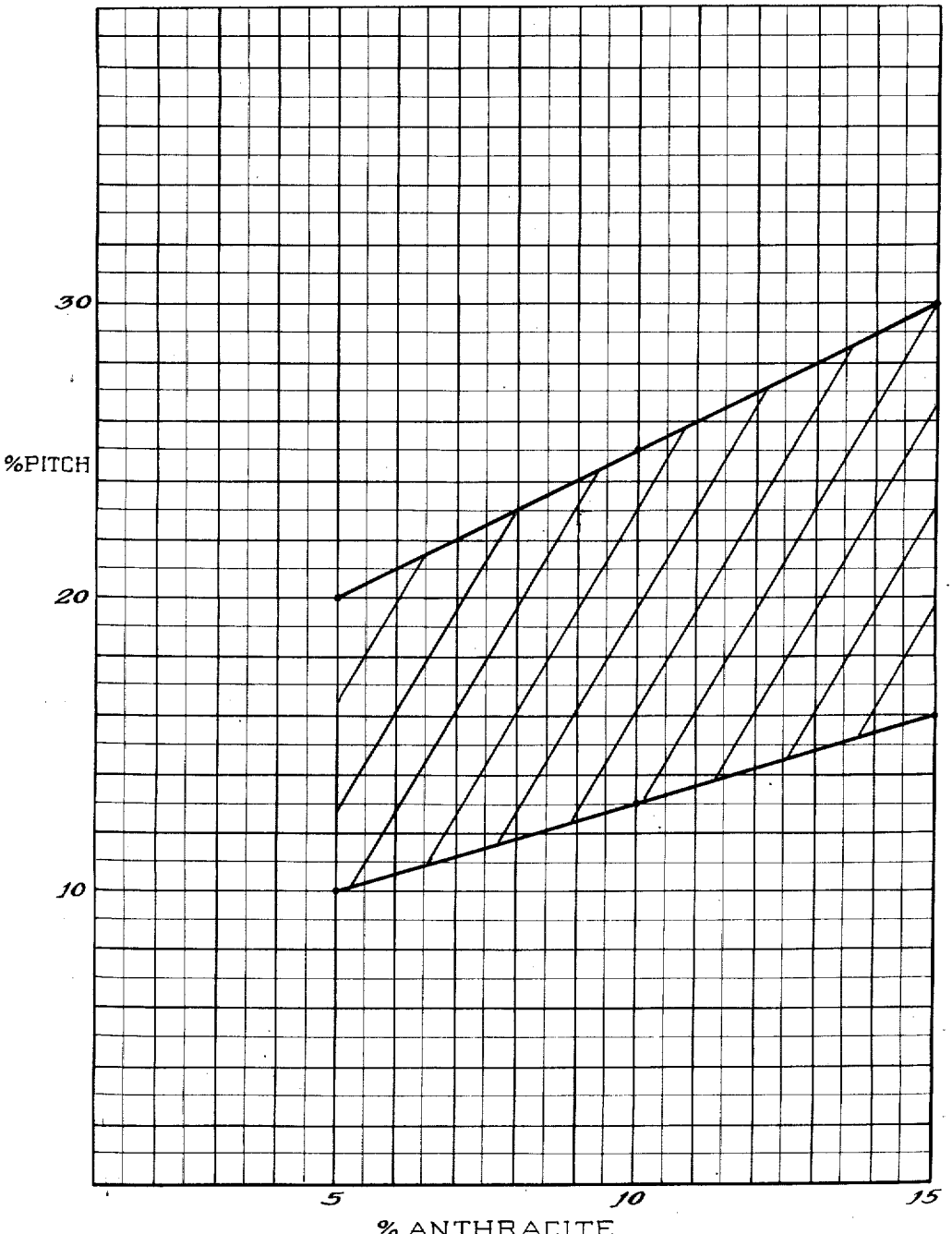
Oct. 1, 1957 T. G. BOWERS 2,808,370

METALLURGICAL COKE

Filed Oct. 12, 1953



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United States Patent Office 2,808,370 Patented Oct. 1, 1957

2,808,370

METALLURGICAL COKE

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Application October 12, 1953, Serial No. 385,313

13 Claims. (Cl. 202—33)

This invention relates to the manufacture of metallurgical coke or blast furnace coke. More particularly, this invention relates to a method of producing a new type of coke which contains substantial quantities of raw petroleum coke in admixture with other components, which coke has been found to be particularly suitable in metallurgical processes as for example the melting of ferrous metals in cupolas.

This application is a continuation-in-part of my copending application, Ser. No. 324,399, filed December 5, 1952, for "Metallurgical Coke."

Foundry coke has been produced almost entirely from selected bituminous coals in what is known in the trade as by-product beehive ovens. Various coals of low or high volatile content are ground and blended to provide a more or less uniform or homogeneous mixture which is then placed in the coking apparatus. Beehive oven coke is produced in rows of circular ovens which are nominally 12 feet in diameter, the blended coals being charged to a depth of up to 24 inches. Heat for coking is supplied mainly by the combustion of volatile matter from the coals and expansion during carbonization is unrestricted. At the present time a very small percentage of metallurgical coke is made in this manner. By-product coke is made in batteries of 30 to 75 ovens. Each oven is about 40 feet long, 10 to 14 feet high and 16 to 20 inches wide. The ovens are erected parallel to each other and are heated by combustion of gases in flues placed between each oven. The ovens are charged with from 10 to 20 tons of the coal mixture through top ports, closed tightly and subjected to indirect heat by maintaining flue temperatures between 1800° to 2200° F. Coking temperatures are controlled by careful regulation of the combustion of the gases in the flues which assures even heating and uniform coke quality. The heating cycle may be anywhere from 15 to 30 hours depending upon the flue temperatures, type of coal and properties desired in the final coke.

Foundry coke normally produced in by-product ovens is made by coking a blend of high and low volatile bituminous coals; the types, number and amounts of the components are selected according to the ultimate properties desired in the coke. The resulting coke is usually high in ash content (8 to 10%), the porosity is usually greater than 50% and has shatter values of 90%+2 inches and 70%+4 inches. The apparent specific gravity is normally less than 1.0. When used in a cupola to melt mixtures of scrap, pig iron, etc. and other components normally used in the manufacture of various metals, this coke has a considerable reactivity towards CO_2 and H_2O vapor in that the flue gases will contain appreciable quantities (from 10 to 20% by volume) of CO. Since oxidation of the coke by CO_2 and H_2O vapor is an endothermic reaction this detracts from the efficiency of the cupola. Furthermore, additional coke may be added to the charge to compensate for this type of oxidation which reduces the throughput or melting rate of the cupola.

A few attempts have been made to introduce raw petroleum coke into bituminous coal mixtures in by-product oven practice. For example, from 5 to 15% by weight

of petroleum coke has been mixed with coking coals. While the resulting cokes have been useful as fuel they fall far short of specifications for metallurgical purposes. Several attempts have also been made to manufacture coke in by-product ovens from a mixture of raw petroleum coke and coal tar pitch. The resulting cokes have a distinct "fiingery" structure, are not resistant to rough handling, and fall far short of cupola practice specifications on shatter and hardness values. The same is true for the coke which has been produced in the so-called Knowles oven from a mixture of raw petroleum coke (75 to 95%) and coking coal (25 to 5%).

It is an object of this invention to produce a coke which will substantially reduce coke consumption and increase melting rates in foundry practice, particularly when melting ferrous metals in a cupola.

It is a further object of this invention to produce a foundry coke of improved density and reduced porosity.

It is a further object of this invention to produce a foundry coke having a high degree of combustibility (reaction with oxygen to form CO_2) and of reduced reactivity towards CO_2 and H_2O vapor to produce CO.

It is a further object of the invention to produce a foundry coke which will have a very low ash residue.

It is a further object of the invention to provide a method for the melting of various metals in foundry practice by using the novel coke herein described.

It is a further object of the invention to provide a novel method for by-product oven coking whereby substantial amounts of petroleum coke can be utilized in order to effect marked improvement in the resulting foundry coke.

It is a further object of the invention to produce a novel coke which will raise the carbon content of ferrometals without impairing other properties in the product.

The above objects as well as others which will become apparent upon understanding the invention as herein described are realized by forming a carbonaceous mixture consisting essentially of (*a*) a major portion of petroleum coke having a volatile content between about 5 and about 14% by weight; (*b*) between about 5 and about 15% by weight of anthracite; (*c*) between about 10 and about 30% of a hydrocarbon pitch; (*d*) the balance or remainder of the components comprising essentially a swelling bituminous coal having a volatile content between about 14 and about 22%. The major portion of this mixture, and preferably 90%, should pass a ¼" screen. This mixture is then placed in a by-product oven whose design is described above and also in the Coking Section of the Encyclopedia of Chemical Technology, vol. 3, The Interscience Encyclopedia, New York, 1949. The oven is normally loaded through a top port with the coal mixture filling the oven to about three-fourths of its height. The mixture is then coked by indirect heat generated in the flues at a temperature between about 1800° and about 2200° F. The coking cycle will depend mainly upon the ultimate properties desired in the coke and upon temperatures of the flues. Thus at a final temperature of 1800° F. the cycle will require from between about 20 to 25 hours and at 2200° F. will require between 18 to 20 hours.

The petroleum cokes employed in making the cokes which are the subject of this invention result from the thermal cracking of heavy petroleum residues such as reduced or topped crudes, thermally or catalytically cracked recycle stock, etc. The coking is normally conducted in a vertical cylindrical drum such as those manufactured by Kellogg, Lummus and Foster Wheeler companies. The heavy hydrocarbons are admitted in to the drum at a temperature between 900° and 1000° F. and are permitted to soak and carbonize until the drum is nearly filled with a solid coke. This material is removed from the drum by various decoking methods as known to the

art. Normally the volatile content will be between about 5 to 14% by weight and more usually between 8 to 12%.

The hydrocarbon pitch which is essential to the practice of this invention may be derived either from coal tar or petroleum sources or mixtures thereof. Coal tar pitch is produced by thermal or vacuum distillation of tar recovered in by-product oven practices. Petroleum pitches are prepared by thermal distillation at atmospheric or reduced pressures of heavy petroleum hydrocarbons, cracked recycle stocks or from high boiling material recovered in reforming operations. The coal tar or petroleum pitch should preferably have a melting point (ball and ring) between 300° and 400° F. since these materials have a higher coke residue and improved bonding properties. I have also discovered that it is essential to the realization of satisfactory and acceptable physical properties of the coke that the ratio of pitch:anthracite be kept within certain limits, namely between about 4:1 and 2:1 when the amount of anthracite is 5% and between 2:1 and 1:1 when the amount of anthracite is 15%, the amount of pitch increasing progressively and substantially uniformly within the limits of this ratio as the percent of anthracite in the mixture is increased from 5 up to 15%. This is shown clearly in the accompanying drawing.

The amount of pitch incorporated in the overall carbonaceous mixture to be coked will depend somewhat upon the specific requirements of the end-use of the coke and upon the specifications of plants where it will be used. Thus, a mixture high in pitch (but within the aforementioned prescribed pitch:anthracite ratio) will produce a harder, more dense coke but less resistant to impact, and the opposite result obtains at the lower pitch:anthracite ratios. I have found that coke of the greatest size and shatter resistance is produced from a carbonaceous mixture having a pitch:anthracite ratio of about 1.4:1. Mixtures containing pitch:anthracite ratios outside the shaded area of the drawing are not encompassed by this invention and produce inferior cokes.

The bituminous coals required in practicing this invention must have a volatile content between 14 to 22% by weight and preferably between 16 to 20%. Since it is desired to maintain the ash residue of the final coke at a low value, the ash content of the coal should also be low and will normally not be in excess of 7% by weight. The coal must be present in amounts of 10% or more, the maximum amount depending upon the amounts of other ingredients in the mixture as specified herein.

Between about 5 to 15% by weight of anthracite is required in the mixture to be coked according to this invention. The use of anthracite has been found to increase the blockiness (increased portions of the large sized pieces of coke) so essential to foundry coke. Again, the ash content of the anthracite should be as low as possible and will normally not exceed 15% by weight. Usually the size of the anthracite employed will be No. 5 Buckwheat. It is preferable to pulverize the anthracite to −100 mesh but pulverization to 25% −40 mesh will give good results.

The metallurgical cokes produced according to this invention will have a carbon content in excess of 95%; ash less than 4%; volatile matter less than ½%; porosity less than 50%, preferably less than 40%; shatter not less than 50% +4 inches and not less than 70% +2 inches; apparent density greater than 1.0 and usually about 1.25; and sulfur less than 1%.

In describing and claiming the metallurgical coke of this invention and the method for manufacturing the same, some definitions have been adopted as follows:

Apparent or bulk density of the coke is the weight in pounds per cu. ft. according to ASTM Method D292–29.

Porosity or cell space is the ratio between the apparent and true specific gravities as determined by ASTM Method D167–24.

Volatile matter (VM).—This is exclusive of the moisture and free oil which would be removed by heating to temperatures of 400° to 500° F. Volatile matter is determined in a platinum crucible placed in electrically heated furnace maintained at temperatures of 1742° F.±36° F. A one gram sample of dry −60 mesh coke is heated for 7 minutes and the resulting weight-loss is termed volatile matter.

Ash.—Ash is the residue from a one gram sample of coke ignited in an oxygen atmosphere at about 1742° F.

Combustibility.—This is the rate of reaction of the coke with oxygen and is described herein in terms of flue gas analysis in cupola operation.

Reactivity.—The reactivity of coke toward carbon dioxide to produce carbon monoxide is determined by analysis of flue gas in cupola operation.

Shatter.—This is determined by ASTM D141–23 and consists of dropping approximately a 50 pound sample of coke (+2 inches) four times upon a heavy steel plate from a height of 6 feet. A screen analysis is made of the broken material and the total percentage is used as an index of strength.

In a preferred embodiment of the invention foundry coke is manufactured by preparing a mixture of the following components:

	Percent by weight
Petroleum coke (8 to 12% VM)	40 to 75
Anthracite (12% ash)	5 to 10
Coal tar pitch (350° M. P.)	10 to 20
Bituminous coal (16 to 20% VM)	10 to 30

The above components were ground so that 90% of the particles would pass a ¼" screen. This mixture was charged in a deep bed into a vertical by-product coking oven and coked by indirect heat for 20 to 22 hours at a temperature between 1800° to 2200° F. The resulting coke had the following analysis:

Free carbon	96% by weight.
Ash	3.0%.
Sulfur	0.5%.
Volatile matter	0.5%.
Shatter	90%+2 inches; 70%+4 inches.
Porosity	35%.

In a further embodiment of the invention foundry coke is manufactured by preparing a substantially uniform blend of the following components:

	Percent by weight
Petroleum coke (10 to 12% VM)	50 to 55
Coal tar pitch (330° M. P.)	10 to 15
Pocahontas coal (bituminous, 18% VM)	20 to 25
Anthracite	11 to 13

The above components were ground so that 90% of the particles would pass a ¼" screen. This mixture was then charged in a deep bed into a vertical by-product coking oven and coked by indirect heat for 22 hours at a temperature between 2000° to 2200° F. The resulting coke had the following analysis:

Free carbon	96% by weight.
Ash	3.0%.
Sulfur	0.4%.
Volatile matter	0.6%.
Shatter	92%+ 2 inches; 75%+4 inches.
Porosity	35%.

In preparing the carbonaceous mixture to be coked according to this invention, the petroleum coke should be the major component (by weight) and the total amount of pitch (coal tar or petroleum) and swelling bituminous coal should be either equal to or less than the weight of the petroleum coke in the mixture. If the amount of the petroleum coke is less than 40% of the total mixture, the beneficial results herein described are not realized. This is also true if the petroleum coke exceeds 75% by weight of the total mixture as in that event the shatter values fall below accepted specifications.

It is believed that the improved results in cupola practice are due to a combination of the physical and chemical properties of this novel coke including specifically: high density, low porosity and low ash. Since combustion is maximized and reactivity considerably reduced, the cupola operation is much more efficient and has higher melting rates. By employing the coke which is the subject of this invention it has been possible to reduce cupola coke requirements as much as 300% thereby permitting greater quantities of metal charge as compared to the amounts of coke and flux required.

A major and important use of the coke manufactured according to this invention is in the cupola melting of ferrous metals. A cupola is a furnace of the vertical shaft type and briefly consists of a cylindrical shell usually of boiler plate and lined with refractory. Cupolas vary in size, such as 18" to 84" I. D. The furnace is equipped with a windbox and tuyeres for the admission of air. An iron charging door is positioned in the side of the stack usually from 16 to 22 feet above the bottom through which melting stock and fuel are introduced. Near the bottom of the shaft, and generally on opposite sides thereof, are holes or spouts for the tapping of molten metal and slag.

In operation, the bottom of the shaft is filled with coke to form a bed. The coke bed heated above the tuyeres will be between 20" to 53". This is ignited after which charges of coke, fluxing agents and melting stock (pig iron, scrap steel, etc.) are introduced until the stack contains the desired number of charges or it is level with the charging door. In charging the cupola a layer of limestone or other flux is placed on top of the coke bed followed by a charge of metal, a charge of coke and another charge of flux, etc. The limestone charge is usually about 20% of the coke charge by weight and may vary from 4 to 90 pounds per charge of metal and coke depending on the size of the cupola. Air is introduced through the tuyeres into the coke bed and the heat produced by the combustion of the coke causes the metal to melt and flow down through the coke to the bottom of the shaft. The slag which is formed by the action of the flux on the ash of the coke and impurities in the charge float on the surface of the molten iron and is periodically drawn off through the slag tap hole.

The heating cycle will vary in length, for example from 1 to 16 hours. The ratio of iron to coke with conventional foundry coke is between 6 to 1 and 12 to 1. When employing the coke of the present invention, metal to coke ratios as high as 20 to 1 have been realized.

In order to further describe the coke which is the subject of this invention and its method of manufacture the following examples are recited:

EXAMPLE I

The following components were ground to 90% −¼" and thoroughly blended:

Petroleum coke (12% VM)_____percent by weight__	60
Coal tar pitch (300° F. M. P.)_____percent__	14
Bituminous coal (Pocahontas 18% VM)_____do____	18
Anthracite (12% ash)_____do____	8

The above mixture was coked in a vertical by-product oven while maintaining the flue temperatures between 2000° to 2100° F. over a 20 hour cycle. The coke resulting from this operation had the following analysis:

Carbon	96%.
Ash	3.5%.
Sulfur	0.5%.
Volatile matter	Less than 0.5%.
Shatter:	
+4"	55%.
+3"	72%.
Apparent density	1.20%.

This coke was used in melting a mixture of pig iron, foundry returns, steel scrap, etc. in a cupola having a nominal diameter of 65" at the tuyeres and 72" in the melting zone. A coke bed of about 6000 pounds was used. Normal iron to coke ratios in such a cupola are 6 to 1, each metal charge being 1 ton. It was found that the iron to coke ratio could be increased to as high as 18 to 1 by employing the novel coke described above thereby increasing the melting rate of the cupola from a normal rate of 17 tons up to 23 tons per hour. Temperatures at the metal spout were between 2750° to 2800° F. Also, the carton content of the metal averaged 3.5 to 3.7% as compared to values of 3.1 to 3.2 for normal foundry coke. Photomicrographs of the melt samples showed higher percentages of graphite inclusion but the density and other physical properties of the metal were not lowered indicating a better distribution of the graphite throughout the metal than in the case of high carbon iron produced with regular foundry coke.

Flue gas analyses were obtained throughout this run and the concentration of CO averaged about 6.0% by volume. This is to be contrasted with a CO analysis in normal foundry practice which averages between 11 to 12% by volume. This at least partially explains the outstanding results obtained and the observed increase of iron to coke ratios.

In preparing the carbonaceous mixtures to produce the coke of the invention, I regulate the quantity of the pitch component according to the amount of anthracite present, or vice versa. The pitch tolerance and requirement of the mixture increases within defined limits, as the amount of anthracite increases from 5 up to 15% by weight of the total mixture. Thus, for a mixture containing 5% anthracite, from 10 to 20% of pitch can be used; similarly

Percent Anthracite	Percent Pitch	Pitch: Anthra. Ratio
(5)	(10 to 20)	(4–2:1)
10	10 to 25	2.5–1:1
15	15 to 30	2.0–1:1

are typical ratios of pitch to anthracite which are required.

Additional samples of metallurgical coke were prepared within the scope of this invention with the following mixtures:

Table I

Ex. No.	Pet. Coke		Bit. Coal		Coal Tar Pitch		Anthra., Percent	Pitch: Anthra. Ratio
	Percent	VM	Percent	VM	Percent	M. P., ° F.		
2	45	12	25	20	20	400	10	2:1
3	50	8	25	20	17	400	8	2.1:1
4	60	10	17	18	15	350	8	1.9:1
5	70	12	13	16	10	350	7	1.4:1
6	75	10	10	15	10	300	5	2:1

The components in each of the above examples were ground so that the majority of the particles would pass a ¼" screen and to produce an intimate mixture of the components. The coking operation was similar to that described in Example 1. All of the cokes produced in Examples 2 to 6 show improved characteristics in cupola operation and permitted increased iron to coke ratios and higher melting rates. All of these cokes had a porosity less than 50%, usually 35 to 40%; volatile matter was less than 1.0%; shatter more than 80% +2 inches and more than 60% +4 inches; ash less than 4%. All of the cokes showed a reactivity considerably lower than that observed in normal foundry coke practices even when mixing low volatile and high volatile coals with small proportions of anthracite fines.

Having thus described the invention with particularity, but without intention of being limited to the exact details

expressed herein but only by the scope of the appended claims, what is desired to be secured by Letters Patent is:

1. A method for manufacturing foundry coke which comprises forming an intimate mixture consisting essentially of a major portion of petroleum coke having a volatile content between about 5 and 14% by weight, between about 5 to 15% by weight of anthracite, an essentially hydrocarbon pitch binder in amounts between 10 to 20% when the amount of anthracite is 5% and between 15 to 30% when the amount of anthracite is 15%, the amount of pitch increasing as the amount of anthracite in the mixture increases, and the balance a swelling bituminous coal having a volatile content between about 14 and about 22% by weight, the major portion of the particles in said mixture passing a ¼" screen, forming a deep bed of said mixture in a narow vertical coking zone and coking the mixture by indirect heat at a temperature between about 1800 to 2200° F.

2. The method according to claim 1 wherein the pitch is coal tar pitch having a melting point between about 300° and about 400° F.

3. The method according to claim 1 wherein the pitch is petroleum pitch having a melting point between about 300° and about 400° F.

4. The method according to claim 1 wherein the petroleum coke and the bituminous coal have a volatile content between about 8 to 12 percent, and between about 16 to 20 percent by weight, respectively.

5. A method for manufacturing foundry coke which comprises forming an intimate mixture consisting essentially of between 40 to 75% by weight of petroleum coke having a volatile content between about 8 to 12% by weight, between about 5 to 15% by weight of anthracite, an essentially hydrocarbon pitch binder in amounts between 10 to 20% when the amount of anthracite is 5% and between 15 to 30% when the amount of anthracite is 15%, the amount of pitch ratios increasing as the amount of anthracite in the mixture increases, the balance a sweling bituminous coal having a volatile content between about 16 to 20 percent, more than 90 percent of the particles of said mixture passing a ¼" screen, forming a deep bed of said mixture in a narrow, vertical coking zone and coking the mixture by indirect heat at a temperature between about 1800° and about 2200° F.

6. A method for manufacturing a high carbon, low ash metallurgical coke which comprises forming an intimate mixture consisting essentially of a major portion of petroleum coke having a volatile content of about 5 to 14% by weight, between about 5 to 15% by weight of anthracite, the remainder of the mixture consisting essentially of hydrocarbon pitch binder and a swelling bituminous coal having a volatile content between about 14 to 22%, the total amount of pitch and bituminous coal being less than the weight of the petroleum coke in the mixture and the pitch being present in amounts between 10 to 20% when the amount of anthracite is 5% and between 15 to 30% when the amount of anthracite is 15%, the amount of pitch increasing as the amount of anthracite in the mixture increases, the major portion of the particles of said mixture passing a ¼" screen, forming a deep bed of said mixture in a narorw vertical coking zone and coking the mixture by indirect heat at a temperature between about 1800 to 2200° F.

7. A method for manufacturing a high carbon, low ash metallurgical coke which comprises preparing a substantially uniform blend of the following components; petroleum coke having a volatile content of 10 to 12% by weight in amount between 50 to 55% by weight; coal tar pitch in amounts between 10 to 15% by weight; a swelling bituminous coal of the Pocahontas type having a volatile content of about 18% by weight in amounts of 20 to 25% by weight; and anthracite in amounts between 11 to 13% by weight, 90% of said mixture passing a ¼" screen, forming a deep bed of said mixture in a narorw vertical coking zone and coking the mixture by indirect heat at a temperature between about 2000 to 2200° F.

8. A method for manufacturing foundry coke which comprises forming an intimate mixture comprising essentially a major portion of petroleum coke having a volatile content between about 5 and about 14 percent by weight, between about 5 and about 10 percent by weight of anthracite, between about 10 and about 25 percent of an essentially hydrocarbon pitch, and the balance a swelling bituminous coal having a volatile content between about 14 and about 22 percent by weight, the major portion of the particles of said mixture passing a ¼" screen, forming a deep bed of said mixture in a narrow, vertical coking zone and coking the mixture by indirect heat at a temperature between about 1800° and about 2200° F.

9. The method according to claim 1 wherein the pitch is coal tar pitch having a melting point between about 300° and about 400° F.

10. The method according to claim 1 wherein the pitch is petroleum pitch having a melting point between about 300° and about 400° F.

11. The method according to claim 1 wherein the petroleum coke and the bituminous coal having a volatile content between about 8 to 12 percent, and between about 16 to 20 percent by weight, respectively.

12. A method for manufacturing foundry coke which comprises forming an intimate mixture consisting essentially of between 40 to 75 percent by weight of petroleum coke having a volatile content between about 8 to 12 percent by weight, between about 5 to 10 percent of anthracite, between about 10 to 20 percent of coal tar pitch, and between about 10 to 30 percent of a swelling bituminous coal having a volatile content between about 16 to 20 percent, more than 90 percent of the particles of said mixture passing a ¼" screen, forming a deep bed of said mixture in a narrow, vertical coking zone and coking the mixture by indirect heat at a temperature between about 1800° and about 2200° F.

13. A method for manufacturing a high carbon, low ash metallurgical fuel which comprises forming an intimate mixture consisting essentially of a major portion of petroleum coke having a volatile content between about 5 and about 14 percent by weight, a minor portion (about 5 to 10 percent) of anthracite, the remainder consisting essentially of hydrocarbon pitch and a swelling bituminous coal having a volatile content between about 14 and about 22 percent, the total amount of pitch and bituminous coal being less than the weight of the petroleum coke in the mixture, the major portion of the particles of said mixture passing a ¼" screen, forming a deep bed of said mixture in a narrow, vertical coking zone and coking the mixture by indirect heat at a temperature between about 1800° and about 2200° F.

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