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J. F. HARDY ET AL

3,369,871

PREPARATION OF METALLURGICAL CARBON

Filed July 15, 1965

2 Sheets-Sheet 1

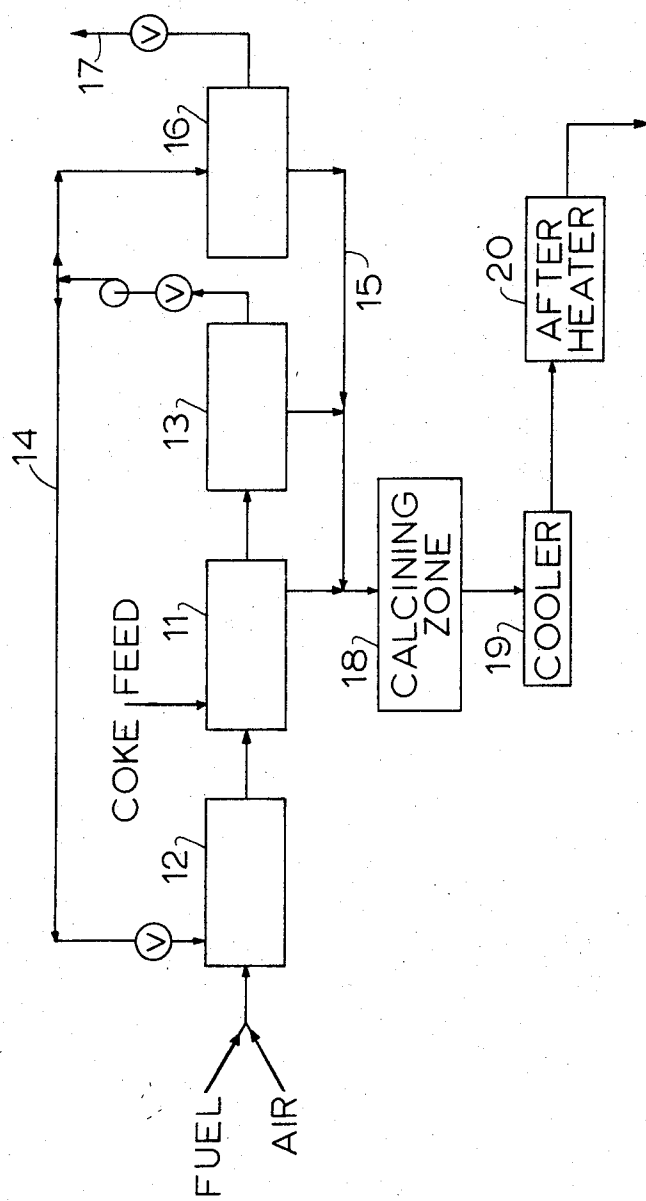


FIG. 1

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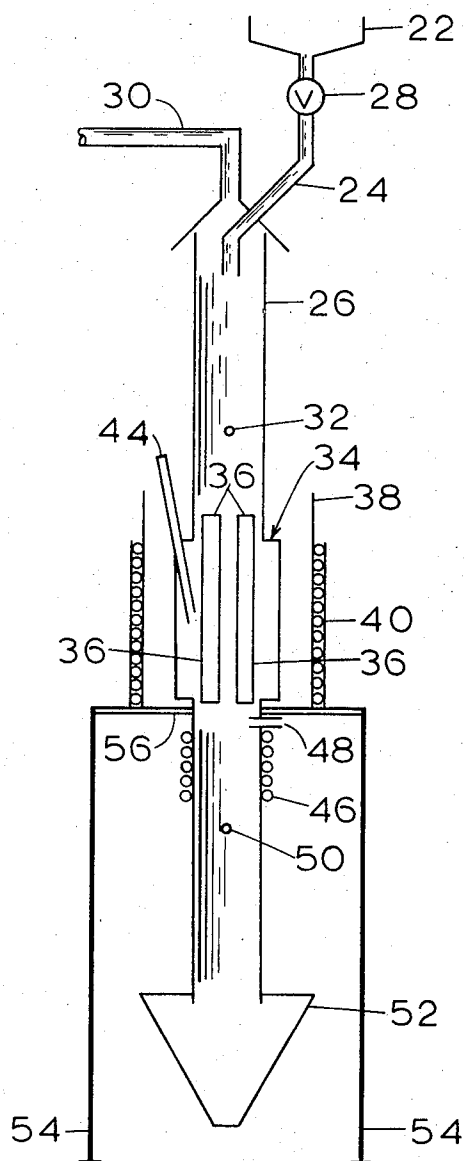


FIG. 2

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PREPARATION OF METALLURGICAL CARBON

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6 Claims. (Cl. 23—209.9)

This invention relates to a process for treating green petroleum coke to improve the properties thereof. More particularly, this invention relates to a method of preparing a metallurgical carbon from green petroleum coke.

Petroleum coke is extensively used in industry, notably as the major constituent of carbon electrodes as packing material in the baking of carbon electrodes and in metallurgy. The greatest proportion of petroleum coke currently available is the product obtained in delayed coking of heavy refinery residual oils and tar. This coke is not pure carbon, but is believed to be a complex substance composed of carbon crystallites embedded in a matrix of heavy hydrocarbon compounds. The coke is wholly unsuitable for the uses mentioned above, and must be calcined. In this step, the hydrocarbons are converted by pyrolysis to carbon and volatile matter. The green coke sometimes absorbs a small amount of lighter hydrocarbon material during its original formation. This material is also driven off during the calcination operation and is included with that evolved during pyrolytic decomposition of the hydrocarbon coke. The volatilized products—commonly referred to as volatile matter—can amount to as much as 10 or 15% of the green coke and include tarry matter, light hydrocarbon gases, and hydrogen. The calcined coke is substantially pure carbon plus inorganic impurities. The carbon crystallites have increased in number and size and resemble more nearly true graphite structure.

However, to make this calcined coke generally useful in metallurgical processes such as the making of ductile iron requires that sulfur content be lowered much further, for example to about 0.1% sulfur or even lower. Were a reduction of sulfur content realized, the resulting material would have low cost, the requisite low sulfur content, large crystallite dimensions somewhat similar to those of graphite, an inoculating efficiency which has been related to crystallite size, wetting efficiency in metallurgical melts which efficiency has also been related to the aforesaid crystallite dimensions, and low ash content.

Heretofore, however, the high sulfur content of about 5% or more common in fluid petroleum cokes has presented a barrier to economic utilization of such cokes as metallurgical carbon.

Therefore, it is an object of the present invention to provide a process useful in improving the properties of green petroleum cokes.

It is another object of the invention to provide a carbon prepared from green petroleum cokes which carbon is useful in the metallurgical industries, for example, useful in the preparation of ductile iron.

It is a further object of the invention to provide economic means for reducing the sulfur content of green petroleum coke.

Other objects of the invention are in part obvious and in part pointed out hereinafter.

It has now been discovered that petroleum coke which is subjected to an economic multi-step process is generally useful in forming metallurgical carbon. The aforesaid

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steps provide a series of effects on the raw coke being treated which effects taken together make the objects of the invention attainable.

The first step is the treatment of raw petroleum coke by oxygen. Although this step may be carried out in air at temperatures as low as 300° F., it is preferred that it be carried out at a temperature from 600° F. to 900° F. and in an atmosphere which is mostly composed of inert gases such as nitrogen, but which contains at least 1% of free oxygen. The time the raw coke is subjected to the aforesaid temperature may vary somewhat depending upon the amount of sulfur in the coke and the particular coke being treated but, advantageously, the material will be treated from about 1½ to 3 hours before being transported into a second step which is a calcining step. During this first step a large portion of the sulfur is oxidized. This is especially true of that sulfur which is relatively near to the surface of the coke particles and that part of the sulfur which is only a small distance below the surface of said coke particles.

The material having received the initial heat treatment is passed into a calcining zone wherein it is subjected to temperatures of at least about 1600° C., and preferably about 1800° C. to 3500° C. or more, for a period of time ranging from several minutes to three or four hours depending on the temperature. When these higher calcining temperatures are utilized, the calcining period may be more than proportionately shortened. During this calcining step the sulfur content of the material is decreased again by volatilization of some of the more readily volatilized sulfur. Furthermore, the sulfur most remote from the surfaces of the coke particles tends to be transported toward the surface of the carbon during this high-temperature heating. Another very important effect of this calcining step is the growth of the crystallite dimensions, i.e. the partial graphitizing of the carbon crystallites being treated. Typical increases in crystallite dimensions would include an increase in L_c of from 32 to 104 angstroms and an increase in L_a from 31.8 to 73.7 angstroms. However, it is to be emphasized that these specific figures are merely exemplary and in no way limiting. The point is merely being made that during the calcining step, the carbon crystallites do increase in size to the extent that they are potentially useful in metallurgical processes. The exact meanings of crystallite dimensional parameters L_a and L_c are known to the art and are described specifically in the section on Carbon Black in the Encyclopedia of Chemical Technology, Interscience, New York, 1964.

In the high temperature treating zone used for the calcining step, it is advantageous that air and contaminating gases be substantially excluded inasmuch as the temperature is so high that the excessive quantities of carbon would be oxidized were the step carried out in an oxidizing atmosphere.

In general the first step of the process herein disclosed can be carried out according to the manipulative steps set forth for the first step disclosed in the process set forth in U.S. Patent 2,755,234. To achieve the high temperatures required for the calcining step however, it is usually convenient to utilize induction heating. One method of accomplishing this heating is to place the coke to be heated in a vessel of graphite or other conductive material, place the vessel within coils to which a radio frequency of, for example, about 17,000 c.p.s. is applied thereby causing the conductive vessel to be heated to sufficiently high temperatures to heat the carbon material therein.

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The coke being removed from the high temperature treatment mentioned above is cooled in an inert atmosphere to about 1000° F. At this point in the process the material still contains too much sulfur to be generally useful as a metallurgical carbon. However, it is an important aspect of the invention that it has been discovered that the sulfur in the coke leaving the calcining zone is in such condition that it can be removed with relative ease from the coke.

Therefore, as a final processing step the coke is, after being cooled to about 1000° F., subjected to hot air or other oxidizing gas which is advantageously passed over the coke at from about 600° F. to about 900° F. This final heat treatment oxidizes a sufficient quantity of residual sulfur to reduce the total sulfur content to about 0.2% or less preferably 0.1% and thus makes the material useful for metallurgical applications. Preferably, this treatment with oxidizing gases lasts from two to four hours but this as will be obvious to those skilled in the art, depends upon the amount of sulfur which was removed or made oxidizable by the first two process steps.

In the drawings:

FIGURE 1 is a flow diagram schematically descriptive of the process.

FIGURE 2 is a section in elevation showing an apparatus particularly useful for the process of the invention.

Referring to FIGURE 1, raw green coke is delivered to treater 11 where it is retained for the requisite period of time. Hot combustion gases generated in furnace 12 flow over and/or through the bed of coke in treater 11 and then into a dust settling chamber 13. From there a portion will ordinarily be recycled to furnace 12 through pipe 14 and the remainder may be used as a dust carrier in dust collection line 15. A dust collector 16 may also be provided for convenience. Unused gases are vented from the system through stacks 17. The treated coke is passed into calcining zone 18 wherein it is subjected to the temperatures of 1800° C. or more. Thence the coke is quenched in cooler 19 and subjected to the final oxidation step in after heater 20.

FIGURE 2 shows a reactor especially useful in practicing the process of the invention. This reactor comprises a feed hopper 22 and a conduit 24 leading from the hopper into graphite reactor tube 26. Feed from hopper 22 to tube 26 is controlled by manipulation of ball valve 28. An exhaust hood 30 is mounted above tube 26 providing means to remove excess heat and noxious sulfur fumes from the reactor zone. A tap 32 for a thermocouple is mounted in tube 26.

An induction heating zone 34 is placed about mid-way along tube 26. Zone 34 comprises graphite reactor cores 36, silica shell 38, and induction heating coil 40. An insulating material, in this case amorphous carbon black, is placed between shell 38 and tube 26. A slight tube 44 is positioned in one reactor core 36 for use in optical determinations of temperature.

Below reactor core 36, cooling coils 46 are wound about tube 26. Gas line 48 provides means for putting any desired gas into the tube 26. Another thermocouple tap 50 is placed in the cooled portion of the reactor tube. A vibrational feeder 52 is utilized in discharging material which has been processed in the described apparatus. The entire apparatus is supported on legs 54 on top of which is an insulating barrier 56 of 1½ inch thick transite slab.

In operation petroleum coke which has already been subjected to the first step may be fed into the apparatus of FIGURE 2. It will be heated by heat transferred from the walls of tube 26. This heat is supplied by induction heating of the graphite in zone 34. The heating is a result of a high radio frequency induced by the current supplied to coils 40, this frequency is advantageously 15,000 cycles or more per second.

After being heated the material will be cooled in the part of tube 26 at and below cooling coils 46 and discharged through feeder 52.

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In order to point out more fully the nature of the present invention the following specific examples are given as illustrative embodiments of the present process and products produced thereby.

In each of the following examples a typical green petroleum coke having the following analysis was utilized as a raw material.

Sieve analysis, cumulative, percent retained on, mesh—	
10	2
20	5
48	11
60	20
80	44
100	65
150	88
200	95
Through 200	5
Particle density, g./cc.	1.3
Bulk density, lb./cu. ft.	61.0
Calorific value, Btu./lb. (ASTM D-271)	14,100
Proximate analysis, wt. percent (ASTM D-271):	
Moisture	.3
Volatile matter	6.0
Fixed carbon	93.4
Ash	.3
Ultimate analysis, wt. percent (ASTM D-271):	
Carbon	90.0
Hydrogen	2.0
Sulfur	6.0
Metals: Wt. percent on coke	
Nickel	.013
Vanadium	.034
Iron	<.01
Calcium	<.01
Silicon	<.005
Titanium	<.001
Sodium	<.02

Example 1

A quantity of green petroleum coke is heated at 900° F. for 90 minutes while being mechanically agitated and while exposed to a gas stream containing 2% of oxygen and 98% of substantially inert gases. At the end of this period, the material is transferred to a graphite container enclosed in the coils of an induction heater having a 40 kw. power output and about a 17,000 cycles per second frequency rating. The material is then heated to 2000° C. and calcined at this temperature for twenty minutes.

Thereupon the material is cooled to 950° F. and air at a temperature of 750° F. is passed thereover for four hours. The carbon product recovered has an L_c of 96 angstroms as measured by X-ray techniques known to the art and a sulfur content of 0.09.

Example 2

A quantity of green petroleum coke is heated at 600° F. for 200 minutes while being mechanically agitated and while exposed to a gas stream containing 2% of oxygen and 98% of substantially inert gases. At the end of this period, the material is transferred to a graphite container enclosed in the coils of an induction heater having a 40 kw. power output and about a 17,000 cycles per second frequency rating. The material is then heated to 1800° C. and calcined at this temperature for forty minutes.

Thereupon the material is cooled to 950° F. and air at a temperature of 850° F. is passed thereover for three hours. The carbon product recovered has an L_c of 90 angstroms as measured by X-ray techniques known to the art, and a sulfur content of 0.1.

Example 3

A quantity of green petroleum coke is heated at 900° F. for 150 minutes and while being mechanically agitated while exposed to a gas stream containing 1% of oxygen

and 98% of substantially inert gases. At the end of this period, the material is transferred to a graphite container enclosed in the coils of an induction heater having a 40 kw. power output and about a 17,000 cycles per second frequency rating. The material is then heated to 1900° C. and calcined at this temperature for twenty minutes.

Thereupon the material is cooled to 950° F. and air at a temperature of 900° F. is passed thereover for four hours. The carbon product recovered has an L_c of 82 angstroms as measured by X-ray techniques known to the art, and a sulfur content of 0.085.

It is of course, to be understood that the foregoing examples are intended to be illustrative and that various changes can be made in the ingredients, proportions and conditions set forth therein without departing from the spirit of the invention as defined in the appended claims.

What is claimed is:

1. A process for making a carbon product from petroleum coke which product is useful in metallurgical applications, said process comprising the steps of (1) heating said coke at a temperature of over about 300° F. while flowing an oxygen-containing gas thereover thereby reducing the sulfur content of said coke, (2) subjecting the coke so treated to a temperature of at least 1600° C. thereby partially graphitizing said coke, (3) cooling said coke to about 1000° F., and (4) subjecting said coke to oxidizing gases at a temperature between about 600° F. and 900° F. until the sulfur content of said partially graphitized coke is reduced below 0.2%.

2. A process as in claim 1 wherein in step (1) said petroleum coke is subjected to said oxygen-containing gas for from about 1½ to about 4 hours at temperatures between 600 and 900° F.

3. A process for making a carbon from petroleum coke which product is useful in metallurgical applications, said process comprising the steps of (1) heating said coke to a temperature of over about 300° F. while flowing an oxygen-containing gas thereover for 1½ to 4 hours, (2)

subjecting the coke so treated to a temperature of at least 1800° C. thereby partially graphitizing said coke, cooling said coke to about 1000° F., and (3) subjecting said partially graphitized coke to oxidizing gases at a temperature between about 600° F. and 900° F. until the sulfur content of said partially graphitized coke is reduced to below 0.2%.

4. A process as in claim 3 wherein in step (3) said subjecting of partially graphitized coke to oxidizing gases is carried out between 600° F. and 900° F. for about two to four hours thereby producing a partially graphitized coke having a sulfur content below 0.1%.

5. A process for making a metallurgically useful carbon from a petroleum coke which has been pretreated by subjecting to oxygen at elevated temperatures of over 300° F. to reduce the sulfur content, said process comprising the steps of subjecting the coke so treated to a temperature of at least 1600° C. thereby partially graphitizing said coke, cooling said coke to about 1000° F., and subjecting said partially graphitized coke to oxidizing gases at a temperature between about 600° F. and 900° F. until the sulfur content of said partially graphitized coke is reduced to below 0.2%.

6. A process as in claim 4 wherein said subjecting of partially graphitized coke to oxidizing gases is carried out between 600° F. and 900° F. for about two to four hours thereby producing a partially graphitized coke having a sulfur content below 0.1%.

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EDWARD J. MEROS, *Primary Examiner*.