June 19, 1923. 1,458,964

A. H. BAILLE-BARRELLE

PROCESS OF MANUFACTURE OF COKE FOR METALLURGICAL USES

Filed May 28, 1921 2 Sheets-Sheet 1

Fig. 1

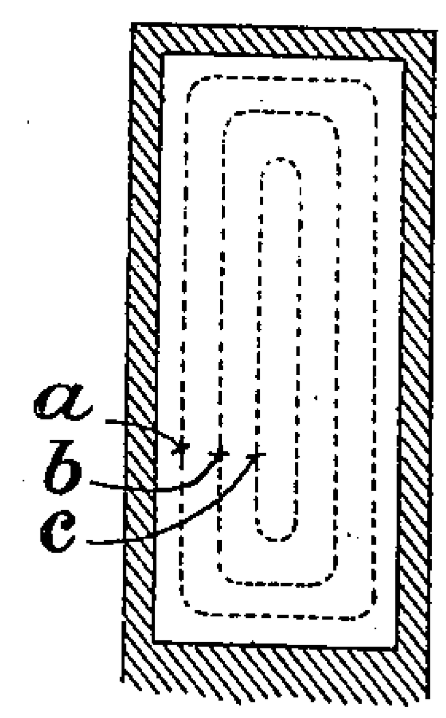

Fig. 2

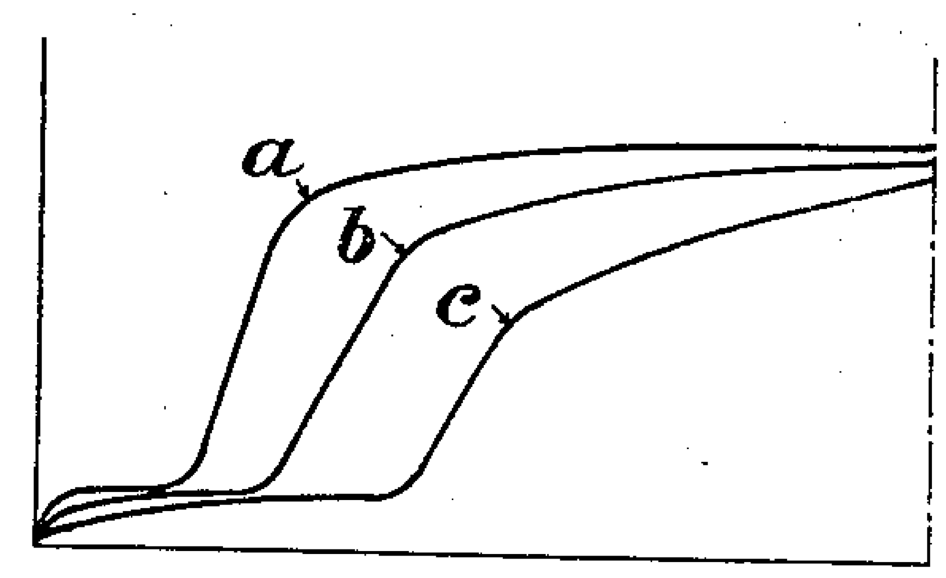

Fig. 3

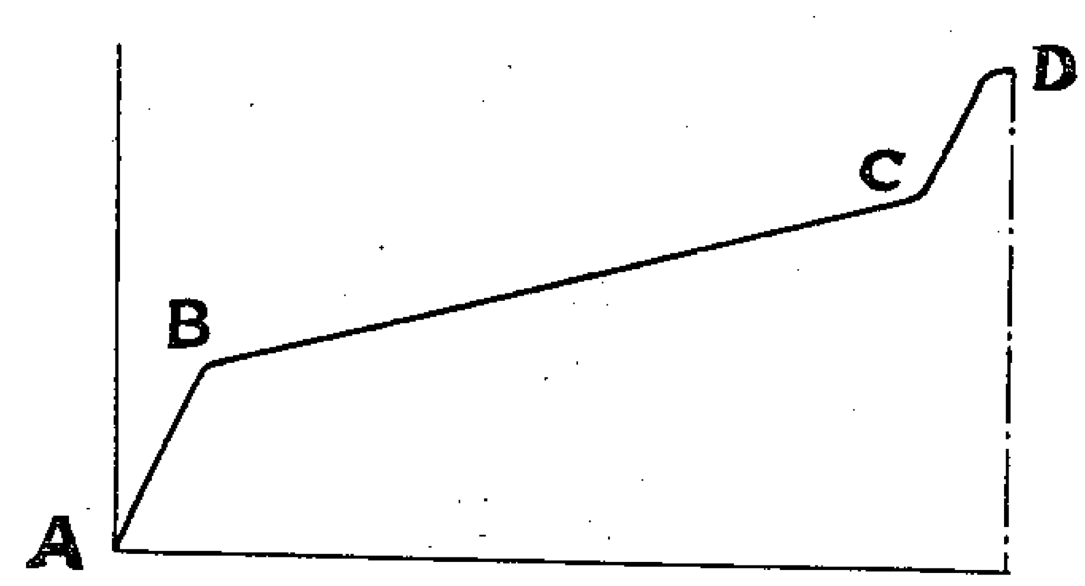

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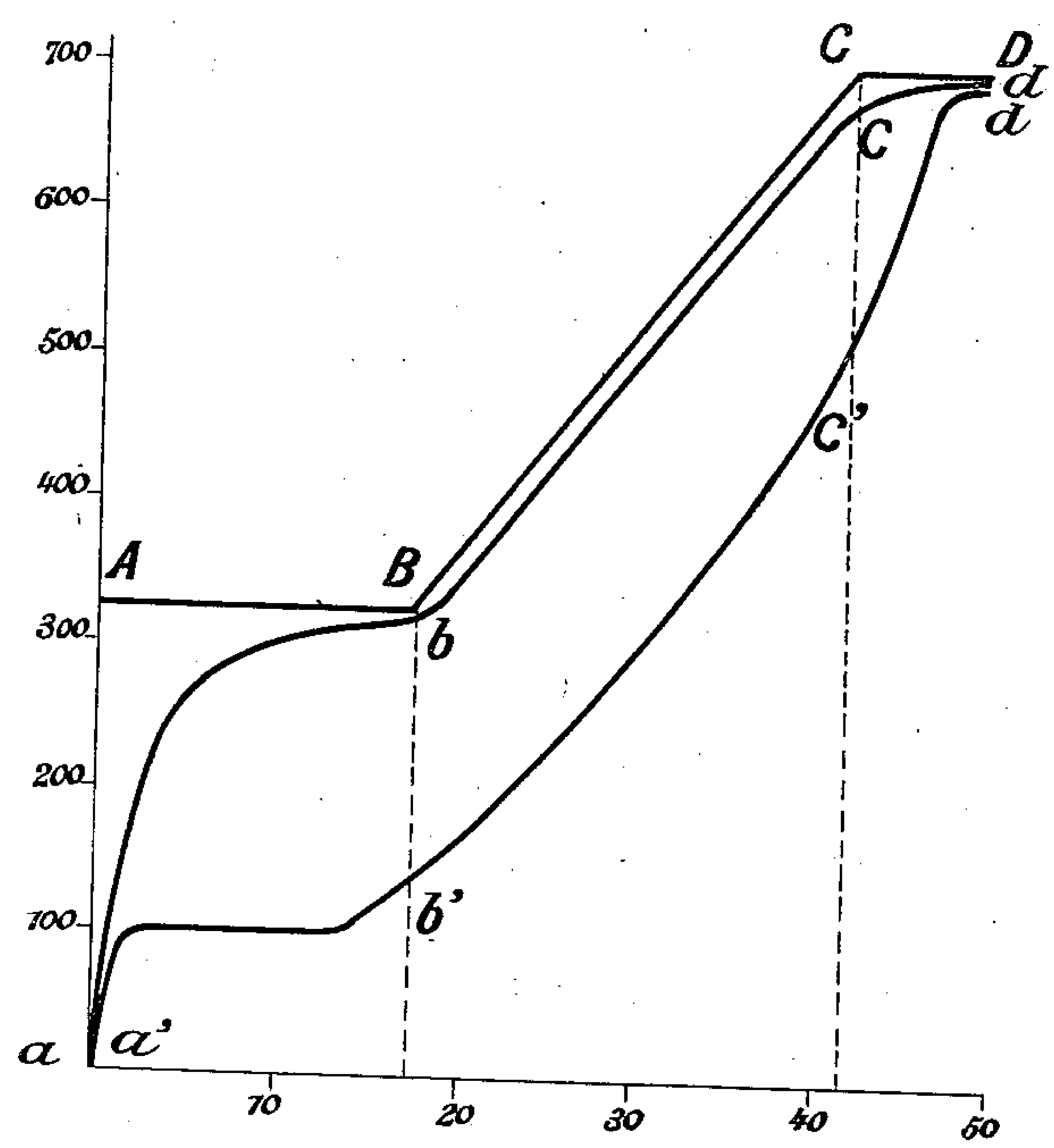
Fig. 4



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UNITED STATES PATENT OFFICE.

ANDRÉ HENRI BAILLE-BARRELLE, OF PARIS, FRANCE.

PROCESS OF MANUFACTURE OF COKE FOR METALLURGICAL USES.

Application filed May 28, 1921. Serial No. 473,341.

To all whom it may concern:

Be it known that I, André Henri Baille-Barrelle, a citizen of the Republic of France, and residing at Paris, Seine Department, No. 126 Rue de Provence, in the Republic of France, have invented certain new and useful Improvements in Processes of Manufacture of Coke for Metallurgical Uses, of which the following is a specification.

This invention relates to a process of manufacture of coke for metallurgical uses.

In the known coking process, when the coal is fed into a coke oven which is brought to a high temperature, this will effect the immediate distillation of the coal coming in contact with the oven walls, whereupon vapors of a tarry nature are produced which condense within the mass of coal which has not had sufficient time to become heated. In this manner there is constituted at a short distance from each wall of the coke oven a region termed screen region, which is very rich in tar and is entirely impervious to gases and to heat. The said region which becomes completely destroyed at the outer side which is submitted to the action of the heat, is formed anew at the inner side thereof, and thus moves gradually towards the center of the furnace, leaving between this region and the oven wall a certain amount of perfectly formed coke, while the coal situated between the said screen region and the center of the furnace has not as yet undergone any appreciable decomposition.

The thickness of the said coking region is very small, this being at most 2 or 3 centimeters. By measuring the temperatures at any desired point within the mass of coal in a coke oven which is heated in the known manner, it will be observed that the temperature will reach 100° C. rather rapidly, then remains stationary and will thereafter rise very slowly until the point under consideration is attained by the said coking region. In this case the temperature rises rapidly, or in 4 to 5 hours, from 200° or 300° to 800° or 900° C. and then increases very slowly up to the final temperature of the operation. It will therefore be noted that the coal is coked in successive layers in which the variations of heat are very rapid.

When applied to coal whose decomposition is attended by phenomena of considerable changes in volume, a process of this kind will afford only a coke of inferior quality, for at each instant the coal in decomposition which is enclosed between the shell of already-formed coke and the inner mass of non-decomposed coal, is prevented from undergoing free expansion and contraction, thereby giving rise to considerable local tensions and resulting in a product of a cracked and fragile nature analogous to a badly annealed glass. In the special case of coal which becomes reduced in volume in the coking process, the first layer of coke surrounding a core which may be put out of shape will become broken in pieces, and subsequently such pieces will serve as a support for the successive films of coke in formation. At the end of the operation the process will yield long needle-like masses disposed perpendicular to the oven walls, these being more or less intermingled but not adhering to each other. Coke of this character, which is very fragile, is known as coke formed in needle-like crystals, and is unsuitable for use in large blast furnaces.

The said phenomenon of the screen region is produced not only upon feeding coal into a coke oven which is sufficiently heated to effect a sudden distillation of the outer layers, but it likewise occurs under all circumstances in which in the case of a mass of coal submitted to the action of heat—in the interval of temperature wherein condensable volatile products are given off—there exists a sufficient difference of temperature between two portions of the mass whereby one portion is enabled to serve as a condensation region for the vapors given off by the other. The phenomenon when once started will increase very rapidly in extent, for when the said screen is once formed, the lack of equilibrium of temperature which gave rise thereto must necessarily go on increasing.

The process according to this invention consists in so regulating the heating of the coke oven as to obtain certain determined temperatures in the said oven at stated moments, such as will prevent the formation of the screen region. By reason of the said process, the different regions of the mass of coal will be subjected to simultaneous expansion and contraction, even though these may not have exactly the same temperature, thereby obtaining a coke which is free from cracks and is not of a fragile nature.

Fig. 1 is a horizontal sectional view through a coal mass, the dotted and indicated lines representing the standard curve of variations of temperature,

Figs. 2 to 4 inclusive are diagrams indicative of the temperature curves of the furnace, the surface and the center of the coal mass.

The said process will be more particularly described hereunder as applicable to the coking of coal of the variety termed "Fettkohl", that is, having the character of the coal obtained from the lower region of Sarrebruck.

By gradually heating such Fettkohl out of contact with air, the following phenomena are observed:

1. Between ordinary temperature and 330° C. the coal loses water as well as very small quantities of non-combustible gases (occluded air, CO^2) and remains practically unchanged. Its percentage of volatile substances and its agglutinating power are only reduced by a small amount, but this on condition that the coal shall be heated in an entirely neutral atmosphere, inasmuch as the smallest admission of air, at temperatures above 100°, would give rise to a rapid oxidation which in the case of certain varieties of coal may proceed as far as a complete combustion. This represents the phase of heating under neutral conditions.

2. The decomposition of the coal appears to commence about 330° C. at which temperature the beginning of the disengagement of gas and the appearance of tar vapors are observed at the same time. This decomposition takes place without any change in the physical state, and all that might happen in certain cases would be that the coal would lose all cohesion and would fall in powder, but this effect is marked by a considerable diminution of the agglutinating power. This represents the phase of the first decomposition or the transition phase, and it ends at about 400° C.

3. Between 400° and 420° C., the action whereby volatile substances are given off (gases and tars), is now observed to increase at a rapid rate. The coal changes its physical state, being transformed for a certain time into the pasty state, whereupon it becomes agglomerated and is subsequently solidified. This represents the phase of agglomeration, or the coking phase.

4. From 420° to the final temperature of the operation, the product obtained from the solidification of the coal paste is transformed into coke suitable for metallurgical purposes. This transformation is effected without any other change in physical state, or even, any change in structure, inasmuch as the substance which is obtained at the end of the third phase loses only its volatile substances while contracting and increasing in hardness. This represents the phase of contraction.

As concerns the heating phase, it is advantageous to reduce this phase as much as possible in order to lessen the effects of oxidation. It is advisable to make use of coke ovens which are made gas-tight as far as possible and to maintain the same at a slight excess of pressure therein. It is likewise advantageous to reduce the duration of the phase of the first decomposition. In fact, the Fettkohl begins to decompose at about 330° C. and even though the first decomposition is not made manifest on the outside save by a slight amount of volatile substances given off, it nevertheless modifies the essential properties of this coal, and in particular its aptitude for melting and its agglutinating power may entirely disappear. In order to prevent this agglutinating power from descending below the minimum limit necessary for obtaining a suitably agglomerated coke, it is required to pass through the interval of temperature from 330° to 440° within a time not exceeding H hours, H representing a number which is to be determined experimentably for each variety of coal. The duration of this phase of agglomeration or coke formation, which is the most essential, should be situated between two limiting points. Examination of the phenomena taking place during this period leads to the following conclusion: The rate of heating during the phase of agglomeration should lie between the two extreme values V and V′, V being a minimum rate compatible with a suitable agglomeration, and V′ a maximum rate compatible with obtaining a homogeneous mass of coke without spongy formation.

Above 420° C. the coke contracts and hardens. As already stated, this contraction and what is termed the screen region phenomenon, are the cause of the great degree of cracking and the defective quality of the Fettkohl cokes which were formerly produced. This great drawback may be obviated by effecting a sufficiently gradual heating during the contraction phase whereby all points of the coke mass will have at all times substantially the same temperature, for in this case the contraction will take place throughout the entire mass at the same time and without giving rise to local tensions which are the primary cause of cracking. But by reason of the slowness of the exchanges of temperature throughout the mass of coal, it is found preferable to adopt extremely low rates of heating. In practice it is not essential that the coke for metallurgical uses shall be entirely free from cracks, and it will suffice to suitably reduce the amount of cracking of the Fettkohl coke in order to enable its use for metallurgical purposes.

In practice, it is found sufficient to obtain the following conditions:

1. At the time when the outer shell begins to contract, it is required to allow a sufficient thickness of plastic pasty mass between this shell and the main body of the coal which is not as yet melted and cannot lose its shape, whereby the said shell is enabled to contract without bursting, that is, it should possess from the beginning of the contraction phase a regular temperature curve whose rate is below g° per centimeter between the inner and outer part of the said space.

2. The phase of contraction occurs in such manner that at each instant the masses having the same rate of heating shall be provided in sufficient amount in order that the internal tension effects arising from unequal contraction shall produce cracks of large size which are widely spaced apart, on the contrary to a network of small crackling such as is formed by the contraction of thin layers successively submitted to the coking action, in the case in which a screen region is formed.

The practical rules to be observed may be finally stated as follows:

1. The phase of contraction is not to be commenced, that is, the temperature of the outer shell of the coke mass is not to be brought to more than 420°, before the interior has exceeded (420—N)°, N being equal to g 1/2 L. (In which L represents the width of the coke oven measured in centimeters).

2. The phase of contraction is to be passed through at a rate of speed such that the difference of temperature from exterior to interior shall in all cases remain equal to N°, for should this difference tend to increase from the start, experience shows that it will then continue to increase until the interior reaches 500°–550°, and after this time it suddenly commences to decrease, whereby the temperature at the central part will very soon become almost the same as at the outer part. The rate of heating at the central part is considerably higher than that of the outer shell, and consequently the interior of the coke mass will become very much cracked. But if the initial difference N has a tendency to decrease from the start, the temperature at the center will very gradually become equal to that of the exterior, thereby producing a grade of coke which is but very slightly cracked.

To recapitulate, the conditions required to obtain a good quality of coke for metallurgical use from Fettkohl, may be stated as follows:

1. Oxidation of the coal is to be avoided during the neutral phase.

2. The transition phase is to be passed through in less than H hours.

3. The agglomeration phase is to be passed through at a rate of speed comprised between the rates V and V′.

4. From the start of the contraction phase, a temperature curve is to be employed whose rate is below g° per centimeter, between the exterior and the center of the coke mass.

5. The phase of contraction is to be passed through at a rate of speed v such that the difference of temperature between the center and the exterior shall have no tendency to increase.

According to tests which have been hitherto carried out with relatively small masses, the following approximate values have been found for the coefficients H, V, V′, g and v:

H=8 hours.

V=15° per hour (for packed coal).

V′=80°–100° per hour.

g=15° per centimeter.

v is to be made lower as the mass of coke becomes thicker; for a rectangular section having about 25 centimeters on the short side, V=15° per hour.

The rules to be followed for the coking of Fettkohl may be more simply stated when the operation is carried out upon considerable masses as in the actual industry:

The operation consists in bringing as rapidly as possible the entire mass which is simultaneously submitted to the coking action to a temperature not under (420°—N)°, wherein no point shall be allowed to exceed 420°; then the temperature of the mass is to be gradually raised to 700° in such manner that at no time during this second period of operation shall the maximum temperature difference between two points of the mass go beyond N°.

Under these conditions a suitable coke without cracks will be obtained. This coke will be furthermore in a better state of agglomeration if the following is carried out:

1. No point of the said mass shall have passed through the phase of agglomeration at a speed below v.

2. No point thereof shall have remained more than H hours between 330° and 400°.

3. The coal shall not have been oxidized.

To conform to these rules, it appears advantageous to carry out the operation as follows: The small coal or slack of the Fettkohl variety is disposed and very strongly pounded down in coke ovens having a width of 25 centimeters wherein the temperature is maintained at 320° until the interior of the coke mass shall have attained 700°. During a series of tests upon coal containing 15% water, which was pounded down in a sheet metal receptacle of 24 centimeters width, it was found that the optimum duration of treatment at constant temperature is 18 hours at 320° and 6 hours at 700° C. The standard curve of variations of temperature in the said space with reference to the time is thus determined in a very complete manner, and the same is represented in the accompanying drawings together with the curves for the heating effects which were actually observed for the exterior and the center of the coke mass. A, B, C, D indicates the temperature curve of the furnace, and *a*, *b*, *c*, *d* and *a'*, *b'*, *c'*, *d'* the temperature curves for the surface and the center of the coke mass respectively.

This optimum curve may be modified to a certain extent. It is evident that the isothermic line for 320° may be replaced by any suitable curve situated thereunder on the sole condition that the second part of the curve shall not be attained before the interior of the coke mass shall have reached 150°. Experiments have also shown that N may vary between 130° and 240°, and that the rate of heating at the center of the mass is subject to variations between 14° and 20° per hour. It is likewise possible to replace the inclined straight line by a series of steps which are spaced apart by about 100°.

The heating could be carried out in various types of coke ovens such for instance as impelling ovens, tunnel ovens, Hoffmann ovens and in general all types of coke ovens wherein the temperature may be varied within a considerable range.

Claims—

1. A process of manufacture of coke for metallurgical uses, consisting in the operation of raising the coke as rapidly as possible to the temperature after which it commences to agglomerate, and then in heating the same gradually and with a suitable degree of slowness whereby there shall not exist at any moment such differences of temperature between any two points in the mass of coal as would be susceptible of giving rise to the phenomenon of the screen region, and lastly, when the coal has become agglomerated throughout the entire mass thereof, in heating the same rapidly to the final temperature which is required for giving off substantially the whole amount of the volatile substances.

2. A process of manufacture of coke for metallurgical uses, consisting in the operation of rapidly heating the coal to the temperature of 400° C. whereupon it commences to decompose, in raising the temperature of the coal from 400° to 420° C. in 8 hours or less, in maintaining the degree of heating in such manner that the rate of heating of the coal during the phase of agglomeration shall be at least equal to 15° C. per hour, the temperature of the outer shell of the coal mass not being raised above 420° until the center of the mass has attained 420°—N°, N being approximately equal to the product of 15° C. by one-half the thickness of the mass measured in centimeters, and in effecting the final heating in such manner that the temperature difference between the surface and the center of the mass shall not exceed N°.

3. A process for the manufacture of coke for metallurgical uses, consisting in the operation of heating a mass of coal of approximately 25 centimeters thickness and well pounded down, in such manner that the temperature of the coke oven shall be maintained at approximately 320° C. until the center of the mass shall have attained approximately 150° C., and then gradually raised by 15° C. per hour up to approximately 700° C., remaining at that temperature until the interior of the coke mass shall have attained 700° C.

4. In a process of manufacture of metallurgical coke, the operation whereby the heating is so effected that at the instant when the surface of the coal is at the temperature of agglomeration T°, the center of the mass shall be at the temperature T—N, N being approximately equal to the product of 15° C. by one-half the thickness of the mass measured in centimeters, and that subsequently the temperature difference between the surface and the center of the mass shall not exceed N°.

In testimony, that I claim the foregoing as my invention I have signed my name in presence of a subscribing witness.

ANDRÉ HENRI BAILLE-BARRELLE.

Witness:
MAURICE ROUX.