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(54) **Title**: REDUCED PUFFING NEEDLE COKE FROM COAL TAR DISTILLATE

(57) **Abstract**: A reduced puffing needle coke is formed, which includes a reduced nitrogen content within the coke so that the coke particles do not experience as much puffing during the formation of graphitized carbon articles produced from such coke upon heating to graphitization temperatures.

REDUCED PUFFING NEEDLE COKE FROM COAL TAR DISTILLATE

BACKGROUND OF THE INVENTION

TECHNICAL FIELD

[0001] The present invention relates to needle coke useful for various applications including forming graphite electrodes. More particularly, the present invention relates to a process for producing needle coke exhibiting reduced puffing characteristics from a coal tar distillate starting material. The invention also includes the reduced puffing needle coke.

BACKGROUND ART

[0002] Carbon electrodes, especially graphite electrodes, are used in the steel industry to melt both the metals and supplemental ingredients used to form steel in electrothermal furnaces. The heat needed to melt the substrate metal is generated by passing current through a plurality of electrodes and forming an arc between the electrodes and the metal. Currents in excess of 100,000 amperes are often used.

[0003] Electrodes are typically manufactured from needle coke, a grade of coke having an acicular, anisotropic microstructure. For creating graphite electrodes that can withstand the ultra-high power throughput, the needle coke must have a low electrical resisitivity and a low coefficient of thermal expansion (CTE) while also being able to produce a relatively high-strength article upon graphitization.

[0004] The specific properties of the needle coke may be dictated through controlling the properties of the coking process in which an appropriate carbon feedstock is converted into needle coke. Typically, the grade-level of needle coke is a function of the CTE over a determined temperature range. For example, needle coke is usually classified as having an average CTE of from about 0.00 to about $5.00 \times 10^{-6}/C^{o}$ over the temperature range of from about 30ºC to about 100ºC.

[0005] To evaluate the CTE of a coke, it is first calcined to a temperature of about 1,000 to 1,400℃. It is then admixed with a molten pitch binder and the pitch/coke mixture is extruded to form a green electrode.

The electrode is then baked to about 800-900°C and then heated from 2,800-3,400°C to effect graphitization. The CTE is measured on the graphitized electrode using either a dilatometer or the capacitance method (the capacitance method is described in the publication titled "Capacitance Bridge Measurements of Thermal Expansion", presented at the 1986 International Conference on Carbon at Baden-Baden Germany. The procedure for evaluating coke CTE is found in publication by E.A. Heintz, Carbon Volume 34, pp. 699-709 (1996), which are incorporated herein by reference in their entirety).

[0006] In addition to low CTE, a needle coke suitable for production of graphite electrodes must have a very low content of sulfur and nitrogen. Sulfur and nitrogen in the coke generally remain after calcination and are only completely removed during the high temperature graphitization process.

[0007] If the needle coke contains too great a concentration of nitrogen or sulfur, the electrode will experience "puffing" upon graphitization. Puffing is the irreversible expansion of the coke particles, which creates cracks or voids within the electrode, diminishing the electrode's structural integrity as well as drastically altering both its strength and density. More specifically, macro stress from puffing develops from temperature gradients during graphitization, because the exterior and interior portions of the electrode pass through the puffing range at different times. Micro stress occurs at the coke particle/binder coke interface during puffing because the coke particle is expanding significantly and the surrounding binder coke is expanding at a much lower rate due to the normal expansion. Both macro and micro stresses degrade the physical properties of the electrode and can cause cracking in the extreme case.

[0008] The degree of puffing generally correlates to the percentage of nitrogen and sulfur present in the needle coke. Both the nitrogen and sulfur atoms may be bonded to the carbon within the feedstock through covalent bonding typically in a ring arrangement. The nitrogen-carbon and sulfur-carbon bonding is considerably less stable than carbon-carbon bonding in high temperature environments and will rupture upon heating. This bond

rupture results in the rapid evolution of nitrogen and sulfur containing gases during high temperature heating, resulting in the physical puffing of the needle coke.

[0009] A variety of methods have been attempted to reduce the puffing of needle coke during the graphitization process, with most of the focus directed to the effects of sulfur. The approaches used involve either treating the needle coke feedstock with a catalyst plus hydrogen to remove sulfur prior to coking or to introduce chemical additives to the coke which inhibit the puffing process.

[0010] One such approach has been the use of an inhibitor additive to either the initial feedstock or the coke mixture prior to the graphitization to an electrode body. U.S Patent No. 2,814,076 teaches of the addition of an alkali metal salt to inhibit the puffing. Such salts are added immediately prior to graphitizing an electrode. Notably, sodium carbonate is added by impregnating the article through a sodium bicarbonate solution.

[0011] U.S. Patent No. 4,312,745 also describes the use of an additive to reduce the puffing of sulfur-containing coke. Iron compounds, such as iron oxide are added to the sulfur-containing feedstock with the coke being produced through the delayed-coking process. In some instances the inhibitors may increase the CTE and the coke would not be as suitable for making an electrode.

[0012] Orac et al. (U.S. Patent No. 5,118,287) discloses a process for treating high sulfur petroleum coke to inhibit puffing wherein particles of the petroleum coke are contacted with a compound containing an alkali or alkaline earth metal selected from the group consisting of sodium, potassium, calcium and magnesium, at an elevated temperature above that at which the alkali or alkaline earth metal compound begins to react with carbon, but below the temperature at which the coke particles would begin to puff in the absence of the compound. The coke particles are maintained at an elevated temperature for a sufficient period of time to permit the reaction to proceed and allow products of reaction to penetrate into the particles and form an

alkali-or alkaline-earth-metal-containing deposit throughout the mass of the particles; and then cooling the so-treated coke particles.

[0013] Jager (U.S. Patent No. 5,104,518) describes the use of sulphonate, carboxylate or phenolate of an alkaline earth metal to a coal tar prior to the coking step to reduce nitrogen puffing in the 1400℃-2000℃ temperature range. Jager et al. (U.S. Patent No. 5,068,026) describes using the same additives to a coke/pitch mixture prior to baking and graphitization, again to reduce nitrogen-based puffing.

[0014] Other attempts have been made to preclude the puffing of electrodes through the use of carbon additives or various hydro-removal techniques. In U.S. Patent No. 4,814,063, Murakami et al. describes the creation of an improved needle coke through the hydrogenation of the starting stock in the presence of a hydrogenation catalyst. This removes the sulfur from the coke feedstock as H_2S. Subsequently, the hydrogenated product undergoes thermal cracking with the product being cut into different fractions. In Japan Patent Publication 59-122585, Kaji et al. describes hydrorefining a pitch in the presence of a hydrogenating catalyst to remove nitrogen and sulfur, followed by coking of the pitch to give a reduced puffing needle coke.

[0015] Goval et al. (U.S. Patent No. 5,286,371) teaches of passing a feedstock through a hydrotreating reaction zone to produce a hydrotreated residual product wherein the product can undergo a solvent extraction process.

[0016] Didchenko et al. (U.S. Patent No. 5,167,796) teaches the use of a large pore size hydrotreating catalyst with hydrogen to remove sulfur from a petroleum decant oil prior to coking.

[0017] Unfortunately, needle coke produced by the prior art usually fails to address the problems of nitrogen remaining in the needle coke that is to be graphitized into an electrode. The additives used to reduce the puffing characteristics of needle coke counteract the sulfur components which would otherwise be liberated from the needle coke but fail to preclude puffing resulting from the nitrogen components. It is commonly believed that

nitrogen puffing inhibitors are not effective. Since nitrogen puffing is not controlled, the use of such additives result in a finished electrode product of inferior quality as the electrode will likely possess both a lower density and a lower strength. The addition of chemicals to the coke feedstocks or to the pitch can lead to the presence of solids during mesophase formation which could raise the CTE of the derived coke. Furthermore, hydrogenation processes require a significant energy input as high temperature are needed for extended heat treatments to remove a substantial amount of nitrogen from the feedstock. Furthermore, hydrogen must be applied for the hydrogenation and accompanying removal of the sulfur and nitrogen from the feedstock.

[0018] What is desired, therefore, is a process for producing reduced puffing needle coke which does not require the use of puffing inhibitor additives and therefore does not decrease the strength and density of the final electrode. Furthermore, a process is desired requiring less thermal energy for the removal of nitrogen from the feedstock as well as no input stream of hydrogen. Indeed, a process which is superior in removing nitrogen from a feedstock for the production of needle coke and/or binder pitch for producing a graphitized electrode article has been found to be necessary for producing high strength, reduced-puffing electrodes. Also desired is the inventive reduced-puffing needle coke with reduced nitrogen content for the production of graphite electrodes.

BRIEF DESCRIPTION

[0019] The present invention provides a process which is uniquely capable of reducing the nitrogen content of a coal tar distillate feedstock for creating reduced-puffing needle coke. Preferably, the feedstock comprises heavy creosote oil, middle creosote oil and light creosote oil, although other coal tar distillate feedstocks may also be employed, as would be familiar to the skilled artisan. The inventive process provides a method where neither additives nor high temperature hydrogenation steps are necessary to remove the nitrogen from the coal tar distillate feedstock in the process of making needle coke. Such reduced-puffing needle coke resists expansion during

graphitization and provides electrode articles with improved density and strength characteristics, a combination of needle coke characteristics not heretofore seen. In addition, the inventive process for producing needle coke provides a reduced-puffing needle coke from coal tar distillate without the excessive expenditures of both hydrogen and thermal energy.

[0020] More particularly, the inventive process reduces the nitrogen present in the coal tar distillate feedstock by means of a nitrogen removal system. The nitrogen removal system allows the nitrogen-containing components of the coal tar distillate to be physically removed with the use of an adsorbent. Such nitrogen removal systems allow for the entering coal tar distillate feedstock stream to have a nitrogen content of from about 0.4% by weight to about 2% by weight and will produce a calcined needle coke product having a nitrogen content of from about 0.03% to about 0.4% by weight. An important characteristic of this inventive process is the ability for the nitrogen removal process to function throughout a wide range of temperatures. Specifically the nitrogen removal system can function at ambient conditions as well as the standard temperatures required for the flow of a coal tar distillate feed stock. For the removal of nitrogen, the coal tar distillate feedstock can flow through a variety of reactor designs, including absorption beds and multiple reactors arranged for the continuous treatment of the coal tar distillate feedstock while a reactor is offline.

[0021] The inventive nitrogen removal system for producing reduced puffing needle coke carbon may use a nitrogen removal method which can operate without the addition of excessive thermal energy or hydrogen gas to facilitate nitrogen removal from the coal tar distillate feedstock. An example of one such nitrogen removal system may be an adsorption system, the nitrogen-containing molecules are adsorbed on specific sites on an article. In one embodiment, the nitrogen removal system may include an activated carbon article as the primary nitrogen removal element of the nitrogen removal system. The activated carbon article acts to bind and physically remove the nitrogen containing components from the coal tar distillate feedstock as the feedstock passes through the nitrogen removal system.

[0022] Alternatively, the nitrogen removal system may contain other adsorbent materials such as activated carbon fibers, activated alumina, silica alumina, silica gel, and xeolites, such as gamma alumina, which can optimally reduce the nitrogen content of the feedstock to about 0.4% or less by weight, preferably about 0.2% or less, and more preferably down to or below about 0.03%.

[0023] In addition, it has been found highly advantageous to have a restoration system for the nitrogen removal system. The restoration system acts to regenerate the removal properties of the nitrogen removal system, through the disengagement of the nitrogen containing components from the removal system. In nitrogen removal systems incorporating an activated carbon structure, the restoration system removes the nitrogen components from the nitrogen binding sites of the activated carbon. Similarly, in nitrogen removal systems incorporating alumina or silica-based adsorbents, the restoration system removes the nitrogen components from the adsorption sites, freeing the active sites for future nitrogen adsorption.

[0024] After the coal tar distillate feedstock exits the nitrogen removal column, the feedstock enters a delayed coking unit for the conversion of treated coal tar distillate feedstock to needle coke. Delayed coking is the thermal cracking process in which the liquid coal tar distillate feedstock is converted into the solid needle coke. The delayed coking of the reduced puffing coal tar distillate feedstock may be a batch-continuous process where multiple needle coke drums are utilized so that one drum is always being filled with feedstock. In another embodiment, the batch-continuous process may be considered a semi-continuous process.

[0025] Additionally, an embodiment disclosed herein, is a process for using a coal tar distillate to produce a reduced puffing needle coke to be employed in applications such as production of graphite electrodes.

[0026] Another embodiment disclosed herein is a process for creating reduced puffing needle coke having a nitrogen reducing system incorporating activated carbon as a nitrogen compound adsorbing agent.

[0027] Still another embodiment disclosed herein is a process for creating reduced puffing needle coke having a nitrogen reducing system incorporating an alumina or silica containing adsorbent for the removal of nitrogen compounds from the coal tar distillate feedstock.

[0028] Yet another embodiment disclosed herein is a reduced puffing coke which contains substantially less nitrogen and exhibits very low or no expansion upon graphitization.

[0029] These aspects and others that will become apparent to the artisan upon review of the following description and can be accomplished by providing a coal tar distillate feedstock having an average nitrogen content of from about 0.5% to about 2% by weight and treating the coal tar distillate feedstock with the nitrogen removal system under relatively mild conditions at temperatures no great than 140℃. A disclosed process advantageously reduces the nitrogen content of the coal tar distillate feedstock to about 0.4% or less by weight, preferably about 0.2% or less, more preferably down to or less than about 0.03%, allowing the feedstock to be converted into reduced-puffing needle coke. If necessary, the viscosity of the coal tar distillate can be reduced by mixing with a suitable solvent in order to facilitate adsorption of the nitrogen-containing species.

[0030] Another disclosed process can utilize a nitrogen removal system with a variety of agents, especially activated carbon as well as activated alumina, silica gels, silica alumina and xeolites. Such adsorbents are readily available from commercial sources such as Aldrich Chem. Co. and have been used in chromatographic separations and for separating heterocyclic components from petroleum-derived diesel oil. (Y. Sano et al., Fuel 84, 903 (2005))

[0031] It is to be understood that both the foregoing general description and the following detailed description provide embodiments of the invention and, when read in light of the attached drawing, are intended to provide an overview or framework of understanding to nature and character of the invention as it is claimed.

BRIEF DESCRIPTION OF THE DRAWING

[0032] Fig. 1 is a schematic flow-diagram of the process to produce reduced puffing needle coke from coal tar distillate feedstock.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0033] Referring now to Figure 1, coal tar distillate 14 is directed toward the nitrogen removal system 16. In nitrogen removal system 16, the coal tar distillate 14 can be heated to facilitate the removal of nitrogen components during the processing within the nitrogen removal system 16, as well as to melt or dissolve any crystalline particles which may be present in the distillate at room temperature. Specifically, slight heating can be utilized to decrease the viscosity of the coal tar distillate 14 and provide better contact between the distillates and the reactive surfaces within the nitrogen removal system. Alternately, the viscosity of the coal tar distillate can be decreased by mixing with and dilution by a solvent. Treatment of certain coal tar distillate feedstocks may require both dilution with a solvent and heating to bring about the most efficient use of the nitrogen removal system. .

[0034] In one embodiment the nitrogen removal system 16 comprises a column loaded with nitrogen removing material. The system may include one or more columns in a parallel arrangement. Multiple columns are ideal so that when one goes off line, nitrogen removal system 16 can still be continuously operated.

[0035] In one alternative, the components of the nitrogen removal system are fixed-bed (static) columns. In these columns the nitrogen-removing material is fixed and the reactor must be taken off-line from coal tar distillate processing to remove or regenerate the nitrogen-removing material. In another alternative, the columns within the nitrogen removal system are moving bed reactors. In moving bed type columns, the unit contains a fluidized bed of nitrogen removing material wherein the material is continuously removed and added to maintain desired activity of the nitrogen removal system.

[0036] One type of nitrogen removing material is activated carbon. One example of preferred type of carbon is a carbon that has been treated to

possess a pore system throughout the carbon structure, resulting in a large internal specific surface area. It is also preferred that the carbon has a large number of active sites for adsorption of nitrogen containing species. Specifically, the activated carbon in the nitrogen removal system 16 can have a surface area in excess of 200 m^2/g, with upper limits above about 3000 m^2/g. Such activated carbon for the nitrogen removal system 16, can be created from a variety of organic sources, including, but not limited to hardwoods, coal and coke products, cellulosic materials, and polymer resins. In many cases the source of activated carbon is coal. Additionally, the activated carbon can be activated carbon fibers, rather than typical activated carbon in granular formation. Typically, the activated carbon will have a trimodal pore distribution of micropores, mesopores, and macropores, with the pore size ranging from less than 2 nanometers for micropores to greater than 50 nm for macropores.

[0037] The primary means of removing nitrogen components from the coal tar distillate feedstock within nitrogen removal system 16 is through adsorption by activated carbon . The two primary physical considerations of the activated carbon to consider in best selecting activated carbon for the adsorption of nitrogen components from a coal tar distillate feedstock are the total surface area and pore structure. A large total surface of the activated carbon permits the availability of more active sites for the interaction with nitrogen components of the coal tar distillate feedstock.

[0038] While any form of activated carbon is effective at nitrogen removal in accordance with the present invention, pH-neutral activated carbon has been found to be especially effective. In addition, in another embodiment of the use of activated carbon in nitrogen removal system 16, acid-washed (or partially neutralized) activated carbon or activated carbon with surface functional groups having high nitrogen affinity is employed, either in substitution for pH-neutral activated carbon, or in combination therewith. Reference herein to “activated carbon” refers to activated carbons generally or to any or all of pH-neutral activated carbon, acid-washed or

partially neutralized activated carbon, activated carbon with surface functional groups, or combinations thereof

[0039] The use of acid-washed or partially neutralized activated carbon may be more effective at the removal of nitrogen-containing heretocyclic componds (typically Lewis bases) from coal tar distillates. The acid-washed or partially neutralized activated carbon would have additional acidic functional groups as compared with pH-neutral activated carbon, which can make bonding interactions with nitrogen-containing species more likely. Activated carbons having surface functional groups with high nitrogen affinity, such as those impregnated with metals such as $NiCl_2$, can more effectively form metal species complexes with nitrogen species, and so trap the nitrogen compounds within the carbon.

[0040] An additional component of nitrogen removal system 16 is the structural elements which maintain the activated carbon while the coal tar distillate passes through the bed. Typical to adsorption with activated carbon, the activated carbon may require a substantial retention time with the coal tar distillate feedstock for the removal of nitrogen. The coal tar distillate may be in contact with the activated carbon on the order of hours to adequately remove nitrogen from the feedstock. To make possible the immobility of the activated carbon, a fixed bed vessel type column is a preferred embodiment, as this style column is commonly used for the adsorption from liquids. In an additional embodiment, the activated carbon can be housed in a moving bed column wherein the activated carbon is slowly withdrawn as it becomes spent.

[0041] For the optimal removal of nitrogen from coal tar distillate 14 by the nitrogen removal system 16, processing parameters can be designed for best reaction conditions between the activated carbon and the coal tar distillate. As adsorption usually increases with decreasing temperature, coal tar distillate 14 may be fed into nitrogen removal system 16 at the lowest temperature consistent with adequate flow of the coal tar distillate. Furthermore, the acidic or basic nature of the distillate can optionally be

altered to also facilitate adsorption if preferable, in some cases allowing the nitrogen within the coal tar distillate to be in a more adsorbable condition.

[0042] Other process considerations may include the time in which the coal tar distillate feedstock is in contact with the activated carbon. An efficiency factor for adsorption may be the total time in which the nitrogen components are able to be in contact with the activated carbon. Increasing contact time between the activated carbon and the coal tar distillate feedstock may allow for a greater proportion of the nitrogen to be removed. Some methods of increasing contact time include reducing the flow rate of the coal tar distillate feedstock, increasing the amount of activated carbon within the bed, or providing activated carbon with a greater surface area.

[0043] Upon diminished performance of the adsorption of nitrogen from the coal tar distillate feedstock, the activated carbon component may be either discarded or reactivated for continued use. Dependent upon the costs of thermal energy and the current price of activated carbon, economics might dictate the disposal of the activated carbon and the deposit of fresh activated carbon within the static beds of nitrogen removal system 16. If nitrogen removal system 16 includes one or more moving bed reactors, the activated carbon can continuously be drawn off as the catalyst becomes spent. Otherwise, the reactor can be shut down and the activated carbon can be removed in a batch wise fashion.

[0044] In a further alternative, the activated carbon of the reactors of nitrogen removal system 16 can undergo regeneration where the activated carbon is significantly freed of adsorbed nitrogen components. In one embodiment, the spent carbon is allowed to flow from nitrogen removal system 16 to the regeneration unit 20 via connection 18. Possible mechanisms for travel of the activated carbon from nitrogen removal system 16 to regeneration unit 20 include either a gravity-induced flow or a pressurized flow arrangement for transport of the spent activated carbon to regeneration unit 20. Alternatively, the static bed containing the spent activated carbon can be completely taken off line and the spent activated

carbon can be removed in a batch-wise fashion and inserted into the regeneration system 20.

[0045] In one embodiment of the regeneration system 20, the nitrogen removal system utilizes a thermal regeneration technique to reactivate the spent activated carbon. Specifically, the regeneration unit may include a furnace or rotary kiln arrangement for the thermal vaporization of adsorbents on the activated carbon. Typical temperatures for vaporizing the absorbed molecules can range from about 400ºC up to about 1000ºC. In one embodiment, the absorbed molecules are vaporized at a temperature of no more than about 900ºC. In another embodiment, the temperature may range from about 400ºC up to about 600ºC. In a further embodiment, the temperature may range from about 700ºC to about 1000ºC. Alternatively, the spent activated carbon can be stripped by steam for the removal of contaminants. In steam stripping regeneration the temperature of the steam can vary from about 100ºC up to about 900ºC for the removal of most adsorbents.

[0046] With the above regeneration techniques the activated carbon will eventually have to be replaced as the thermal regeneration techniques as well as the steam regeneration techniques, do oxidize a portion of the activated carbon each time. Approximately 10% by weight of the activated carbon is lost during each thermal regeneration while about 5% by weight of the activated carbon is lost when utilizing steam regeneration techniques.

[0047] In an alternative embodiment of the nitrogen removal system 16, a variety of inorganic adsorbents can be used in a column type arrangement to function as nitrogen removal system under conditions less severe than prior art processes. The adsorbents can be of a variety of high surface area metallic materials, which include preferably activated alumina, as well as gamma alumina, silica alumina, silica gel, charged silica, titania, zirconia, zeolites, and a variety of high surface area active metal oxides including those of nickel, copper, iron and so on. These supports with their high surface areas provide a large number of active sites for the removal of nitrogen components from the coal tar distillate feedstock.

[0048] Specifically, gamma alumina can have a surface area of from about 1 m^2/g to over 100 m^2/g, is quite rigid and can be formed in a variety of shapes for placement within the nitrogen removal system 16. These shapes include a variety of sized pellets, honeycomb, helical, and a variety of polygonal arrangements typical for fixed bed reactors.

[0049] The alumina adsorbents with an appropriate pore size and surface area for the adsorption of nitrogen components can be used in different forms and shapes including, but not limited to a variety of sized pellets, honeycomb, helical, and a variety of polygonal arrangements typical for fixed bed reactors.

[0050] Similar to activated carbon, inorganic adsorbents such as gamma alumina can also be recycled as their disposal would be quite costly in the production of reduced-puffing needle coke. In one embodiment, larger contaminants can be removed through a steam stripping process wherein the adsorbent material is exposed to steam in a temperature range of from about 100ºC to about 500ºC and a pressure of from about 10 psig (69 kPa(g)) to about 50 psig (345 kPa(g)). If so desired, the upper temperature range may be increased to above 500ºC. Any contaminants not removed from the adsorbent can be removed through a subsequent thermal treatment to regenerate its adsorption activity. The thermal treatment process includes temperatures in the range of from about 500ºC to about 900ºC. Total processing time for regeneration is dependant upon the selected thermal treatment temperature allowing the user to optimize the regeneration specific to the overall needle coke production process. Over repeated regenerations, the adsorbent will lose activity and require replacement or reconstruction.

[0051] Upon exiting the nitrogen removal system 16, the treated coal tar distillate feedstock stream 24 is directed to the coking unit 26. A variety of methods exist for coking a coal tar distillate feedstock, with delayed coking being the most common method for creating needle coke.

[0052] A standard delayed coking unit preferably comprises two or more needle coke drums operated in a batch-continuous process. Typically,

one portion of the drums is filled with feedstock while the other portion of the drums undergoes thermal processing.

[0053] Prior to a needle coke drum being filled, the drum is preheated, by thermal gases recirculated from the coking occurring in the other set of needle coke drums. The heated drums are then filled with preheated coal tar distillate feedstock wherein the liquid feedstock is injected into the bottom portion of the drum and begins to boil. With both the temperature and pressure of the coking drum increasing, the liquid feedstock becomes more and more viscous. The coking process occurs at temperatures of from about 400ºC to about 550ºC and pressures from about ambient up to about 100 psig (690 kPa(g)). Slowly, the viscosity of the treated coal tar distillate feedstock increases and begins to form needle coke.

[0054] The coke produced by the aforementioned process is then calcined at temperatures up to or about 1400ºC. The calcined reduced puffing needle coke preferably has a CTE below about 0.20 $*10^{-6}$/ºC, more preferably below about 0.125 $*10^{-6}$/ºC, and most preferably below about 0.1 cm/cm $*10^{-6}$ /ºC, when measured at a temperature range of 30ºC to 100ºC. Furthermore, the calcined reduced puffing needle coke has less than about 0.4% by weight, more typically about 0.2% by weight, and most preferably down to or less than about 0.03% by weight nitrogen content while having less than about 1.0% by weight sulfur content, allowing the needle coke to exhibit very low nitrogen-induced physical expansion during graphitization to temperatures well above 2000ºC.

[0055] Without intending to limit the scope of the invention, the following examples demonstrate the advantages of the practice of the present invention in removing nitrogen from a coal tar distillate.

Example 1

[0056] A 20 cubic centimeter (cc) sample of coal tar distillate having a nitrogen content of 12,266 parts per million (ppm) is diluted with toluene at a 1:1 ratio by volume, and blended with an absorbent. The absorbent is an activated carbon commercially available from Kansai Coke & Chemical Co. having a surface area of 2700 square meters per gram (m^2/g) and pore volume

of 1.31 milliliters per gram (ml/g). Before the adsorption experiment, the adsorbent is pretreated under vacuum at 80°C in order to remove water and other contaminants, which might inhibit the adsorption of nitrogen compounds. The coal tar distillate/toluene blend is heated to 100°C to have sufficient fluidity and is then mixed with adsorbent at a blend/adsorbent weight ratio of 5:2. Adsorption is performed for 2 hours. After adsorption, the treated coal tar distillate is separated from adsorbent and toluene is removed by evaporation under N_2 flow. The treated distillate is found to have a nitrogen content of 9322 ppm, a decrease of 24%.

Example 2

[0057] In order to remove further nitrogen compounds, two-stage adsorption experiments are performed at the same adsorption conditions. The coal tar distillate produced in Example 1 is separated from the adsorbent, and then immediately mixed with fresh activated carbon for second stage adsorption. The second stage adsorption is also performed at 100°C for 2 h. The resulting coal tar distillate is found to have a nitrogen content of 5650 ppm, a 54% decrease from the original sample.

[0058] Based on the results shown in Examples 1 and 2, the inventive adsorption process at mild operating conditions (low temperature and pressure) can significantly reduce the nitrogen concentration in coal tar distillate, resulting in the production of improved needle coke feedstock.

[0059] Also disclosed is another method of creating reduced puffing needle coke. The method includes a) selecting coal tar distillate; b) passing the coal tar distillate through an activated carbon nitrogen removal system to produce reduced nitrogen coal tar distillate; c) coking the reduced nitrogen coal tar distillate; and d) calcining the coke obtained from step (c) to create calcined reduced puffing needle coke. The activated carbon nitrogen removal system of step (b) may include activated carbon with a surface area of from about 200 m^2/g to about 3000 m^2/g. The activated carbon may have surface functional groups. Also the activated carbon may be impregnated. The activated carbon nitrogen removal system may include one or more columns, and the column may be either a fixed-bed vessel type reactor or the column

may be a moving-bed type. The activated carbon nitrogen removal system of step (b) may also include a regeneration unit wherein the regeneration unit utilizes steam stripping regeneration at a temperature of at least about 100ºC.

[0060] Another method disclosed herein is a method of creating reduced puffing needle coke. Such method may include a) selecting coal tar distillate; b) passing the coal tar distillate through an adsorption zone to produce reduced nitrogen coal tar distillate; c) coking the reduced nitrogen coal tar distillate; and d) calcining the coke obtained from step (c) to create calcined reduced puffing needle coke. The adsorption zone of step (b) may include an inorganic adsorbent wherein the adsorbent is selected from the group consisting of alumina, silica gel, charged silica, silica alumina, titania, zirconia, zeolite, nickel oxide, copper oxide, iron oxide and combinations thereof. A support for the adsorbent may be activated alumina. The adsorption system may further include a regeneration unit, and preferred regeneration unit may steam strip the contaminants from the adsorbent. Alternatively, the regeneration unit may include thermally stripped contaminants from the adsorbent.

[0061] The disclosures of all cited patents and publications referred to in this application are incorporated herein by reference.

[0062] The above description is intended to enable the person skilled in the art to practice the invention. It is not intended to detail all of the possible variations and modifications that will become apparent to the skilled worker upon reading the description. It is intended, however, that all such modifications and variations be included within the scope of the invention that is defined by the following claims. The claims are intended to cover the indicated elements and steps in any arrangement or sequence that is effective to meet the objectives intended for the invention, unless the context specifically indicates the contrary.

What is claimed is:

1. A method of creating reduced puffing needle coke, comprising:
   a. selecting coal tar distillate;
   b. passing the coal tar distillate through an activated carbon nitrogen removal system to produce reduced nitrogen coal tar distillate;
   c. coking the reduced nitrogen coal tar distillate
   d. calcining the coke obtained from step (c) to create calcined reduced puffing needle coke.

2. The method of claim 1 wherein the coal tar distillate of step a) has a nitrogen content of from about 0.5% by weight to about 2% by weight.

3. The method of claim 1 wherein the activated carbon nitrogen removal system of step b) includes activated carbon with a surface area of from about 200 m^2/g to about 3000 m^2/g.

4. The method of claim 3 wherein the activated carbon is in the form of activated carbon fibers.

5. The method of claim 3 wherein the activated carbon is acid-washed or partially neutralized.

6. The method of claim 3 wherein the activated carbon has surface functional groups.

7. The method of claim 3 wherein the activated carbon nitrogen removal system comprises one or more columns.

8. The method of claim 1 wherein the activated carbon nitrogen removal system of step b) further comprises a regeneration unit.

9. The method of claim 8 wherein the regeneration unit utilizes thermal regeneration at a temperature of from about 400ºC to about 1000ºC.

10. The method of claim 1 wherein the calcined reduced puffing needle coke of step d) has a nitrogen content of less than about 0.4%.

11. The method of claim 1 wherein the calcined reduced puffing needle coke of step d) has a nitrogen content of less than about 0.2%.

12. A method of creating reduced puffing needle coke, comprising:
   a. selecting coal tar distillate;

b. passing the coal tar distillate through an adsorption zone to produce reduced nitrogen coal tar distillate;

c. coking the reduced nitrogen coal tar distillate;

d. calcining the coke obtained from step (c) to create calcined reduced puffing needle coke.

13. The method of claim 12 wherein the adsorption zone of step b) includes an inorganic adsorbent.

14. The method of claim 12 wherein the calcined reduced puffing needle coke of step (d) has a nitrogen content of less than about 0.2%.

15. A calcined reduced puffing needle coke derived from coal tar distillate comprising needle coke with a nitrogen content of less than about 0.2% nitrogen.

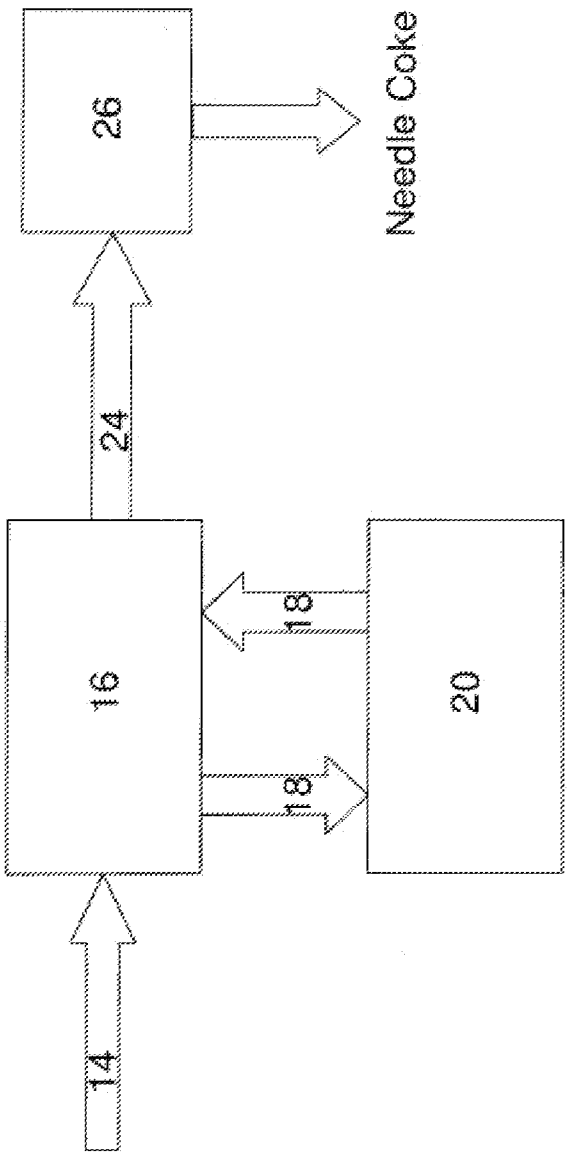


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 09/44055

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C10B 55/00 (2009.01)
USPC - 423/445R; 423/447.4; 208/50
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC: 423/445R; 423/447.4; 208/50

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 423/445R; 423/447.4; 208/50 and all USPC classes (text search - see keywords below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST(USPT,PGPB,EPAB,JPAB); Google; Google Scholar.
Search Terms: calcine, needle, premium, sorbent, absorbent, coke, nitrogen, puff, CTE, coefficient of thermal expansion, activated carbon, GAC, contaminant, coker, creosote, coal tar, tar distillate, regenerate, reactivate, acid washed, neutralized, surface area, BET.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,894,144 A (NEWMAN et al.) 16 January 1990 (16.01.1990), col 1, ln 47-49, col 2, ln 18, col 6, ln 15, 32.	1-15
Y	US 2006/0211906 A1 (BEREZUTSKIY) 21 September 2006 (21.09.2006), para [0032], [0034], [0067], [0106], [0108], [0154].	1-14
Y	US 6,248,230 B1 (MIN et al.) 19 June 2001 (19.06.2001), col 7, ln 61-63, col 8, ln 20-21, 28-32.	10, 11, 14, 15
Y	US 7,028,434 B2 (WAYNICK) 28 March 2006 (28.03.2006), col 4, ln 58.	4
Y	US 7,202,195 B2 (CANNON et al.) 10 April 2007 (10.04.2007), col 3, ln 28.	5
Y	US 6,391,185 B1 (SHVAREV et al.) 21 May 2002 (21.05.2002), col 1, ln 24.	9

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 June 2009 (18.06.2009)	29 JUN 2009
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (April 2007)