as governing the prior process, would obviously exclude sodium carbonate from consideration, since all of the facts previously known to those practicing methods of graphitization, are inconsistent with its employment in the 70 manner in which silica or iron oxid or their equivalents are employed in such process.

Sodium is a substance which is not capable of reacting or combining with carbon to form a compound therewith at 1000° C. 75 which is below the ordinary working temperature of the electric furnace, as a carbid of sodium cannot exist at the temperatures of the electric furnace, a fact well known to such authorities as Moissan, Acheson and 80 Fitzgerald.

When sodium carbonate is heated under such conditions as obtain in this process, it is decomposed, forming sodium oxid, Na₂O, the carbon dioxid passing off into the surrounding atmosphere; and the reaction of 85 the resultant sodium oxid and carbon proceeds as follows:

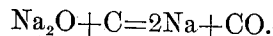


That is the carbon reduces the sodium oxid, forming metallic sodium and carbon monoxid. If it were possible at a low temperature for the sodium to combine with the carbon to form a compound, the reaction would 95 take place as follows:



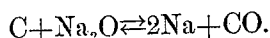
This reaction, however, resulting in the carbid of sodium, obviously could not take 100 place at the temperature of an electric furnace, as sodium carbid could not form at the temperature of 1000° C. which is passed under working conditions. In order, therefore, that those skilled in the art may understand 105 the action of sodium carbonate in this connection to properly use the same and to properly select chemical equivalents for carrying out the process, I will set forth the laws governing the process and the selection 110 of materials therefor.

When carbon and sodium oxid are heated together to a sufficient temperature, the following reaction will take place, as stated 115 above.



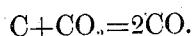
That is, the carbon reduces the sodium oxid forming the metallic sodium and carbon monoxid. As the temperature in the furnace 120 is above the boiling point of sodium, it can only exist here in the gaseous state. Both products of the reaction are consequently gases. On the other side, the sodium oxid on the left hand has quite an appreciable 125 vapor pressure at the temperature in question. The vapor pressure of carbon is also of importance. The reaction discussed,

therefore, is not complete, but represents an equilibrium between gases, thus



5 A certain equilibrium will establish itself for each temperature, in such way that with rising temperature more sodium is formed *i. e.*, the reaction proceeds from left to right until reaching a new equilibrium. If the
10 temperature is lowered, however, the opposite takes place and sodium reduces carbon monoxid, depositing carbon and forming sodium oxid. In the electric furnace these reactions take place. The sodium oxid is in
15 contact with the carbon, as stated, and therefore a reduction of the sodium oxid into sodium vapors and carbon monoxid to an extent, determined by the temperature prevailing, will occur. The gases, thus formed,
20 will diffuse into the adjoining parts of the carbon articles of a somewhat lower temperature. As stated the reverse reaction then takes place, carbon being deposited and sodium oxid reformed. As the temperature
25 then further rises, in the furnace, this sodium oxid will again be reduced and thus gradually be transported toward the interior of the baking compartment.

It is generally known that graphite, at
30 least at temperatures above a few hundred degrees (C), is the most stable modification of carbon. The relative properties of the different modifications of carbon, amorphous carbons, diamond and graphite have
35 been studied very thoroughly by means of the reaction



According to this, carbon reduces carbon
40 dioxid, forming carbon monoxid. This reaction is favored by high temperature, being nearly complete at 1000° C. On the other hand carbon monoxid decomposes into free carbon and carbon dioxid. At about 400°
45 this opposite reaction is almost complete. In the intermediate temperature range the equilibrium changes gradually with rising temperature in favor of the carbon monoxid, a certain equilibrium between the gases
50 corresponding to each temperature. But this equilibrium is different according to the modification of carbon in contact with the gas mixture. This circumstance has made it possible to compute the relative vapor
55 pressures of the different modifications of carbon and their variation with the temperature. In this way it was found that graphite has the lowest vapor pressure and amorphous carbon the highest. Thus the
60 vapor pressure of amorphous carbon is 3.7 times higher than that of graphite at 500° C., but 5.4 times higher at 641° C. From the rate of this change it may be concluded that at the temperatures around 1500° the

amorphous carbon has a vapor pressure 65 many times larger than that of graphite. This fact will be referred to later.

Another result of these investigations was that carbon monoxid, when decomposing to a certain extent into carbon dioxid and free
70 carbon, when no kind of carbon was present at the start, assumed the equilibrium corresponding to the segregation of graphite carbon. This occurrence is only a natural consequence of the fact that graphite has the
75 lowest vapor pressure or, in other words, is more stable. This phenomenon has a direct bearing upon the process in my furnace.

From the above reasons, as advanced for the reaction last described, it is obvious that
80 the carbon deposited from the reduction of carbon monoxid by sodium in my furnace, must be graphitic carbon. It could be feared that when the sodium oxid is again reduced on account of the rising temperature the graphite carbon, just deposited with
85 it, would be consumed in the reduction. There is, however, no danger of this loss, since the amorphous carbon present has so much higher vapor pressure and consequent
90 reducing activity. Further, as mentioned in connection with the discussion of the equilibrium between carbon and carbon dioxid on one side and carbon monoxid on the other, the equilibrium is different according
95 to the modification of carbon present. The same will be the case with the equilibrium between carbon and sodium oxid on one side and sodium and carbon monoxid on the other side, assumed in my furnace. The
100 amorphous carbon demands one equilibrium, the graphite formed, another, on account of the difference in their vapor pressures. The equilibrium, established in the system with amorphous carbon, therefore, cannot exist
105 in a stable condition in the presence of graphite, just as water, cooled below the freezing point, cannot exist in the presence of ice. Carbon will consequently be deposited as graphite from the amorphous carbon
110 system. This one will then continuously reestablish itself as long as there is any amorphous carbon left. Thus a transfer of the carbon baked, into graphite will gradually take place at sufficiently high
115 though constant temperature.

The specific process of graphitizing, outlined above as involving the use of sodium carbonate is obviously based upon the reduction of sodium oxid by carbon into the
120 metal sodium as vapor and carbon monoxid and consequent reduction by the metal vapors of the carbon monoxid, depositing graphitic carbon. An essential condition for the success of this process is that the
125 metal in question does not form a carbid with the carbon present in excess, when liberated, thus preventing the possibility of

the cycle described. It is known that sodium does not form a carbid at the temperatures employed, and to this fact is due the graphitizing in my furnace as set forth.

5 Having described my invention, I claim:

1. The process which consists in subjecting to heat carbon and sodium carbonate in an electric furnace above the temperature at which sodium carbid can be formed.
- 10 2. The process which consists in subjecting to heat carbon articles packed in a packing containing sodium carbonate, at a temperature above that at which sodium carbid can be formed.
- 15 3. The process which consists in subjecting to heat carbon and a substance capable of decomposition or reduction to sodium oxid in an electric furnace above the temperature at which sodium carbid can be formed.
- 20 4. The process which consists in subjecting to heat carbon and a compound, with a part of the constituent elements of which compound said carbon will combine to form
- 25 a gas and liberate another part of the constituent elements in gaseous form, the carbon-containing gas being reduced to deposit graphite upon disturbing the equilibrium between the gases formed.
- 30 5. The process which consists in subjecting to heat carbon and a compound, with a part of the constituent elements of which

compound said carbon will combine to form a gas and liberate another part of the constituent elements in gaseous form, the carbon-containing gas being reduced to deposit 35 graphite in the presence of graphite, when the temperature is lowered below that at which the first mentioned reaction takes place.

40 6. The process which consists in subjecting to heat carbon and a compound, with a portion of the constituent elements of which compound the carbon will combine to form a gas, capable of being reduced by the remaining portion of said compound in the 45 presence of graphite upon disturbing the equilibrium of the vapors by a reduction of temperature.

50 7. The process which consists in subjecting to heat carbon and a compound, a part of the constituent elements of which compound will combine with carbon to form a gas, the remainder of the constituent elements of which compound will not combine 55 with carbon, reducing said carbon containing gas to deposit graphite by disturbing the equilibrium of the system.

In testimony whereof, I hereunto affix my signature in the presence of two witnesses. 60

CARL FREDRIK JAKOB FORSELL.

Witnesses:

E. B. GILCHRIST,
J. M. WOODWARD.