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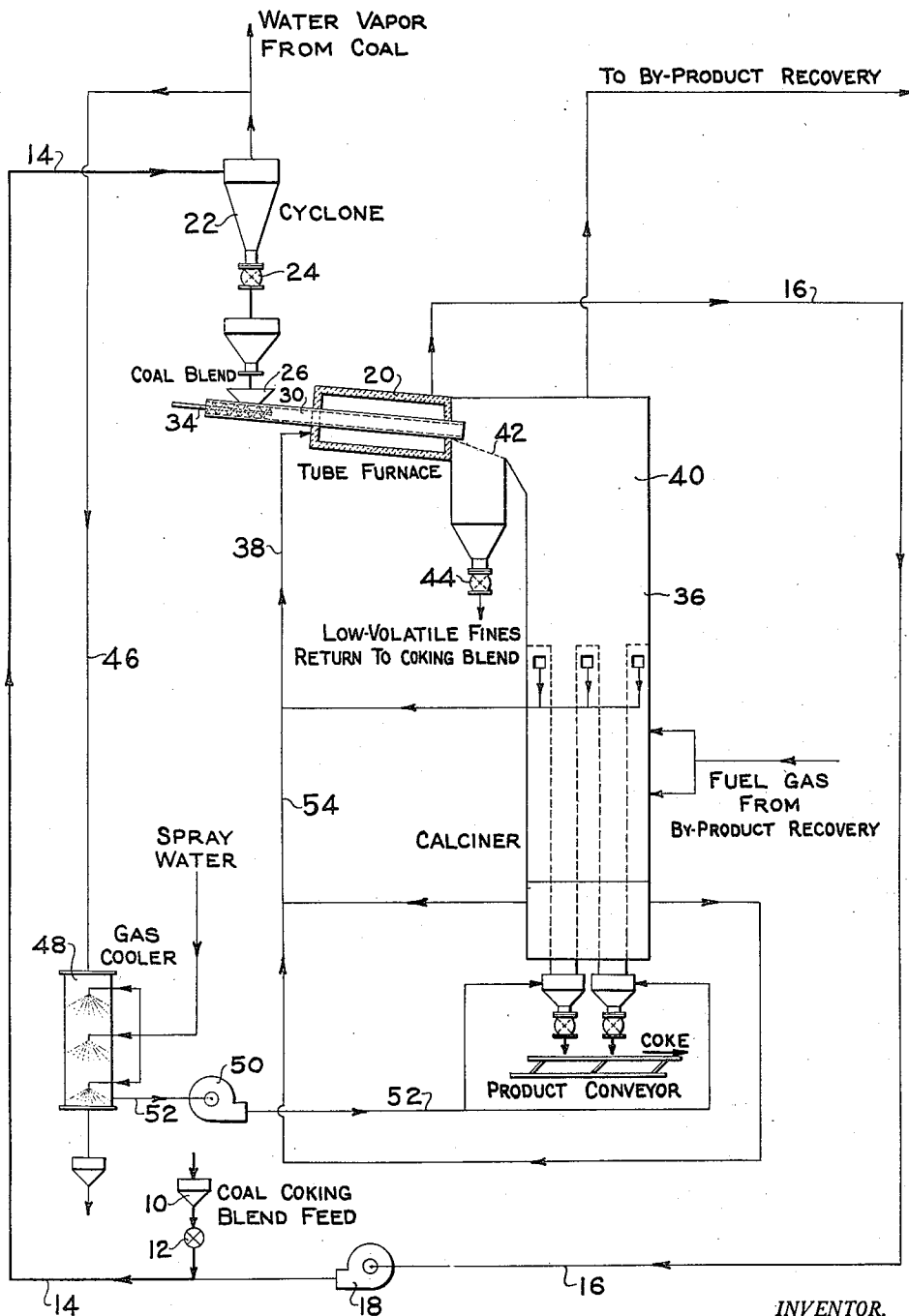
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2,922,752

CONTINUOUS CARBONIZATION PROCESS AND APPARATUS

Filed March 7, 1957

3 Sheets-Sheet 1



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FIG. 1.

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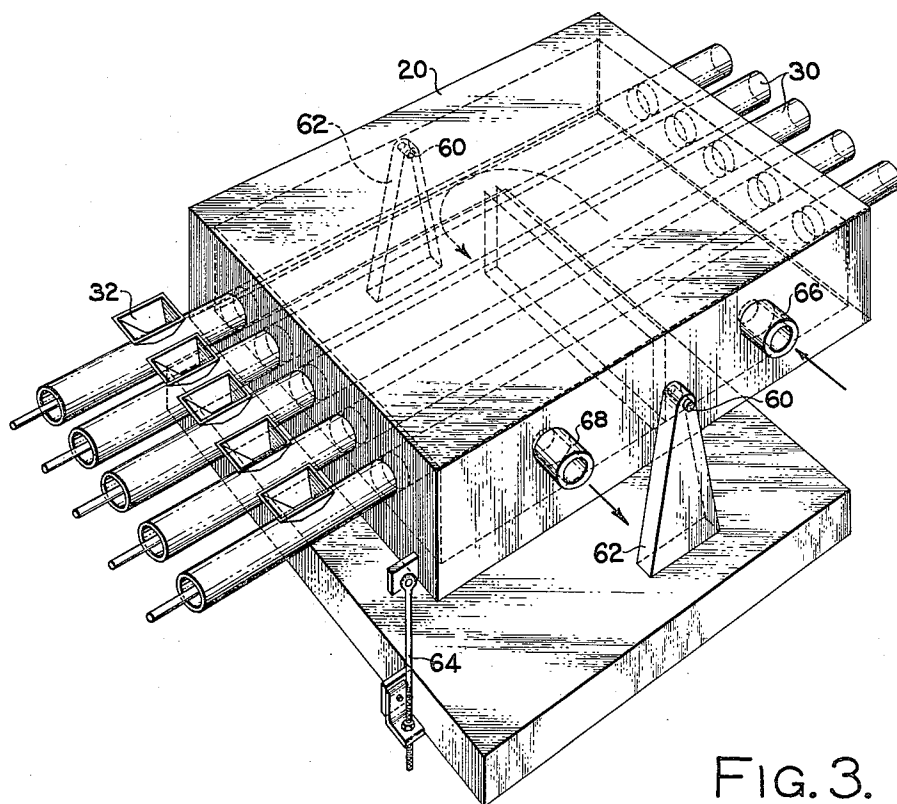


FIG. 3.

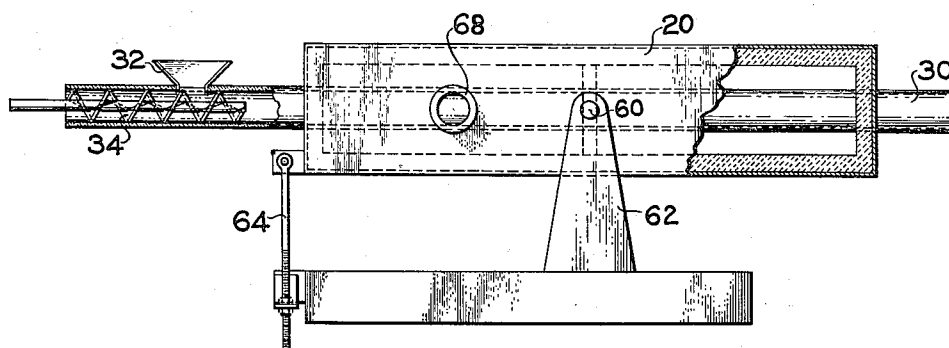


FIG. 4.

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CONTINUOUS CARBONIZATION PROCESS AND APPARATUS

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Application March 7, 1957, Serial No. 644,602

8 Claims. (Cl. 202—22)

This invention relates to a novel process for the production of solid carbon and includes within its scope a novel carbon product obtainable therefrom. More particularly, it relates to the production of solid carbons especially useful in the metallurgical industries for the reduction of ores and for metal winning and refining. Depending upon the raw material fed to the process, carbon suitable for incorporation in electrode forming masses or in many types of metallurgical furnace charges, can be produced thereby. The novel process of this invention is further distinguished by being continuous in operation, which is unique in this art.

Solid carbon is extensively used in many industrial processes. Most commonly it is obtained in the form of coke from the distillation of coal and residual petroleum oils and tars. When such materials are heated at sufficiently high temperatures and for sufficient periods of time in the absence of oxygen, the volatile hydrocarbons and other elements and compounds are driven off to leave behind essentially elemental carbon in the form of hard, cellular lumps. These lumps may be introduced as is into a charge of ore, for example, or ground, mixed with a binder and molded to a desired shape, e.g. electrode shape. Because of the different characteristics of the various different cokes, e.g. petroleum as contrasted with coal cokes and cokes produced in slot ovens as contrasted with shaft furnaces, each type of coke has its typical use.

In the production of coke from petroleum oils the oil must first be converted by suitable distillation from the liquid to the solid state and thereafter calcined to eliminate the remaining volatilizable matter associated with the solid. This conversion may be accomplished by delayed coking or by shallow bed coking in a sole heated oven. In either case, a second stage of heat treatment is required after the solid coke first evolves to remove the volatiles. Such treatment is presently carried out in a rotary calciner or shaft furnace.

To convert coal to coke the coal must be heat treated likewise to eliminate the volatilizable matter. This is customarily carried out in slot or sole fired ovens or shaft furnaces heated indirectly. If the coal is of the expanding type, it cannot satisfactorily be coked in a slot oven or shaft furnace but only in the sole fired oven.

Since the process of this invention is concerned only with raw material already in the solid state, i.e. green petroleum coke and coal, the initial step of converting the oil to coke is not material to this specification. These carbonaceous solids are readily procurable.

It will be evident that basically both green petroleum coke and raw coal are treated alike when undergoing conversion to elemental carbon or metallurgical coke. In other words, both are heated at elevated temperatures in the absence of oxygen until substantially all volatile matter is eliminated and hard, essentially elemental carbon is left behind as the desired product. However their

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end uses are somewhat different depending upon their physical and chemical properties. Coal coke produced by ordinary coking procedures is principally used for the reduction of metal bearing ores and in other metallurgical applications, while petroleum and purified coal cokes go almost entirely into electrodes.

It is also evident that heretofore there has been no truly universal process for the production of high quality carbon from both coal and green petroleum coke and which also is adapted to the production of such carbon in physical form best fitted for its intended use. It is the principal object of my invention to provide such a process.

It is a further object of this invention to provide a process in which can be utilized heretofore relatively unusable petroleum coke fines, fluid coke and the like as carbonaceous raw material.

It is another object of this invention to provide such a process which is continuous and is simpler, less expensive, more efficient and productive of better results than conventional processes.

It is a further object of this invention to provide such a process by which it is possible to produce both metallurgical coke and coke suitable for electrode use.

It is another object of this invention to provide a novel carbon product.

In U.S. Patent No. 2,764,539, Horvitz, there is described a new electrode forming mass which contains carbon briquets of great hardness and high purity. To the extent that the process of my invention may produce a carbon of comparable hardness and purity even better adapted than briquets for incorporation in electrodes, this invention may be said to be an improvement over that of the said Horvitz patent. Reference is likewise made to the extensive discussion in said Horvitz patent of the art of manufacturing carbon electrodes, much of which is applicable to the carbon product of this invention as will hereinafter be elaborated on.

The process of this invention comprises forcing the solid green carbon, i.e. either green petroleum coke or raw coal, with or without a fluid binder depending upon the thermo plastic nature of the carbon, under a slight to moderate pressure through a smooth walled, externally heated metal tube from which oxygen is substantially excluded. The green carbon is continuously supplied to one end of the tube and withdrawn in the state of more advanced carbonization from the opposite end thereof, the extent of treatment accomplished being dependent upon the length of the tube, temperature therein and the speed of transit of the carbon. The pressure applied need be only just sufficient to overcome the friction between tube wall and carbon plus the gravitational weight of the carbon column if the tube is oriented other than horizontal and flow of carbon is upward. It appears that a positive pressure of about 1–20 lbs. per sq. in. is adequate for the purpose no matter what the attitude of the tube, and the pressure should be substantially uniform throughout the entire coking mass.

The treated coke is continuously extruded from the tube as a substantially solid cylinder which is not, however, monolithic owing to the shrinkage cracks and fissures caused by escaping vapors evolved by the heat treatment. Consequently, the cylinder of coke as it flows from and overhangs the discharge end of the tube will break off into lumps which may be further reduced in size by mechanical means if desired.

The temperature at which the treatment is carried out will be at least 800° F. and preferably considerably higher, that is, in excess of 1100° F. It may be advantageous to provide zones of different temperature

along the length of the tube since it is usually desirable to increase temperature as the conversion of carbonaceous raw material to coke progresses.

Although a finished product may be obtained from the steps of the process thus far described, it is advantageous to effect further calcination at temperatures somewhat higher than are good for the metal tube. In such case the coke is conducted directly from the tube to a refractory shaft furnace indirectly heated to internal temperatures in the neighborhood of 2000° F. or slightly higher.

Whether or not the green carbon is mixed with a binder before treatment in the tube will depend entirely upon the type of carbon fed. Thus, green petroleum coke will always be mixed with a carbonaceous binder, ordinarily pitch, while raw coal will be so mixed only if it is of the so-called non-coking type, i.e. coal which does not become plastic during carbonization. Since the coking coals, on the other hand, become plastic on heating a supplemental binder is not required.

The process of this invention is particularly useful for producing superior cokes for electrode forming masses. Because of the fragmentary, irregular shape of the coke aggregates and the relatively higher density of the coke, it is noticeably superior to other cokes and to the briquets described in the above-mentioned Horvitz patent. Briquets have the additional disadvantage of being so smooth that they do not bond well, hence for best results in electrodes must be completely ground to irregular small size lumps. On the other hand, the product of this invention is already almost completely in suitable physical forms and only the very largest fraction, which is but a minor proportion of the total, need be reduced by grinding to effective size. In any event, the aggregates need not be reduced to as small a size as is customary for other cokes since the relatively higher density of the coke of this invention permits of the use of relatively larger aggregates. Accordingly, less binder is required and a shorter baking time is necessary to finish the electrode than is the case for heretofore known cokes, and production cost is concomitantly reduced. When compared to conventional petroleum coke heretofore used almost exclusively in electrodes, the product of this invention imparts to the electrode greater compressive strength and lower electrical resistivity.

As I have said, the invention is particularly suited to integration with a subsequent calcination step and the integrated process is included within the scope of this invention. Two embodiments of such process are illustrated in the accompanying drawings, in which:

Fig. 1 is a view, partly in section of a flow diagram of the process adapted to the treatment of coal to produce metallurgical coke, and

Fig. 2 is a similar view for the process adapted to the treatment of petroleum coke to produce electrode carbon.

Figs. 3 and 4 are sectional views of a suitable tube furnace including means for adjusting the slope of the unit for optimum operation with different raw materials.

As shown in Fig. 1 and Fig. 2, the raw material is charged to the system from feed hopper 10 through lock valve 12 into hot gas transport conduit 14 supplied with hot furnace exhaust gases through conduit 16 and fan 18. The raw material is thus preheated while being conveyed to tube furnace 20 in which the heat treatment is carried out, separation of the material from the gas being effected by means of cyclone 22 from which the material is locked out through valve 24 into treater feed hopper 26. The raw carbon is then fed from hopper 26 into furnace 20 directly as shown in Fig. 1 or indirectly through a mixer 28 as shown in Fig. 2. Mixer 28 is required when the raw carbon must first be mixed with a pitch binder prior to coking.

Furnace 20 in which the heat treatment is effected according to this invention consists of a heat insulated

chamber through which extend a plurality of metal tubes 30. Feed inlets 32 (Figs. 3 and 4) are provided adjacent the outer ends of tubes 30 and means, for example, screw feeders 34, are provided to force solid raw material through each tube under positive pressure as stated above. Alternative means for achieving satisfactory propulsion of raw material through the tube, such as a plunger, may be used.

The treating unit composed of furnace 20 and tubes 30 is preferably integrated with a secondary calciner 36 constructed with a plurality of vertically disposed, indirectly heated shafts. One suitable type of calciner is described in copending application, Ser. No. 455,532, filed September 13, 1954, of Hughes et al., now Patent No. 2,847,369, issued August 12, 1958. When such type of calciner is associated with the process the hot combustion product gases from the heating flues of the calciner may be conducted to furnace 20 through conduit 38 for the heating of tubes 30. Likewise, tubes 30 may be disposed to discharge directly into top area 40 of calciner 36 whence the treated carbon from the tubes will flow by gravity through the calciner for completion of the treatment. Advantageously, the carbon discharged from tubes 30 will be flowed over screen 42 to separate the fines and small size coke lumps therefrom which can be drawn off from the system through lock valve 44 and segregated as a separate product or recycled for blending with fresh raw material. When petroleum coke is treated in admixture with a binder there will be a minimum of fines and small lumps in the product from tubes 30 but what amount thereof is produced has utility in the production of electrodes, hence no screen is required and is omitted from the embodiment of Fig. 2.

While furnace 20 is advantageously integrated with the secondary calciner 36 it will be understood that it is not essential to the practice of this invention. Thus tubes 30 can be arranged to discharge into any suitable receptacle and furnace 20 may be heated by any suitable means, including burners firing directly into the furnace.

As previously described, hot exhaust gases from furnace 20 are cycled to the raw material supply through conduit 16 for the dual purpose of preheating the raw material and conveying it to the treating furnace. However, it is obvious that other means can be employed as well for delivering raw material to the furnace, and preheat, while highly advantageous, is not essential to the process.

The coke in retort 36 must, of course, be cooled before it can be discharged to the atmosphere. It is accordingly convenient to cycle the raw material conveying gas from cyclone separator 22 to the bottom of calciner 36. The solids-free hot gas is thus conducted through pipe 46, gas cooler 48, fan 50 and conduit 52 into the bottom of the calcining shafts. As the gas flows upwardly through the coke it extracts the heat therefrom and may then be flowed through conduit 54 to furnace heating gas line 38, or otherwise used.

In Figs. 3 and 4, furnace 20 is shown as being mounted on pivots 60 journaled in supports 62. The furnace thus may be tilted longitudinally to direct discharge from tubes 30 either upwardly or downwardly. An adjusting rod assembly 64 is provided to hold the furnace in the selected position. Hot gas inlet 66 and outlet 68 are likewise provided in the furnace wall, the former being connected to conduit 38 and the latter to conduit 16 when this furnace is incorporated in the systems of Figs. 1 and 2.

Practice of the invention according to the preceding description is illustrated by the following examples.

EXAMPLE 1

A coal coking blend, formulated to produce foundry grade coke as contrasted to blast furnace coke, was delivered to transport line 14 at the rate of 5.22 tons per

hour into hot gas of 1200° F. temperature flowing at the rate of 274,000 s.c.f.h. As a result of the preheat the coal was dried and hence was delivered to treater feed hopper 26 at the rate of 4.7 tons per hour and at a temperature of 500° F. The coal flowed through tubes 30 under an initial pressure of approximately 12 lbs. per sq. in. and at a linear rate of 1½ ins. per minute, and was heated to about 1150° F. by hot gases from the calciner delivered to the furnace through conduit 38 at a temperature of 1860° F. The coke thus formed was then flowed through calciner 36 where it was heated to about 1800° F. for sufficient time to complete calcination to metallurgical foundry grade coke having the following properties.

Coke properties based on screened 8" x 4" lumps

Shatter test ¹ -----	+2"	3 95
Tumbler stability ² -----	+1"	3 48
Tumbler hardness ² -----	+¼"	3 57
Apparent specific gravity -----		1.2

¹ The shatter test of the example is described in ASTM designation D141-48.

² The tumbler tests of the example are described in ASTM designation D294-50.

³ Percent retained on sieve designated.

The apparatus consisted of three furnaces each containing ten 20 foot tubes of 12" diameter, inclined downwardly at an angle of 7° from the horizontal, and connected into a unitary twin shaft calciner, the heated section of which being 25 ft. high and being 4.5 ft. wide on the heated sides and 2 ft. wide on the unheated sides.

EXAMPLE 2

In apparatus similar to that of Example 1, except that all tubes 30 were 8" in diameter, and inclined upwardly at an angle of 10° from the horizontal, raw petroleum coke was delivered at the rate of 4.71 tons per hour to 1200° F. carrier gas flowing at the rate of 274,000 s.c.f.h. The dried, preheated coke flowed to mixer 28 at the rate of 4.24 tons per hour and at a temperature of 600° F. where it was mixed with 0.47 ton per hour of binder pitch. The mixture was forced through tubes 30 under positive pressure of 16 lbs. per sq. in. at a linear rate of approximately 3.5 ins. per min. during which time it was indirectly heated to about 1150° F. by hot gases supplied from the calciner as previously described. Treatment was continued in calciner 36 to a temperature of about 2150° and the coke product was discharged therefrom at a temperature of 300° and at a rate of 3.96 tons per hour. The product has the following properties:

Coke Properties	Semi-Coke	Calcined Coke	Prior Art Coke
Ave. particle size, in.-----	2.5	1-2	0.2-0.4
Particle Density-----	1.4	1.3-1.6	1.1-1.3
True Density-----	1.4	2-2.1	2-2.1
Resistivity, ohms/in.-in. ³ -----		0.035-0.045	0.035-0.045
Volatile Matter-----	5-8	0.1	
Ash-----	0.3	0.3	
Sulfur-----	1.5	1.5	

From these data it will be noted that the product of the process of my invention is unique in particle size and particle density which accounts principally for its improved behavior in electrode forming masses.

While under most conditions the green carbon with or without binder flows smoothly through the calcining tube, there are some circumstances under which the material tends to stick to the wall and build up a cake. In such cases I provide a protective envelope around the material being treated, this being another feature of

my invention. This protective envelope consists of a substantially uniform layer of loosely consolidated, small particle size coke maintained against the inner wall of the tube. This layer is preferably about one inch thick and is composed of particles about 6 to 20 mesh in size. The green carbon is thus prevented from making contact with the metal wall. Furthermore, the porous lining provides an ideal path for the flow of gases evolved from the carbonizing materials whereby these gases are conducted away from the treating zone without excessive disruption of the carbon being treated.

Supplementary benefits are likewise derived from this added feature of my invention. By reason of the travel of vapors through the hottest zone in the tube they will be cracked more nearly in a manner to produce high temperature tar which has greater value than low temperature tar. The protective layer of coke flows through the treating tube along with the carbon being treated and is easily separated therefrom on discharge.

Having thus described my invention, I claim:

1. A process for coking carbonaceous materials of predominantly fixed carbon content a portion at least of which is plastic at elevated temperatures and which evolve vapors at such temperatures, which comprises introducing such material in particulate form into one end of an externally-heated, smooth-walled tube of uniform cross section throughout its length from which oxygen is excluded, forcing the material through the tube under a pressure in excess of one pound per sq. in. applied over the entire cross sectional area thereof at the feed end of the material in the tube, heating the material to a temperature in excess of 800° F., thereby plasticizing the plasticizable component thereof, compacting the mass and evolving vapors therefrom, retaining the particulate material in flowable condition and under pressure in the tube until coking is completed to a substantially uniform density throughout the mass of material, and recovering the vapors and coke product from the tube.

2. The process of claim 1 in which the carbonaceous material is petroleum coke.

3. The process of claim 1 in which the carbonaceous material is coal.

4. The process of claim 1 in which the carbonaceous material is initially mixed with a carbonizable fluid binder.

5. The process of claim 1 further characterized by heating the coke recovered from the tube to a temperature higher than that prevailing within the tube in the absence of oxygen.

6. The process of claim 1 in which the carbonaceous material is preheated prior to introduction into the metal tube.

7. The process of claim 1 in which the carbonaceous material is conveyed to the vicinity of the metal tube in tail gases from the heating zone.

8. An integrated process for producing electrode and metallurgical grade coke from green solid heat plasticizable carbonaceous materials of predominantly fixed carbon content, which comprises suspending said material in particulate condition in hot gases obtained as herein-after described, drying and conveying the material therein to a smooth walled, externally heated coking zone of uniform cross section throughout its length, forcing said particulate material through said zone under superatmospheric pressure applied over the entire cross-sectional area of the material at the feed end thereof and converting it to coke of substantially uniform density throughout during transit therethrough, thereafter conducting said coke product through an indirectly heated, vertically disposed calcining zone and recovering the thus treated material as ultimate calcined coke product, and providing hot gases for both heating indirectly and conveying the carbonaceous material by burning a combustible fuel against the exterior of the calcining zone and conducting the combustion products therefrom to the

carbonaceous solids pick up zone and to the exterior
of the coking zone:

References Cited in the file of this patent

UNITED STATES PATENTS

849,947	Wagner	Apr. 9, 1907
1,471,647	Chance	Oct. 23, 1923
1,805,109	Runge et al.	May 12, 1931

1,828,586	Archbald	Oct. 20, 1931
1,930,377	Archbald	Oct. 10, 1933
2,755,234	Reintjes	July 17, 1956
2,764,539	Howitz	Sept. 25, 1956

OTHER REFERENCES

U.S.D.I. Bureau of Mines Monograph 5, "Gas, Coke, and By-Product Properties of American Coal," 1934, TP321, F459, page 34.