

Aug. 15, 1972

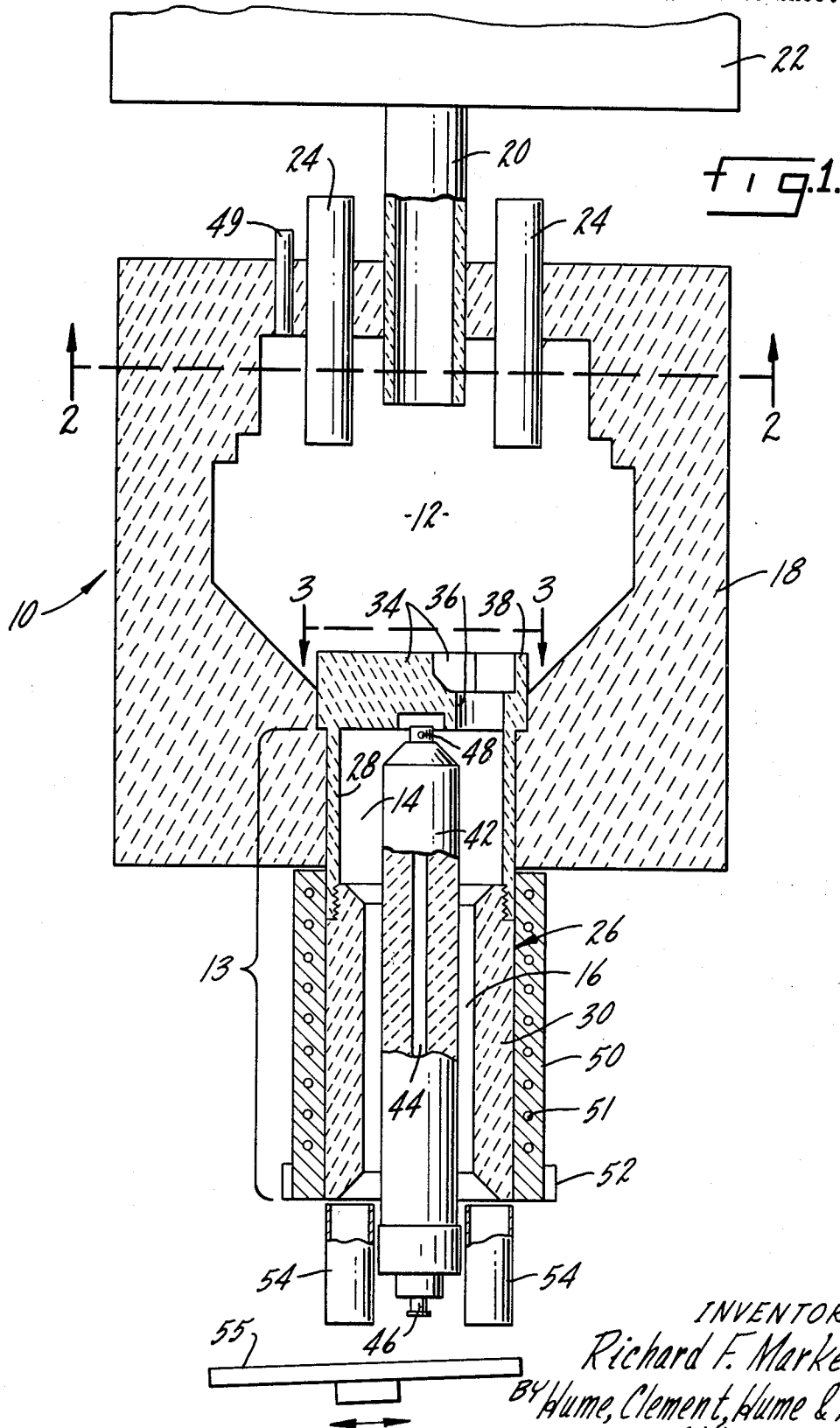
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3,684,446

METHOD FOR HIGH-TEMPERATURE TREATMENT OF PETROLEUM COKE

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2 Sheets-Sheet 1



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fig. 2.

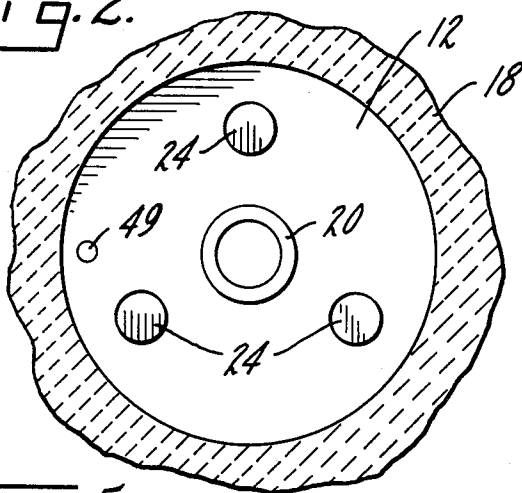


fig. 3.

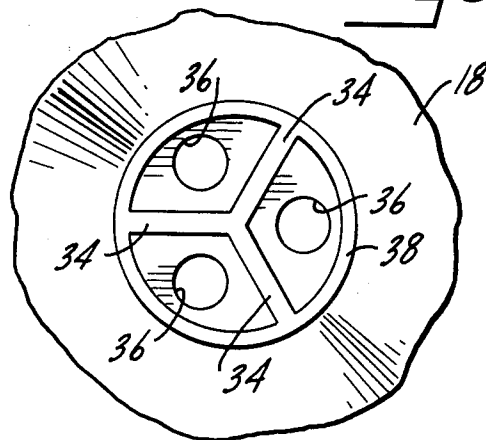


fig. 5.

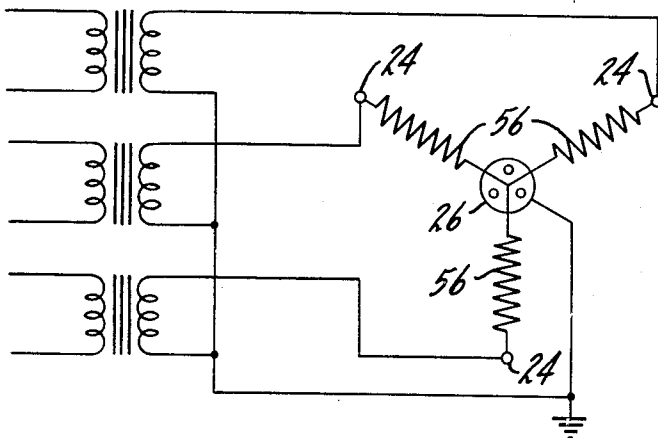


fig. 4.

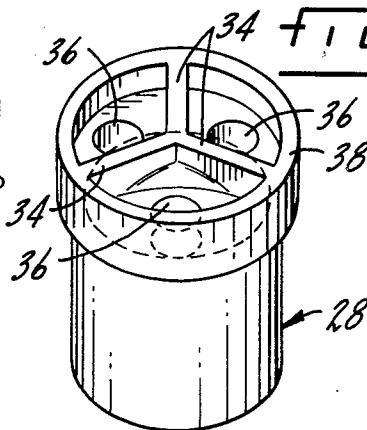


fig. 6.

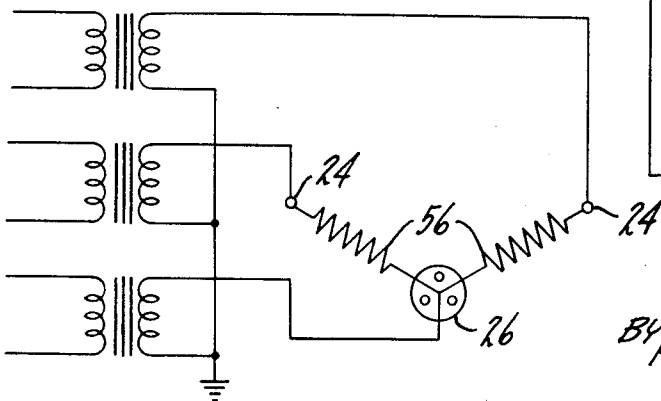
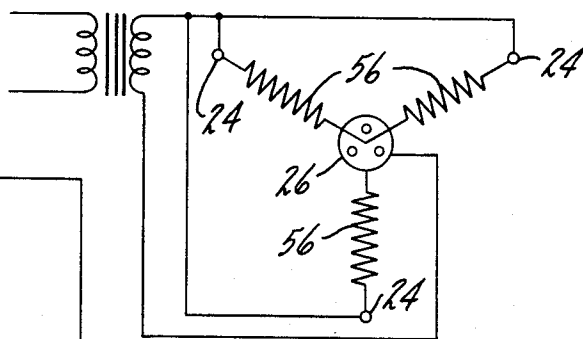


fig. 7.



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1

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METHOD FOR HIGH-TEMPERATURE TREATMENT OF PETROLEUM COKE

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12 Claims

ABSTRACT OF THE DISCLOSURE

The invention provides a method and apparatus for high-temperature treatment of petroleum coke. In carrying out the method, calcined petroleum coke, which is preferably hot, is introduced into a graphitizing zone and heated by direct electrical resistance. The coke is continuously agitated during the heating, and is moved downwardly through the graphitizing zone. After passing through the graphitizing zone, the coke is continuously transferred to a tempering and cooling zone, where it is continuously agitated. If it is desired to desulfurize the coke, it is heated to at least about 1700° C., while graphitization requires a temperature of at least about 2200° C.

The present invention relates to an improved method for the high-temperature treatment of petroleum coke.

The desulfurization and graphitization of petroleum coke require heating to very high temperatures. Desulfurization generally requires a temperature of at least about 1700° C. and preferably about 2000° C., while graphitization requires a temperature of at least about 2200° C., and preferably at least about 2500° C. Because of these very high temperatures, it has not heretofore been possible to desulfurize or graphitize petroleum coke in a continuous process on a commercial scale.

Generally, the present invention provides a method and apparatus for the continuous high temperature treatment of petroleum coke. In carrying out the method, petroleum coke is first calcined by heating it to a temperature of at least about 900° C. The calcined coke is continuously delivered to a heating zone, preferably while it is still hot. The coke is heated in the heating zone by direct electrical resistance to a temperature of at least about 1700° C. If it is desired to graphitize the coke, it must be heated to at least about 2200° C. While in the heating zone, a central portion of the coke is continuously agitated by applying a rotational force to the coke about a vertical axis. Such agitation maintains a static layer of material adjacent to the walls of the heating zone, thus providing a layer which insulates the walls against high temperatures. At the same time that the coke is agitated, it is moved downwardly through the zone. The coke moves out of the heating zone at the bottom where it is continuously transferred to a tempering and cooling zone. In the upper tempering portion of the tempering and cooling zone, the coke is agitated without further heating to allow the temperatures to equalize, and to allow for the treatment of any portion of the coke that did not reach the desired temperature in the heating zone. The treated coke is then moved to the lower, cooling portion of the tempering and cooling zone, where agitation is continued to provide for uniform cooling.

The present invention also provides improved apparatus for the high-temperature treatment of petroleum coke. The apparatus comprises means defining a heating zone together with coke input means communicating with an upper portion of the heating zone and at least one electrode in an upper portion of the heating zone. Means defining a tempering and cooling zone are located below the heating zone, and an agitator-electrode is positioned

2

at the bottom of the heating zone and mounted for rotation in a horizontal plane. The agitator-electrode has at least one aperture providing communication between the heating zone and the tempering and cooling zone.

The invention, its construction and method of operation, together with the preferred embodiments thereof, will be best understood by reference to the following detailed description, taken together with the drawings, in which:

FIG. 1 is a cross-sectional elevation view of an apparatus embodying the features of the present invention;

FIG. 2 is a cross-sectional view taken along line 2—2 of FIG. 1;

FIG. 3 is a cross-sectional view taken along line 3—3 of FIG. 1;

FIG. 4 is a perspective view of the agitator employed in the preferred embodiment;

FIG. 5 is a circuit diagram for an apparatus constructed in accordance with the present invention;

FIG. 6 is a circuit diagram for a modified apparatus constructed in accordance with the present invention;

FIG. 7 is a circuit diagram for a second modified apparatus constructed in accordance with the present invention.

In carrying out the method of the present invention coke is calcined in a conventional manner in a conventional calcining furnace by heating it to at least about 900° C., and preferably to about 1350° C. In the preferred embodiment, a continuous calcining furnace is employed, and the coke is continuously transferred to a heating zone while still hot. The hot calcined coke is heated by direct electrical resistance to a temperature of at least about 1700° C. By agitating the coke in the heating zone, it has been found that the heat is evenly distributed, and that the production of channeling and "hot spots" is avoided.

In order to produce a high-quality product, it is essential that the coke all be heated to about the same temperature. Accordingly, in the present invention the coke is transferred to the tempering portion of a tempering and cooling zone wherein it is again continuously agitated without significant heating or cooling in order to mix the coke thoroughly and equalize the temperature throughout the mass. The tempering zone actually forms the upper portion of the tempering and cooling zone, while the cooling zone forms the lower portion. In the cooling portion, the temperature of the treated coke is lowered so that the material can be handled. Agitation of the coke in the cooling portion of the tempering and cooling zone promotes uniform cooling and prevents channeling and blockages.

In the most preferred embodiment of the present invention, an inert gas is passed upwardly through the coke in the heating zone. Any gas that does not react with the coke may be employed, although nitrogen is preferred because of its low cost. Optionally, a minor amount of a halogen-bearing gas may be mixed with the inert gas and simultaneously introduced into the heating zone.

The term "halogen-bearing gas" refers to materials that may be introduced into the heating zone in the gaseous state, and which react with impurities in the coke to produce gaseous halogen compounds of increased volatility. The use of a halogen-bearing gas thus serves two purposes. First, it aids in purifying the coke at high temperatures by increasing the volatility of the contaminants. Second, it aids in maintaining these impurities in a gaseous state, so that they are removed from the heating zone, rather than being condensed on the interior walls. The purification aspect is of little importance if the coke is being treated to very high temperatures, i.e., around 2500° C. or above. However, even at these high temperatures, the

use of a halogen-bearing gas is valuable in preventing condensation of gaseous impurities within the heating zone.

Suitable halogen-bearing gases are well known in the art. Exemplary gases include chlorine, fluorine, carbon tetrachloride, hydrogen chloride, and the like. Bromine, iodine, and their compounds are not generally considered suitable.

Referring to the drawings, FIG. 1 shows a furnace constructed in accordance with the present invention and generally indicated by reference numeral 10. The furnace 10 is divided into an upper heating zone 12 and a lower tempering and cooling zone 13. The tempering and cooling zone 13 is, in turn, divided into an upper tempering zone 14 and a lower cooling zone 16. The heating zone 12 is defined by a refractory encasement 18.

Coke to be heat-treated is fed into the furnace 10 through a coke inlet conduit 20, which communicates with an upper portion of the heating zone 12. In the most preferred embodiment, the coke inlet conduit 20 communicates with the outlet end of a continuous calcining furnace 22, which is of conventional design. The coke inlet conduit 20 is surrounded by one or more electrodes 24. In the preferred embodiment, as shown in FIG. 2, there are three such electrodes 24 arranged around the coke inlet conduit 20 in a triangular pattern.

As shown in FIG. 1, the heating zone 12 in the preferred embodiment has a lower portion which is formed in the shape of a truncated cone converging toward the bottom. At the bottom of the heating zone 12 is an agitator, generally indicated by reference numeral 26, which is mounted for rotation in a horizontal plane, and which also forms an electrode, an electrical neutral point, or a ground point in the electrical system, as hereinafter described. The heating zone 12 is formed in a shape that produces a static layer of graphite or desulfurized coke against the walls of the zone, insulating the walls from the high temperatures encountered. Because of the positioning of the electrodes 24 and agitator 16, this static layer will be outside the current flow, and will not be heated significantly by electrical resistance.

As shown in FIG. 1, the agitator 26 has an upper portion 28, and a lower, tubular portion 30. The upper and lower portions 28, 30 are joined together by suitable means, such as screw threads.

Referring to FIGS. 3 and 4, the upper portion 28 of the agitator 26 has upstanding agitation blades 34 which separate three apertures 36 as shown in FIG. 1, the apertures 36 providing communication between the heating zone 12 and the tempering zone 14. In the most preferred embodiment, the agitation blades 34 are surrounded by a generally cylindrical wall 38, which aids in feeding treated coke toward the apertures 36 when the agitator is rotated as hereinafter described.

Referring to FIG. 1, a stationary cylinder 42, made of suitable refractory material, penetrates axially within the agitator 26 in spaced relationship with the inside walls thereof, so as to form a tempering zone 14 and cooling zone 16 of annular shape. The stationary cylinder 42 has a central gas channel 44 which provides communication between a gas inlet connection 46 at the bottom of the cylinder 42 and a gas outlet 48 at the top of the cylinder 42. As previously mentioned, in carrying out the method of the present invention, it is preferred to deliver an inert gas, which may be mixed with a halogen gas, upwardly through the coke in the heating zone 12 in order to carry away volatile materials. The gas and volatile materials are removed from the furnace 10 through a vent 49, communicating with an upper portion of the heating zone 12.

The cooling zone 16, which is defined by the stationary cylinder 42 and the lower portion 30 of the agitator 26, is surrounded by a cooling jacket 50 having pipes 51 for circulating a suitable coolant such as water. Cooling means could also form part of the stationary cylinder 42,

either as an alternative or in addition to the cooling jacket 50 shown in the drawings.

Any of a variety of means can be employed to rotate the agitator 26. In the embodiment shown, a straight-out gear 52 is mounted at the base of the cooling jacket 50. This gear 52 may engage a suitable drive gear, not shown in the drawings.

The treated coke is removed from the furnace 10 through a pair of outlet conduits 54 which communicate with the bottom of the cooling zone 16 as shown in FIG. 1. Material moving outwardly through the outlet conduits 54 is delivered to suitable conveying means such as an auger, a belt-type conveyor, or a vibrator 55, as shown in the drawing.

Numerous electrical systems may be employed in order to heat coke by electrical resistance in accordance with the present invention. Referring to FIG. 5, a highly desirable system employs three electrodes, each of which is connected to one of the terminals of a three-phase system. In the arrangement shown, the coke within the heating zone is represented by the electrical resistance symbols 56. In the arrangement shown in FIG. 5, the agitator 26 is grounded so that the electric current will tend to be drawn downwardly from the electrodes 24 through the graphite to the agitator 26. It is possible to also employ the same arrangement wherein the agitator 26 is not grounded. In the latter arrangement, the agitator 26 forms an electrical neutral point in the circuit, and will also tend to "draw" the electric current toward it.

Referring to FIG. 6, a second electrical system employs two electrodes 24, while the agitator 26 itself forms the third electrode, each electrode being connected to one terminal of a three-phase system.

Referring to FIG. 7, a single-phase alternating current system may also be employed in accordance with the present invention. In the embodiment shown in FIG. 7, three electrodes 24 are employed, all of which are connected to the same pole. The agitator 26 forms the opposite pole of the system.

The voltage required to operate the furnace of the present invention will vary, depending mainly on the size of the furnace. Generally, less than 40 volts will be required. Both the voltage and amperage must be adjusted to produce the temperatures desired within the heating zone 12.

The refractory encasement 18 around the heating zone 12 may be made of any suitable refractory material, although it should be designed to withstand the high temperatures encountered at the walls of the heating zone 12. Preferably, the upper portions of the heating zone (where the least heat is encountered) will be surrounded by high-temperature fire brick. In the lower portions of the heating zone 12, where the coke becomes quite hot, materials that are capable of withstanding higher temperatures must be employed. One suitable construction employs graphite walls insulated with carbon black, such as a form of carbon black known under the trade name of "Thermax." The tempering and cooling zone 13 is also preferably surrounded by a high-temperature refractory material such as graphite.

The agitator must also be made of material that can withstand very high temperatures, yet is also capable of conducting electricity. Suitable materials include graphite, tantalum, and tungsten.

The apparatus of the present invention may be employed to treat cold calcined petroleum coke, although it is preferred to employ the apparatus in combination with a continuous calcining furnace, so that the coke will have been raised to calcining temperature before it is introduced into the heating zone 12, avoiding a large wastage of energy. In operation, the tempering and cooling zone 13 will be filled with graphite or desulfurized coke, while the heating zone 12 will be filled at least to the level of the electrodes 24. The flow of material through the furnace 10 is controlled by the speed of the conveyor

55. That is, the outlet conduits 54 will be filled with treated coke and all the material above the outlet conduits 54 will rest on the material below it. The material in the outlet conduits 54 in turn rests upon the material carried by the conveyor 55. Thus, if it is desirable to increase the speed at which coke is moved through the furnace 10, it is simply necessary to increase the speed of the conveyor 55. It may also be necessary to increase the speed of the agitator 26 to maintain smooth, continuous feed. Thus, treated coke is continuously removed from the furnace 10 at the outlet conduits 54, while untreated coke is continuously introduced at the coke inlet conduit 20.

The coke is ordinarily introduced into the furnace 10 at a temperature of at least about 900° C., which is achieved in the calcining furnace 22. The calcining furnace 22 will have removed the bulk of the volatile materials from the petroleum coke.

Under the influence of the rotating or oscillating agitator 26, the incoming coke is mixed with hot material in the heating zone 12. Electric current is delivered to the material by the electrodes 24, heating the coke by electrical resistance. As the coke moves downwardly through the heating zone 12, the temperature is continuously raised until it reaches a maximum of about 1700–3000° C. This maximum will be achieved toward the bottom of the heating zone 12. The continuous agitation during this heating prevents channeling of the coke, and breaks up paths of high electrical conductivity, which could produce "hot spots."

The heating rate must be properly controlled if a high-quality product is to be produced. Control of the heating rate is particularly important in the production of graphite, since this involves a change in the crystalline structure of the carbon. As a general matter, the coke should be heated at a rate that does not exceed about 20° C./minute at temperatures above 1400° C. Heating rates in excess of this tend to produce puffing in the coke, and do not allow sufficient residence time in the heating zone 12 for the coke to be properly treated.

Residence time of the coke in the heating zone 12 must, of course, be controlled as a function of the temperature at which the coke is introduced into the zone, the temperature at which it is removed, and the heating rate.

The bottom of the heating zone 12 is preferably formed in the shape of an inverted cone for two reasons. First, this shape tends to guide the coke toward the agitator 26. More importantly, as the petroleum coke is heated and purified, its electrical conductivity increases. The progressive decrease in the cross-sectional area toward the bottom of the heating zone 12 therefore holds the resistance of the material relatively constant, so that the rate at which heat is generated remains relatively uniform through the heating zone 12.

As the petroleum coke is heated, an inert gas, preferably nitrogen, is delivered to the heating zone 12 through the gas channel 44 and the gas outlet 48. This gas passes upwardly through the heating zone 12, carrying away volatiles which are vaporized and removing them at the outlet vent 49. A minor amount of a halogen-bearing gas, preferably chlorine, may be mixed with this gas. The halogen-bearing gas aids in the volatilization of impurities by converting them into halides, which generally have an increased volatility.

The downward moving material within the furnace 10 passes through the apertures 36 and into the tempering zone 14. Very little cooling takes place in this portion of the apparatus. Instead, the primary function is to equalize the temperature throughout the treated coke, while at the same time allowing any remaining volatile materials to escape. Because the outer wall of the tempering zone 14 is formed by the upper portion 28 of the agitator 26, while the inner wall is formed by the stationary cylinder 42, there will be some agitation of the

coke within the tempering zone. In addition, the rotation of the agitator prevents hang-ups and channeling of the coke within the tempering zone 14.

The treated coke moves from the tempering zone 14 downwardly into the cooling zone 16, where it is cooled by cold water fed into the cooling jacket 50. Within the cooling zone, the temperature of the material is preferably lowered to about 400° C. or below. Finally, the cooled treated coke is delivered through the outlet conduit 54 to the conveyor 55. Again, channeling and hang-ups are prevented by the rotation of the outer wall of the cooling zone 16. Of course, the same objective could be accomplished by suitably modifying the apparatus to have the inner wall rotate, while the outer wall remained stationary. In this instance, the outer wall, of course, would be formed by a member that is not connected to the graphite agitator.

The speed at which the agitator 26 is rotated depends upon a number of factors. The agitator should be rotated at a high enough speed to achieve adequate mixing and uniform heating within the heating zone 12, but should not run so fast as to cause excessive wear on parts or to waste energy. The agitator 26 should also rotate fast enough to achieve uniform feed through the furnace 10. Generally, the agitator should rotate at speeds in the range of about 2 to 200 revolutions per hour, speeds of about 5 to 25 revolutions per hour being preferred. The agitator may either be rotated continuously, or may be oscillated back and forth.

Obviously, many modifications and variations of the invention as hereinbefore set forth will occur to those skilled in the art, and it is intended to cover in the appended claims all such modifications and variations as fall within the true spirit and scope of the invention.

I claim:

1. A method for treating petroleum coke comprising: continuously introducing calcined petroleum coke into a heating zone; heating said coke by direct electrical resistance in said heating zone to a temperature of at least 1700° C.; continuously agitating a central portion of said coke in said heating zone by applying a rotational force to said coke about a vertical axis, whereby a static layer of material is maintained adjacent to the walls of said heating zone while moving said coke downwardly through said heating zone; continuously transferring said coke to a tempering and cooling zone; and continuously agitating and cooling said coke within said tempering and cooling zone.

2. The method as defined in claim 1 wherein said coke is heated to at least 2200° C., whereby to graphitize said coke.

3. The method as defined in claim 2 wherein said coke is heated to at least 2500° C.

4. The method as defined in claim 1 further including the step of first calcining said petroleum coke in a calcining zone by heating said coke to at least about 900° C., and wherein said calcined coke is continuously introduced into said heating zone while still at a temperature of at least about 900° C.

5. The method as defined in claim 4 wherein an inert gas is passed upwardly through said coke in said heating zone.

6. The method as defined in claim 5 wherein said inert gas contains a minor amount of a halogen-bearing gas mixed therewith.

7. The method as defined in claim 6 where said inert gas is nitrogen and said halogen-bearing gas is chlorine.

8. The method as defined in claim 7 wherein said coke is heated to at least 2200° C. in said heating zone, whereby to graphitize said coke.

9. The method as defined in claim 8 wherein said coke is heated to at least 2500° C.

10. The method as defined in claim 2 wherein an inert gas and a halogen-bearing gas are passed upwardly through said coke in said heating zone.

7

11. A method for graphitizing petroleum coke comprising: calcining said petroleum coke in a calcining zone by heating said coke to a temperature of at least about 900° C.; continuously introducing said calcined coke into a heating zone while still at a temperature of at least about 900° C.; heating said coke by direct electrical resistance in said heating zone to a temperature of at least 2500° C.; continuously agitating a central portion of said coke in said heating zone by applying a rotational force to said coke about a vertical axis, whereby a static layer of material is maintained adjacent to the walls of said heating zone while moving said coke downwardly through said heating zone; passing an inert gas upwardly through said coke in said heating zone; continuously transferring said coke to a tempering and cooling zone; agitating said coke in said tempering and cooling zone while permitting the temperature of said coke to equalize; and cooling said coke in said tempering and cooling zone.

12. The method as defined in claim 11 wherein said

8

inert gas is nitrogen, and wherein said nitrogen contains a minor amount of chlorine mixed therewith.

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EDWARD J. MEROS, Primary Examiner

U.S. Cl. X.R.

13—7; 202—265; 423—461