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APPLICATION FOR PATENT

METHOD FOR MAKING METALLURGICAL COKE

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METHOD FOR MAKING METALLURGICAL COKE

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10 Claims

ABSTRACT OF THE DISCLOSURE

Metallurgical coke is made from carbon particles by heating the particles to shrink them. Thereafter, the shrunk carbon particles are mixed with a carbonaceous binder and formed into lumps which are heated in a nonoxidizing atmosphere to drive off volatiles and carbonize the binder.

This invention relates to an improved metallurgical coke and method for making it, and is a continuation-in-part application of my expending application Ser. No. 547,683, filed Apr., 1, 1966, which is a continuation-in-part application of my application Ser. No. 329,090, filed Dec. 9, 1963.

In certain parts of the industrialized work, metallurgical coke (also referred to as foundry, furnace, and cupola coke) must be shipped from relatively great distances, adding to its cost. In these same areas, there is an abundance of basic raw materials which will burn, but which have not been put in the form of metallurgical coke. Examples of such materials are carbon particles known as "petroleum coke," which is produced from the thermal cracking of petroleum and gilsonite coke as available from standard delayed or fluidized coking processes. This invention provides an improved process for converting these carbonaceous materials into a unique metallurgical coke for use in furnaces, cupolas, and the like. Such coke must be mechanically strong to withstand the severe mechanical shock and weight loads to which it is subjected in the cupolas and furnaces. It should also burn freely to a low ash content and have a low sulfur impurity. The coke of this invention meets all of these requirements.

An improvement in this fuel product over those of the prior art is the high carbon content and low impurities. Fuel of low ash content is also desirable in cupola operations, since, among other things, these impurities are a waste byproduct discharged as slag which presents disposal problems. Foundry cokes of the prior art are made from coal, principally bituminous, but sometimes with anthracite additions. Such raw materials include impurities laid down in their natural formation. Highest quality coke products made from carefully selected coals as used in cupolas have ash contents in the range of 6% to 9% by weight. The metallurgical coke of this invention contains less than about 3% ash as a result of the inherent high purity of the raw materials used in its manufacture. This negligible amount of ash does not form a refractory coating on the coke as it burns, and, therefore, does not retard burning or inhibit the dissolving of the carbon into the molten metal in the furnace. Dissolving of carbon permits the use of less expensive metal in cupola operation.

Another disadvantage of conventional foundry coke is that it is discharged from ovens in a solid mass which breaks into lumps of irregular size and shape, and requires costly size selection prior to shipment. The size of the coke of this invention, as well as its shape, is predetermined and made uniform by controlled compaction of individual pieces.

In terms of method, this invention includes a process for forming lumps of metallurgical coke from carbon particles selected from the group consisting of fluid petroleum coke and gilsonite coke. The carbon particles are mixed with a carbonaceous binder. The mixture is compacted and extruded continuously through a die. The extruded mixture is cut off to form lumps of the desired size, and the lumps are subsequently heat processed to carbonize them.

Preferably, the carbon particles are preshrunk by heating prior to mixing with the binder. The mixture is also preferably degassed prior to compaction to improve the coherence of the carbon particles with a minimum amount of binder and permits continuous extrusion at relatively low pressure. The resulting product has good strength because of the improved coherence due to the degassing, and has good porosity and density for fast and complete burning, which is required in the operation of cupola furnaces.

The gilsonite and fluid petroleum coke particles are usually spherical, and are ordinarily difficult to bond together in that form without excessive pressure and relatively large amounts of special binder. In addition to the preshrinking and degassing steps described above, preferably, at least 60% of the carbon particles are fractured to less than 100 mesh by an impact milling and crushing process which destroys the spherical shape of the carbon particles and imparts to them angular and irregular surfaces to obtain the desired agglomeration in the large lumps and to provide high reactivity of the final product.

Preferably, the mixture is extruded through a die at a pressure of 100 to 1200 pounds per square inch. This relatively low pressure extrusion permits the product to be manufactured on a substantially continuous basis, making it available at a price to permit its use as a foundry coke. At the present time, the mixture is extruded into a rod having an external diameter of 2 to 6 inches, and it is cut off at a length of in the range of 2 to 8 inches.

The extruded and cut material is preferably heated in the range of 1100 to 2500° F. for 2 to 15 hours, and preferably about 12 hours. I have found that heating of the product can be accomplished in a direct-fired kiln where air in excess of that required to burn the kiln fuel is freely admitted to the heating chamber. The oxidizing atmosphere entering the kiln is rapidly made reducing by burning volatile hydrocarbons discharged from the product upon heating. The hydrocarbon volatiles form a protective blanket of unburned and reducing gases immediately surrounding the product to avoid its unwanted burning during the heating cycle. After carbonizing, the hot product is quenched in a water spray immediately upon removing from the kiln to avoid air burning.

In those cases where the carbon particles have some sulfur present in an amount in excess of that desired when used as a metallurgical coke, the invention includes the steps of blending desulfurizing agents to the mixture. For example, limestone, soda ash, and other compounds with elements having a high affinity for sulfur, are finely divided and dispersed into the carbon aggregate going into the mixture. The relatively large surface area of the fines of the desulfurizing agent, and the intimate distribution of the agent intimately with the sulfur in the carbon particles greatly increases the effectiveness of the desulfurizing agent and eliminates the extra step required in present practice when it is necessary to add desulfurizing agents separately to molten metals.
In terms of product, this invention provides an improved metallurgical coke comprising lumps of carbon particles bonded together to have an apparent specific gravity of at least about 1.25. The carbon particles are selected from either petroleum or gilsonite coke, or a mixture of both.

The lumps of coke are substantially uniform, i.e., less than 5% of the lumps deviate from an average nominal size by more than about 10%. Preferably, the lumps are at least about 40 cubic inches each. The lumps may be of any desired size greater than this, but normally will not be more than 200 cubic inches. Preferably, the lumps have a bulk density of at least 42 pounds per cubic foot. The compressive strength of each individual lump is at least about 5000 pounds per square inch and ash content is not more than about 3%.

The binder conveniently is charred coal tar, but it can be any suitable carbonaceous material such as petroleum tar.

The majority of the particles in the lumps are preferably smaller than 100 mesh in particle size. These and other aspects of the invention will be more fully understood from the following detailed description and the accompanying drawing, which is a schematic flow sheet of the presently preferred process for making metallurgical coke in accordance with this invention.

Referring to the drawing, carbon particles, such as those produced as fluid coke in petroleum refining, or those available as gilsonite coke from standard delayed coking or fluidizing coking processes, are preshrunk by heating in a nonoxidizing atmosphere between about 1600°F and about 1800°F. until most of the inherent shrinkage of the particles is removed. The preshrunk carbon particles are then cooled in a nonoxidizing atmosphere to a temperature of not more than about 350°F., and subjected to fracturing in an impact mill or roll crushe. This is not a conventional milling operation as such to provide a fixed size of aggregate. Most conventional size milling tends to smooth the surfaces of the particles by rapid attrition and wear. This is exactly what the fracturing step of this process avoids, and is particularly important when handling naturally occurring spherical particles such as those produced from fluid petroleum coke or gilsonite coke. It has been found that particles of this nature are best fractured into surfaces which are irregular or angular by high speed impact milling, or roll crushing, and to fracture at least 60% of the spherical particles to particles with surfaces which are irregular and angular and which are reduced to less than 100 mesh size. This type of fracturing provides the desired agglomeration of carbon particles into large lumps, and provides the required high reactivity of the final product because of the increased angularity and surface area of the agglomerated particles. If desired, the carbon particles are preshrunk after milling instead of before as described above.

When required, the desulfurizing agents, such as limestone, soda ash, and the like, are added with the carbon aggregate into the roll crushe or impact mill for dry grinding and intimate mixing with the carbon. If desired, the desulfurizing agent may be separately ground and added to the mixture with the carbonaceous binders.

The fractured carbon aggregate is dumped into a mixing stage 12, which includes a conventional paddle mixer or pug mill, and mixed thoroughly with a carbonaceous binder. The mixing of carbon aggregate with carbonaceous binders has been practiced for some time in the manufacture of carbon and graphite electrodes. Experience in this prior art has dictated prolonged mixing times of about 50 to 90 minutes. The mixing time can be surprisingly found, therefore, that with similar mixing equipment, a mixing time of only about 3 to 5 minutes is sufficient to produce the improved metallurgical coke of this invention. We have found that the degree of mixing controls the density of the final product to a marked degree. For example, a mixing time of 3 minutes provided a final product with a density of 1.26 grams per cc., whereas a 5-minute mixing time produced a final product with a density of 1.48 grams per cc., other conditions being equal.

Various petroleum and coal tar derivatives are used as binders in this invention, their selection being based on economy and availability. Although satisfactory metallurgical coke has been made with various binders, best results have been obtained using a coal tar which is highly viscous at room temperature, and very fluid at 150°F. to 300°F. Therefore, the binder and aggregate are preferably heated to about 130°F. to about 300°F. in the mixer so that the binder is fluid and thoroughly wets the carbon aggregates. The binder is added in the range of 8% to 18% of the weight of the total mixture with the carbon particles.

The carbon aggregate and binder are mixed until the aggregate is thoroughly wetted by the binder, and a plastic mass is formed. The mixture is degassed by a vacuum pump 13 at the discharge end of the mixer. The vacuum pump subjects the mixture to a vacuum of 5 to 29, and preferably 10 to 29, inches of mercury to remove air which was beaten into the mixture during the mixing step. The removal of the air increases the cohesion of the mixture and permits it to be extruded at a relatively low pressure, which increases its reactivity when used as cupola furnace fuel.

The degassed mixture is passed from the mixer into a hopper 14 of an elongated auger extruder 15 in which is mounted a rotatable feed screw 16. One end of the extruder is closed, and the feed screw drives the mixture in it toward the other end, which includes a tapered reduction section 18 and an extension die 19. The size and configuration of the product is determined by the shape of the die and the operation of the cutter blade 20 at the discharge end of the die. The pressure at which the mixture is extruded through the die affects the properties of the final product, and while the pressure is not entirely critical, it is fairly closely controlled. It is one of the advantages of this invention that the mixture can be extruded at relatively low pressure, and on a continuous basis. The forces generated by the auger extruder are relatively fixed so that variations in pressure on the product are obtained by controlling the ratio of the auger barrel size to the die opening, as well as the configuration of the tapered reduction section connecting the barrel to the die. Lumps formed at 100 to 1200 pounds per square inch in the die provide the improved products of this invention. The die has an inside diameter of 2 to 5 inches so that the mixture is extruded in the form of a rod 22 of that diameter range. The cutter is operated to cut the extruded rod into "lumps" about 2 to 5 inches long.

The extruded and cut mixture 24 is fed onto one end of an endless conveyor belt 25, which carries the cut pieces into the inlet of a kiln 26. A mixture of kiln fuel, such as natural gas and air, is fed into the kiln through a supply line 27, and is burned at burners 28 within the kiln to provide a direct-fired kiln operation. The lumps pass through the kiln in a free standing or unsupported position on graphite trays 29 on the endless belt and are heated to about 1900°F. within a few hours. The lumps can be heated to between about 1100°F. and 2500°F., but preferably about 1700°F. to 2000°F. The unfired product is started in the kiln at about 400°F., and kiln temperature is increased by firing the kiln. Firing time can vary, and depends on the product size and kiln efficiency. Total heating cycles of 2 to 15 hours have been used to produce the improved metallurgical coke of this invention. If the carbon particles are not preshrunk as described above, the preferred heating time is about 12 hours. Pre-shrinking reduces the preferred heating time to about 6 hours. Carbonization techniques in the prior art required reducing atmospheres such as in the coking of coal for foundry coke and in carbon electrode manufacture, in
prior practice, heat was applied by conduction through the heating chamber walls. In the present process, carbonization of the lumps is accomplished in the direct-fired kiln where air in excess of that required to burn the kiln fuel is freely admitted to the heating chamber. The oxidizing atmosphere entering the kiln is rapidly made reducing by the burning of the volatile hydrocarbon matter discharged from the mixture, especially the coal tar, upon heating. The firing cycle of the method assumes that a protective blanket of unburned volatile gases evolved from the product immediately surrounds the product to avoid its burning. These volatile hydrocarbon waste gases are burned within the kiln but spaced from the product to provide a supplemental source of heat.

The fully heated coke discharged at the end of the kiln is quenched in a water spray immediately upon removal from the kiln to avoid air burning. The product of this invention has burning characteristics which are a vast improvement over metallurgical coals made in the prior arts. One example of such an improvement is that the use of this invention has a much higher density than conventional foundry coke, and yet is more reactive, i.e., burns faster and to a greater weight loss. This is contrary to what normally would be expected. For example, coconut oil or water dust with a density in excess of 1.5 gm./cc. is much more reactive than conventional coke, which has a density of about 1.0 gm./cc. The product of this invention has a relationship of burning rate to density which is the opposite from the established pattern. The following table exemplifies the unique characteristic:

<table>
<thead>
<tr>
<th>Test</th>
<th>Material</th>
<th>Density (gm./cc)</th>
<th>Percent weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Foundry coke</td>
<td>0.95</td>
<td>30</td>
</tr>
<tr>
<td>J</td>
<td>Foundry coke</td>
<td>1.05</td>
<td>40</td>
</tr>
<tr>
<td>H</td>
<td>Foundry coke</td>
<td>0.95</td>
<td>25</td>
</tr>
<tr>
<td>H</td>
<td>Product B</td>
<td>1.25</td>
<td>30</td>
</tr>
</tbody>
</table>

The results of the above table are given in terms of percentage loss in weight as the result of burning in air, simultaneously and under the same conditions, two conventional foundry cokes and two samples (A and B) of a product made in accordance with the process of this invention. In both instances, the weight loss of the products of this invention is at least 1/2 times that of the conventional foundry coke burned at the same time, indicating a burning rate of the same order of increase.

In using the cupola furnace fuel of this invention, it is, a fuel with low ash content, high density, and uniform size, in melting iron in a cupola furnace, improvements in melting are obtained by a unique method of operating the cupola. Compared with conventional melting of iron with ordinary foundry coke, available improvements provided by the coke of this invention include a higher carbon content in the metal, higher metal temperatures as tapped from the cupola, and increase in melting rate, less air required, and reduced lining wear during the melt period.

Suitable apparatus for the unique use of the coke of this invention consists of a vertical shaft type furnace comprised of a cylindrical metal shell, refractory lined, and constructed with tuyeres or nozzles in the lower portion for the introduction of air. An opening is provided in the upper portion for charging of metal stock and lump carbon fuel. Holes and spouts for molten metal and slag removal are located near the bottom.

A particular feature of this apparatus is that descending meltite stock is intimately contacted by ascending hot gases providing an efficient and direct heat exchange. Lump carbon burned from the initial bed of fuel is continuously replaced by descending fuel to uniformly maintain the height of this bed.

A conventional cupola fulfills this description and is the preferred unit for this method.

The function of cupola fuel is to provide heat for melting and to provide carbon in the resulting molten iron. The nature of the cupola operation is such that a delicate balance must be established between the metal-to-coke ratio, the air-to-coke ratio, the bed height of the burning fuel and the nature of the metal charge to satisfactorily maintain control. Basic rules of operation must be adhered to for optimum results.

Standard operating procedures for the cupola are based on sound theory. In practice, however, best results are established by trial and error. It has been learned over the years that minor changes carefully made during operation will be followed by certain symptoms, each of which indicates specific conditions within the working cupola. These have been published and successfully practiced for decades.

The use of low-ash compacted coke of this invention in accordance with established operating practice for conventional coke frequently created adverse conditions. This led to the conclusion that the coke of this invention was not satisfactory for cupola furnace operation. However, surprising results were disclosed in further trials when certain changes were undertaken contrary to those of prior normal practice to correct symptoms of imbalance. Over all melting conditions with the coke of this invention were thus improved beyond the optimum heretofore attainable with prior conventional coke.

The following will disclose the individual changes from conventional operating procedure included in this new method:

The height of the coke bed is among the most critical items in the operation of a cupola. Tables are available in which coke bed heights in inches above the tuyeres are established in very narrow ranges for various size cupolas, for example:

| 27" | inside diameter—36" to 42" bed height |
| 44" | inside diameter—45" to 51" bed height |
| 78" | inside diameter—47" to 53" bed height |

The bed heights being established in this new method of operation with the coke of this invention are as much as 1/2 less than conventional, for example:

<table>
<thead>
<tr>
<th>60</th>
<th>Conventional</th>
<th>New method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed height (ft)</td>
<td>Bed height (ft)</td>
<td>Change, percent lower</td>
</tr>
<tr>
<td>43</td>
<td>40</td>
<td>35</td>
</tr>
<tr>
<td>35</td>
<td>35</td>
<td>5</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>5</td>
</tr>
</tbody>
</table>

These consistently downward adjustments made to establish individual optimum bed heights for this new method were undertaken in the face of symptoms indicating that the bed was already too low. For example, the color of the slag is used in checking bed performance. The normally grayish-green color of acid cupola slag becomes dull black in color when the bed has fallen below its normal operating height using conventional coke. In operating trials over 30 individual cupolas with the coke of this invention, the slag consistently became black when initial bed height was set at normal. Instead of adding more coke to raise the bed as dictated by established practice, the bed height was lowered at stated above, resulting in better, instead of worse, operating conditions and product.

The cupola lining is eroded during operations in a band at the operating height of the coke bed due to the high temperature of the melting zone. Examination of the refractory burnout sustained at the end of the melt period is conclusive evidence of the lower bed height maintained during operation by this method. An attendant feature is less lining loss to be replaced per ton of metal melted.

Further, an optimum relationship exists between air input, coke charge and melting rate. Published data is rigidly adhered to for good melting practice. A new norm is automatically established for the combustion process when the air blast is increased or decreased. Here again, a procedure contrary to established practice with
conventional coke is followed to obtain optimum results for the new type of fuel. Conventionally, slower melting in the cupola is obtained by using (1) more conventional coke, or (2) less air; and the rate of melting is increased by using (1) more air, or (2) less coke. With the low-ash compacted fuel of this invention, both less air and less coke are used to get higher melt rates. Reduction in both air volume and fuel charge, then, is a departure from normal prior practice to increase melt rate.

Air volumes established in this new coke are as much as ½ less than conventional, for example:

<table>
<thead>
<tr>
<th>Conventionall air volume, (cf.m.)</th>
<th>New method air volume, (cf.m.)</th>
<th>Change, percent lower</th>
</tr>
</thead>
<tbody>
<tr>
<td>6,000</td>
<td>5,400</td>
<td>10</td>
</tr>
<tr>
<td>5,000</td>
<td>2,900</td>
<td>30</td>
</tr>
<tr>
<td>2,400</td>
<td>1,600</td>
<td>35%</td>
</tr>
</tbody>
</table>

Further, the improved coke charge is consistently 5% to 10% less than that required in conventional practice with ordinary foundry coke.

In general, it is desirable to obtain high metal temperatures, melt rates and carbon pickup. For economy, low fuel usage, air volume and lining loss are also desired.

Higher temperature metal is cleaner and more slag-free; the carbon pickup is improved with temperature contributing to greater fluidity and the undesirable sulfur pickup from coke is lower at high temperature.

It is economically advantageous to obtain the highest melt rate possible from a cupola melting unit. In fact, demands often exceed capacity in periods of expanding business conditions, and increased melt rates are frequently desired.

Carbon pickup from coke fuel in a cupola has a substantial effect on hot metal cost. Metal charged to iron-melting operations is selected from: (1) pig iron high in carbon (about 4%); (2) cast iron scrap having somewhat lower carbon content (3 to 3½%); and (3) steel scrap (less than 1% carbon). Sprues and returns from the casting area automatically become a portion of the charge in most instances. In value, the higher carbon content metal (pig iron) carries the highest cost. This can be as much as double the cost of steel, the lowest cost metal in most instances. The greater the carbon pickup from the coke, then, the lower the cost of charging metals.

The least amount of coke fuel consumed to comply with any particular set of melting requirements is obviously desired for economy.

Similarly, the lowest air volume is desired, not only from the standpoint of horsepower requirements, but also because lower air is conducive to less lining wear or heat loss through the cupola shell.

Most cupolas are refined frequently so that the least amount of lining material required is desirable.

For each melting operation, optimum results are largely dependent on the characteristics of the fuel which govern its overall capabilities. Available conventional foundry coke is limited in its capacity to provide the desirable features itemized above. In practice, over a period of time, each conventional melting operation ultimately reaches the limitations of the fuel.

The compacted carbon fuel of this invention raises the capabilities of cupola furnaces for melting iron for castings to new standards heretofore unavailable from established melting practice with conventional foundry coke.

The new fuel is used to achieve:

(1) Increase in carbon content of the metal as much as 12.5%, e.g., from 3.2% to 3.6%.
(2) Metal temperature increase as much as 150° F.;
(3) Increase in melt rate as much as 15% ;
(4) Reduction in fuel charge as much as 15%;
(5) Reduction in air volume as much as 30%;
(6) Reduction in lining wear as much as 50%.

The fuel is made principally from petroleum coke or gilsonite coke particles compacted into individual lumps of substantially uniform size of at least 40 cubic inches each, with ash content of less than 3%, apparent specific gravity of at least 1.25 grams per cubic centimeter, random bulk density of at least 45 pounds per cubic foot; and compressive strength of at least 5000 pounds per square inch. The actual or real specific gravity of the carbon particles is about 1.95.

The following tabulation indicates the comparison between conventional foundry coke and the compacted carbon fuel used in this process for melting iron:

<table>
<thead>
<tr>
<th>Foundry coke</th>
<th>Compacted carbon fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash, percent</td>
<td>2.0-4.0%</td>
</tr>
<tr>
<td>Apparent specific gravity, g/cm³</td>
<td>3.0-3.2</td>
</tr>
<tr>
<td>Bulk density, lb/ft³</td>
<td>40-45</td>
</tr>
<tr>
<td>Compactive strength, psi</td>
<td>1500-2000</td>
</tr>
<tr>
<td>Particle uniformity, percent weight</td>
<td>95%</td>
</tr>
</tbody>
</table>

The following examples show how the product of this invention is used:

**EXAMPLE 1**

A cupola of 60-inch inside diameter melting 12 tons per hour of gray iron for thin-wall castings had its operating conditions stabilized with conventional foundry coke as follows: the charge consisted of cast iron 70-85% and pig iron 15-30%. This product metal with an average carbon content of 3.35%. It was desirable to increase the carbon content of the gray iron and also to decrease the quantity of pig iron in the charge. In using this melting process which employed the compacted carbon fuel as described herein, the average carbon content of the gray iron was increased to 3.52% while the pig iron portion of the charge was reduced to zero to 10%.

**EXAMPLE 2**

The conventional melting method applied to a 42-inch inside diameter cupola was stabilized to provide a melt rate of 3½ tons per hour with 8-to-1 metal-to-conventional coke ratio, 100% cast iron charge. The average carbon content of the resulting gray iron was maintained at 3.50% by adding lump graphite to the charge in the amount of 12½% of the weight of the foundry coke charged (30 pounds graphite, 240 pounds foundry coke). The product of this invention provided an increased average carbon content of the metal from the cupula at 3.60% with complete elimination of the lump graphite addition. The metal-to-coke ratio was established at 10-to-1, which amounted to a 16.6% reduction in coke charged to the cupula (240 pounds reduced to 200 pounds).

**EXAMPLE 3**

The coke of this invention was used in a 60-inch inside diameter cupula melting gray iron for thin-wall castings to increase the melt rate from the 15 tons per hour maximum attainable from conventional melting practice. The melt rate was increased to 16½ tons per hour for a 10% gain. The metal-to-coke ratio was improved from 10-to-1 to 10½-to-1. Coke weight per charge was reduced from 400 pounds to 380 pounds for a 5% reduction. Metal temperatures were maintained above the 2800° F. minimum requirement. Carbon content of the metal was maintained at 3.58%.

**EXAMPLE 4**

Metal temperature increases have been realized through use of the product of this invention as follows:

<table>
<thead>
<tr>
<th>Inside diameter (in.)</th>
<th>Metal-to-coke ratio</th>
<th>Melt rate, tons/hr.</th>
<th>Conventional coke</th>
<th>Improved coke</th>
<th>Increase, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>9:1</td>
<td>2,260</td>
<td>2,000</td>
<td>160</td>
<td>10%</td>
</tr>
<tr>
<td>42</td>
<td>12:1</td>
<td>2,260</td>
<td>2,000</td>
<td>160</td>
<td>10%</td>
</tr>
<tr>
<td>60</td>
<td>10:1</td>
<td>2,050</td>
<td>2,000</td>
<td>150</td>
<td>0%</td>
</tr>
</tbody>
</table>
EXAMPLE 5

Reduction in air volume has been possible through use of this improved coke as follows:

<table>
<thead>
<tr>
<th>Inside diameter (in.)</th>
<th>Coke rate, tons/hr.</th>
<th>Molding coke</th>
<th>Conventional coke</th>
<th>Improved coke</th>
<th>Percent reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>104.1</td>
<td>215</td>
<td>6,000</td>
<td>5,900</td>
<td>10.0</td>
</tr>
<tr>
<td>42</td>
<td>9.5</td>
<td>120</td>
<td>6,000</td>
<td>5,800</td>
<td>3.3</td>
</tr>
</tbody>
</table>

EXAMPLE 6

Cupola lining replacement material has been reduced by this improved coke principally by virtue of reduced air volume as follows:

<table>
<thead>
<tr>
<th>Inside diameter (in.)</th>
<th>Metal-to-coke ratio</th>
<th>Molding coke</th>
<th>Conventional coke</th>
<th>Improved coke</th>
<th>Percent reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>1.95:1</td>
<td>275</td>
<td>700</td>
<td>700</td>
<td>50.0</td>
</tr>
<tr>
<td>41</td>
<td>8:1</td>
<td>925</td>
<td>1,400</td>
<td>700</td>
<td>50.0</td>
</tr>
</tbody>
</table>

Effect of preheating the carbon particles

A principal factor governing the heating time of the mixture of carbon particles and binder in the kiln is the effect of the variation of heating on the strength of the final fired product. For example, as the heating time is reduced, the resultant strength of the product is lessened.

The measurement of product strength used in this determination is a procedure adopted by ASTM as standard to indicate the resistance to impact of coke. This is designated as the ASTM drop shatter test, and measures the percent by weight of coke reduced in size through repeated dropping under fixed conditions to a size passing a 2 inch square screen size. The greater the quantity not passing the 2 inch screen, the higher the resistance to shatter, or greater strength.

Uniformly high strength is important to all metallurgical coke products. In the field of coke used as cupola fuel, a minimum of 96% retained on a 2 inch screen after the shatter test indicates a product of high quality.

In the method as described in my copending application, the minimum heating time is, among other things, limited by the strength requirements described above. For example, with preheating petroleum coke particles, and under a particular set of heat processing conditions, a heating time of 12 hours provided a product strength of 98% in the drop shatter test. With the firing cycle reduced to 6 hours while maintaining other conditions constant, the drop shatter fell to as low as 47%, well below the commercial requirement for cupola fuel.

When the method of this invention is used in conjunction with that of my copending application above mentioned, product strength can be maintained at the required 98% drop shatter while the throughput of the particular heat processing unit is doubled by reducing the heating period from 12 to 6 hours.

By heating petroleum coke used as the basic raw material (carbon particles) for the metallurgical coke of this invention prior to its mixing with the tar binder and compacting into large lumps, the firing time can be greatly reduced without weakening the finished product. The temperature of such preheating is important. It should be in the range of about 1600° F. to about 1800° F., and preferably at about 1675° F. The lower limit of about 1600° F. has been found to be the minimum required to gain the fullest benefit of this preheating stage. On the other hand, preheating to a temperature over about 1800° F. adversely affects the burning characteristics of the final product, with substantial loss of efficiency.

The carbon particle aggregate is preheated in an atmosphere controlled to minimize loss of solid carbon through oxidation. Any of a number of types of heat processing units can be used for this preheating step. These include, but are not limited to: rotary kilns, multiple-hearth furnaces, fluid bed heaters, rotating-hearth furnaces, and the like.

The aggregate is cooled immediately upon discharge from the preheat unit to a temperature of not more than about 350° F. to facilitate subsequent handling and mixing.

The type of cooling apparatus is not critical providing that the cooling is carried out under conditions which minimize loss of aggregate carbon through oxidation, say, in a nonoxidizing atmosphere.

The preheating step causes a volumetric shrinkage of the petroleum coke aggregate prior to mixing with the binder and firing the mixture. For example, a particular petroleum coke was found to have a shrinkage of 19% by volume when heated to 1700° F. in a nonoxidizing atmosphere. When this coke was used without preheating, 4½ inch diameter pieces of the compacted product were reduced in size to 4½ inch diameter upon firing. This shrinkage of the compacted product in firing is believed to weaken the finished pieces when fired too rapidly. When this same coke was preheated to a temperature within the range of about 1600° F. and 1800° F., no size reduction occurred in firing the compacted lumps, and even when the firing time was cut in half, there was no loss in strength.

Consequently, the preheating is carried out at a temperature sufficiently high to ensure that most of the inherent shrinkage of the aggregate coke is removed prior to compacting and subsequent firing.

The main factor affecting the upper limit of preheating temperature is the result of heating on the reactivity, or burning characteristics, of the finished product. It is generally known to those familiar with the art that the resistance of coke to oxidation is increased by increasing the calcining temperature. It is for this reason, among others, that the coke aggregate making up carbon electrodes, anodes, and similar products, is first preheated or calcined at high temperatures. This is normally carried out at a temperature of at least 2400° F. and preferably is taken to 2800° F.

When the product of this invention has its coke aggregate preheated to those temperatures used in prior art processing of electrodes, and the like, the finished product undergoes a substantial loss in efficiency in its burning characteristics. This is apparently the result of the aggregate not burning as rapidly as the residue remaining from carbonizing the tar binder within the body of the product is heated processed. Severe mechanical loss of aggregate particles has been noted when burning a product made with coke calcined at temperatures in the range of 2400° F. to 2800° F. When the preheating temperature is held to not more than 1800° F., this adverse condition is eliminated.

Graphite trays

This invention also improves the service life of the trays or product-carrier members used to pass the lumps through the kiln when carbonizing the binder of the compacted product. Such carrier members, of necessity, undergo the same temperature cycle as the product. In reuse, this heat cycling is constantly repetitive which causes fatigue in most materials leading to costly replacement. This is greatly accentuated when the supporting members are allowed to go through the water-quenching phase of the process along with the product.

In this invention the product supporting members are made of graphite to carry the product through the kiln. Graphite has a high refractoriness and an outstanding capability to withstand repetitive heating and cooling cycles because of its low coefficient of expansion and high thermal conductivity. The limitations for use of graphite at elevated temperatures are generally recognized as being within nonoxidizing conditions. Specific design features of the kiln used in this invention would normally preclude
the consideration of graphite members within its interior. Direct firing and the remittance of excess air to the kiln will be thought to prevent the use of graphite due to its tendency to oxidize. However, the design and operational features of the kiln of this invention are such that a protective non-oxidizing atmosphere of tar volatiles is maintained in the vicinity of the product. This same condition protects the carrier members when made of graphite because they are immediately adjacent to the product. Thus the nonoxidizing atmosphere produced by the volatile from the carbonaceous binder in the kiln protects both the carbon product and the graphite carrier members from oxidation.

In summary, when the improved cupola fuel compacted from high purity carbon, such as petroleum coke, is used in the cupola melting of iron to prepare gray, ductile, and malleable iron in molten form for castings, improvements in melting results are obtained. Compared with melting with conventional foundry coke, the available improvements include: (1) higher carbon content in the metal; (2) higher metal temperatures as tapped from the cupola; (3) increase in melting rate; (4) reduced air volume; (5) less coke charged; (6) less lining wear during the melt period. The product of this invention can be used as a method to achieve one or more of these without adverse effect on the others.

I claim:

1. A process for forming lumps of cupola furnace coke from carbon particles selected from the group consisting of petroleum coke and gilsonite coke, the method comprising fracturing the carbon particles to have irregular surfaces and pass through 100 mesh screen, mixing the carbon particles with a fluid carbonaceous binder derived from the group consisting of coal tar and petroleum derivatives, degassing the mixture with vacuum, compacting and extruding the degassed mixture continuously through a die at a pressure between about 100 p.s.i. and about 1200 p.s.i., cutting off the extruded mixture to form lumps, adding fuel to a direct-fired kiln independently of the lumps and burning the independently added fuel with air to form a flame in the kiln and raise the kiln temperature to between about 1100° F. and about 2500° F., admitting air to the kiln in excess of that required to burn the independently added fuel, and passing the lumps through the kiln to carbonize the binder and drive off volatiles from the binder to form a protective atmosphere around the lumps.

2. A process for forming lumps of cupola furnace coke from carbon particles selected from the group consisting of petroleum coke and gilsonite coke, the method comprising fracturing the carbon particles to have irregular surfaces and pass through 100 mesh screen, mixing the carbon particles with a fluid carbonaceous binder derived from the group consisting of substantially water-free coal tar and petroleum derivatives, degassing the mixture with vacuum, compacting and extruding the degassed mixture continuously through a die at a pressure between about 100 p.s.i. and about 1200 p.s.i., cutting off the extruded mixture to form lumps, adding fuel to a direct-fired kiln independently of the lumps and burning the independently added fuel with air to form a flame in the kiln and raise the kiln temperature to between about 1100° F. and about 2500° F., admitting air to the kiln in excess of that required to burn the independently added fuel, and passing the lumps through the kiln to carbonize the binder and drive off volatiles from the binder to form a protective atmosphere around the lumps.

3. A process for forming lumps of cupola furnace coke from carbon particles selected from the group consisting of petroleum coke and gilsonite coke, the method comprising fracturing the carbon particles to have irregular surfaces and pass through 100 mesh screen, mixing the carbon particles with calcium carbonate and a fluid carbonaceous binder derived from the group consisting of coal tar and petroleum derivatives, degassing the mixture with vacuum, compacting and extruding the degassed mixture continuously through a die at a pressure between about 100 p.s.i. and about 1200 p.s.i., cutting off the extruded mixture to form lumps, adding fuel to a direct-fired kiln independently of the lumps and burning the independently added fuel with air to form a flame in the kiln and raise the kiln temperature to between about 1100° F. and about 2500° F., admitting air to the kiln in excess of that required to burn the independently added fuel, and passing the lumps through the kiln to carbonize the binder and drive off volatiles from the binder to form a protective atmosphere around the lumps.

4. A process for forming lumps of cupola furnace coke from carbon particles selected from the group consisting of petroleum coke and gilsonite coke, the method comprising fracturing the carbon particles to have irregular surfaces and pass through 100 mesh screen, mixing the carbon particles with a fluid carbonaceous binder derived from the group consisting of coal tar and petroleum derivatives, the binder being present in the amount of about 8% to about 18% by weight of the total mixture, degassing the mixture with vacuum in the range of about 10 to about 29 inches of mercury, compacting and extruding the degassed mixture continuously through a die at a pressure between about 100 p.s.i. and about 1200 p.s.i., cutting off the extruded mixture to form lumps, adding fuel to a direct-fired kiln independently of the lumps and burning the independently added fuel with air to form a flame in the kiln and raise the kiln temperature to between about 1100° F. and about 2500° F., admitting air to the kiln in excess of that required to burn the independently added fuel, and passing the lumps through the kiln to carbonize the binder and drive off volatiles from the binder to form a protective atmosphere around the lumps.

5. A process for forming lumps of metallurgical coke from carbon particles selected from the group consisting of petroleum coke and gilsonite coke, the method comprising fracturing the carbon particles by impact milling, mixing the carbon particles with a fluid carbonaceous binder having volatile hydrocarbons, compacting and extruding the degassed mixture continuously through a die at a rate to keep a protective layer of volatile hydrocarbon vapor around the lumps while they are carbonized.

6. A process for forming lumps of cupola furnace coke from shrinkable carbon particles selected from the group consisting of petroleum coke and gilsonite coke, the method comprising fracturing the carbon particles in a non-oxidizing atmosphere at a temperature between about 1600° F. and about 1800° F. sufficiently to remove most of the inherent shrinkability of the particles, cooling the shrunk carbon particles to a temperature below about 350° F., mixing the shrunk carbon particles with a fluid carbonaceous binder derived from the group consisting of coal tar and petroleum derivatives, compacting the mixture, forming lumps from the mixture, and heating the lumps sufficiently to carbonize the binder and drive off volatiles from the binder.

7. A process according to claim 6 which includes the step of fracturing the carbon particles to form irregular surfaces and pass through a 100 mesh screen.

8. A process according to claim 6 which includes the step of degassing the mixture with vacuum.

9. A process according to claim 6 which includes the steps of extruding the mixture through a die at a pressure between about 100 p.s.i. and about 1200 p.s.i., cutting off the extruded mixture to form lumps, heating the lumps to a temperature between about 1100° F. and about 2500°
F. in a nonoxidizing atmosphere to carbonize the binder and drive off volatiles from the binder to form the non-oxidizing atmosphere around the lumps.

10. A method according to claim 9 which includes the step of placing the lumps on a graphite carrier, and passing the lumps and graphite carrier through a kiln at a temperature between about 1100° F. and about 2500° F.

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DAVID EDWARDS, Assistant Examiner.

U.S. Cl. X.R.

201—8, 22, 23, 32, 37; 264—29
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,444,047 May 13, 1969

Thomas J. Wilde

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 27, "work" should read -- world --. Column 3, line 15, "it" should read -- is --; line 53, "are" should read -- area --. Column 4, line 51, "rangs" should read -- range --. Column 6, line 59, "at" should read -- as --. Column 10, line 49, "heated" should read -- heat --. Column 11, line 2, "remittance" should read -- admittance --; line 5, "opertional" should read -- operational --; line 60, "buring" should read -- burning --; line 63, "250°" should read -- 2500° --.

Signed and sealed this 24th day of March 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents