COATING OF REACTIVE FORM COKE BY CATALYTIC DEPOSITION OF GLANZ CARBON
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U.S. Cl. 44-10 R

5 Claims

ABSTRACT OF THE DISCLOSURE

Form coke, coated with a uniform film of glanz carbon, is described, together with methods for producing the film during the production of the coke by the catalytic action of transition metals, especially tin and zinc.

BACKGROUND OF THE INVENTION

Conventionally, coke has been made from coking coals in "by-product" or "beehive" ovens; the coke is obtained as a mass which is discharged from the furnace in the form of lumps or irregular shape. In handling—particularly in shipping—the edges and corners of these lumps break off as fines, which cause difficulty in maintaining bed porosity in the blast furnace, and rapid plugging of the dust-collecting systems associated therewith. However, the fines produced are relatively coarse and are airborne with difficulty in normal handling. This tendency to produce fines is generally tested according to the American Society for Testing and Materials method ASTM D-294-64, called the Tumbler Test. Results are reported as the "hardness factor"—i.e., the weight of the coke sample that is retained on the ¼" standard sieve after tumbling. In normal operations, any coke that degrades in handling to a size that will pass through the ¼" standard sieve is removed by in-transit screening as the coke moves from the supply dump to the skip car for charging to the blast furnace, so that the hardness factor measures the coke available for actual charging to the furnace.

Many attempts have been made to produce substitutes for standard coke from noncooking coals. One such material is described and claimed in Work et al. U.S. Pat. 3,184,293, issued May 18, 1965; is produced by the methods described in Work et al. U.S. Pat 3,140,241 and 3,140,242, issued July 7, 1964. The product made in accordance with these patents comprises briquettes made by briquetting particles of a reactive coal calcinate with oxidized coal tar pitch, curing the briquettes in an oxidizing atmosphere, and then calcining the briquettes to remove volatiles to under 3% without removing all of the hydrogen. The product is very reactive with carbon dioxide, and has a high hardness factor. Tests run in an experimental blast furnace indicated that the uniform size and shape of the particles facilitated furnace operation. Moreover, the particles do not spall on burning, so that the fines problem in the blast furnace is minimized.

However, when a large-scale test in a commercial installation was made, it was found that the briquettes developed a serious fines problem substantially different from that encountered with conventional coke. After a 1,000 mile rail haul, cars of the coke, when unloaded, produced a dust cloud which surrounded the unloading point so that it was difficult to remain close enough to the unloading area to assist in the unloading. Despite the fact that the percentage of fines was no greater than that produced from conventional coke under similar circumstances, the fines from this new form of coke were easily airborne, whereas the fines from conventional coke were not.

One suggestion for overcoming this problem of airborne dust is disclosed in Trechock et al. U.S. patent application Ser. No. 110,608, entitled "Method of Controlling Ultrasfines from Reactive Form Coke," and filed Jan. 28, 1971. In accordance with that application, the reactive form coke is treated with an aqueous dispersion of a film-forming solid to deposit, on and immediately adjacent the surface, a film which contains 0.5 to 3%, and preferably 0.5 to 3%, of the film-forming solid. This treatment is indeed effective in controlling the airborne dust problem, but has a disadvantage in cost. Even 0.5% of solid is 10 pounds per short ton of coke or 5 kilos per metric ton, and, in addition, preparation of the dispersion and application to the form coke are costly.

In the copending Joseph application Ser. No. 134,982, filed Apr. 19, 1971 entitled "Form Coke Coated with Glanz Carbon and Methods of Production," the objections to the Trechock et al. method are overcome by coating reactive form coke with glanz carbon, by introducing into the briquettes, during coking, a stream of gas carrying high concentrations of hydrocarbon vapors, preferably derived from raw coal introduced into the gas stream used for coking. The results are excellent. However, the raw coal introduced ends as a powder in the cyclones used to clean the flue gas coming from the coker, and it is sometimes inconvenient to handle this powder.

OBJECT OF THE INVENTION

This invention aims to produce a glanz carbon coating on reactive form coke during processing subsequent to the formation of the green briquettes from the hydrocarbons which are evolved during the operation, without the need for adding hydrocarbon vapors from outside sources.

STATEMENT OF THE INVENTION

In accordance with this invention, this objective is attained by processing briquettes of reactive form coke after formation in the presence of a catalyst metal, or a salt thereof—most preferably tin or zinc—adjacent the surface of the briquettes; the hydrocarbon vapors coming out of the briquettes are cracked at the surface to deposit thereon a thin film of glanz carbon covering the entire surface and filling the surface pores up to about 5 microns in size. The resultant coated reactive form coke is nondusting and even nonsmuttering. Since the coating occurs simultaneously with curing or calcination, no additional process step with attendant cost is involved. The process is applicable to other form cokes, and improved briquettes result.
DETAILED DESCRIPTION OF THE INVENTION

As indicated above, this invention is designed to control a problem which seems to be unique with the carbonaceous briquettes made in accordance with U.S. Pats. 3,140,241 and 3,410,242. Briefly, in accordance with these patents, a reactive calcinate is mixed by catalyzing coal particles by heating in the presence of added oxygen (U.S. Pat. 3,140,241) or oxygen in the coal (U.S. Pat. 3,140,242) to a temperature above 250° F. and below tar-distilling temperatures, then shock-heating the particles to tar-distilling temperatures by passing them into a fluidized bed maintained at the desired tar-producing temperatures, removing substantially all of the tars in one or more carbonizing stages, and then calcining the particles at a still higher temperature to not over about 3% of volatiles, while maintaining at least 1% by weight of hydrogen in the calcinate. This reactive calcinate is then briquetted with a bituminous binder; the green briquettes are cured in the presence of oxygen at temperatures to cause oxygen-heat induced interaction between the binder and the reactive calcinate, and the cured briquettes are then calcined to produce the desired reactive product. These porous briquettes are hereinafter referred to in the specification and claims as "reactive form coke."

Reactive form coke withstands the ASTM Tumbler Test better than conventional coke, but after long rail shipments and bulk handling produce the serious dusting problem hereinabove referred to. Investigation of the problem established that the dusting was due to the fact that the abraded particles had much higher proportions of ultrafine than conventional coke, and that the extreme dusting was caused by this high concentration of ultrafine particles in the 5 to 20 micron particle size range. Microscopic investigation indicated that the surface of reactive form coke briquettes contained many pores under 5 micron size, so that abrasion ultrafine particles were developed.

The solution of the dusting problem is complicated by the necessity of not changing the essential characteristics of the product for blast furnace and other uses, and of course by the basic requirement of low cost.

The deposition of glanz carbon on the surface of the briquettes is an excellent way of overcoming this dusting problem, provided sufficient glanz carbon is produced to coat substantially the entire surface and to fill the very fine (—5 micron) pores. The hydrocarbon distilled from the briquettes during curing does not ordinarily produce glanz carbon on the surface; it is necessary to have a 10% volume concentration of hydrocarbons in the gases surrounding the curing briquettes to produce a useful glanz carbon film.

We have found that the vapors coming out of curing briquettes, or out of briquettes during the curing process, will react to produce glanz carbon in sufficient quantity to substantially fill the —5 micron surface pores and coat the larger pores, if there is present adjacent the briquette surfaces some catalyst metal, as such or as a salt, most preferably tin or zinc. The catalyst acts to induce glanz carbon deposition at much lower temperatures, and out of much lower concentrations of hydrocarbon, than without catalyst.

Whereas temperatures above about 1000° F. are necessary to produce glanz carbon in the absence of the catalyst, temperatures of 450 to 500° F. produce nice films of glanz carbon with catalyst present.

The metal need be present in only trace quantities, and may be derived from metal or a metal salt. It can be added in any convenient fashion. It cannot be added to the briquetting mix—metal in the interior of the briquette forms glanz carbon there, which prevents reaction between binder and solid, essential to get nonspalling briquettes. However, it can be added to the briquettes after forming and be present during curing. For example, if the briquettes are cured in the presence of pieces of tin plate or galvanized iron, enough metal is volatilized into the gas stream passing over the briquette surfaces to produce a glanz carbon film on subsequent curing. The same effect is obtained by spraying the green briquette surfaces, before curing, with, as little as 5 x 10^{-4} parts by weight of stannous chloride per part by weight of briquette. Another method of getting the same effect is to hang strips of asbestos paper, carrying tin or zinc chloride, in the curing oven; enough volatilizes to get the desired effect. The catalyst may also be present in the cooking oven with the same results.

Attempts to analyze for catalyst metal on the finished briquettes have given negative results; it is probable that the metals are volatilized during the cooking.

The discovery of the utility of tin was made in a most unusual manner.

Two hundred grams of green briquettes, made from Elkhorn-Adaville seam coal from Kemmerer, Wyo., as described in Work et al. U.S. Pat. 3,184,293, were placed in a 1-gallon tin can which had been perforated with about 100 holes created by punching the walls and bottom with an ordinary ten-penny nail. The can was covered with a matching, double-seal, 1-gallon can cover. The can and contents were placed on a shelf in a "Dispatch" air-circulating oven, so equipped that air, in addition to the air carried through by the oven fan, was introduced at the rate of 10 to 15 c.f.m. This oven was designed to simulate conditions used in a plant-scale curing oven, and the purpose of this test was to attempt to determine the amount of light hydrocarbon oils that may be distilled off during the curing operation.

The "curing" phase of U.S. Pat. 3,184,293 is an exothermic oxidation of hydrogen from the green briquette. As such, considerable heat is produced which, unless it is removed by the passage of large volumes of cooler air over the area wherein this heat is generated, causes an exponential rise in temperature from the 450 to 500° F. desirable reaction temperature to temperatures that can be developed and sustained by burning carbon and hydrocarbon. In the case of this containing green briquettes, the ten-penny nail holes, while numerous, were not sufficient to allow the quantity of air passage necessary to maintain the reaction temperature at the 450 to 500° F. level. As a result, the briquettes therein caught fire. The briquette quality was assumed to have been destroyed. However, on examination of the cooled product, it was observed that the briquette were not consumed by fire, even though some had burned, and that all of the surfaces were covered with a hard, dense, high-gloss coating of silver-colored carbon. The can itself had deposited on its sides and lid a hard brittle pitch that is not characteristic of a residue from binder distillate or residue from binder distillation.

Most unexpected was the observation that when two of these briquettes, which were of poor quality as shown by crushing resistance of only 200 pounds total force, when rubbed together with hand pressure produced no dust. Instead of abrading the surfaces, this rubbing actually polished the carbon lay-down to an almost mirror finish. Samples of the untreated briquettes, which had a crushing strength of about 300 pounds (1/2" x 1" x 5/8" pillows) total force, were extremely dusty when abraded by rubbing under the same light pressure, one against the other.

Following this observation, laboratory and pilot plant tests proved that the desired reaction occurred during curing of properly cured briquettes, and that metals other than tin were useful as catalysts. It was also found that the invention is applicable to form coke briquettes made by briquetting ordinary non-reactive coal chars with bituminous binders, followed by cooking with or without an intermediate curing step in the presence of oxygen. The resultant coated briquettes have the advantage of a clean non-dusting surface, but their
The specific examples of the invention are given by way of illustration, and are not meant to be limiting.

**EXAMPLE 1**

Two-inch briquettes were prepared in pilot operation from a green mix of Elkol-Adaville calcinate and raw tar, produced in commercial operation, using 15% of binder as per instructions in U.S. Pat. 3,184,293. These briquettes were treated with a tin solution containing 10 g. of stannous chloride (10%) per 100 ml. of solution. This tin solution was applied with a 5 mm. wide glue brush to an area of approximately 5 mm. square on the horizontal surface of the briquettes. One brush stroke was used on each briquette, and the amount of stannous chloride applied could not be measured on a standard three-beam balance to the second decimal place. The briquettes weighed 300 g. before and after application. Ten briquettes were used. Following the brushing treatment with stannous chloride solution, these briquettes were cured at 450°F. Within 7 minutes of admission to the curing oven (Dispatch No. 703-6 with 15 c.f.m. of air forced in), a silvery coating appeared.

The coating persisted through carbonization at 1750°F. in a nitrogen gas atmosphere. On cooling, these briquettes were abraded by rubbing together. The hard, dense coating caused no dust and appeared to be polished by the rubbing.

The situation was duplicated using about 0.1 ml. of 10% zine chloride solution for 30 g. of briquettes. The results reported hereafter were duplicated.

The untreated counterparts were dusty, dirty to touch, and produced a black streak on a white cloth surface. When rubbed together, they produced a cloud of airborne dust that persisted for up to 60 minutes.

**EXAMPLE 2**

Four briquettes from the same parent sample as Example 1 were placed in the curing oven, described in Example 1, along with a strip of asbestos sheeting 1" wide and 12" long, which had been stroked once with a 1½" wide flat brush dipped in a 10% stannous chloride solution. On curing and cooking as in Example 1, the hard, dense, abrasion-resistant coating, previously described, developed and persisted.

**EXAMPLE 3**

Carbonized briquettes from a commercial plant were used to produce the product described in U.S. Patent 3,184,293 were surface-treated by spraying with 16 p.p.m. of stannous chloride from a 10% solution and heated in an inert atmosphere of coal volatile matter and nitrogen to 750°F. These briquettes were 1½" x 1½" x ¾" in size. On abrasion in the test described below, they showed a dust index of 0.36% by weight. The control counterpart, a portion of the sample that was cured and cooked without the presence of tin, showed a comparable index of 0.56% by weight and abraded at 149% greater rate.

The test used to determine the dusting potential of carbonized briquettes was developed to stimulate the amount of fines and dust that develops when briquettes are handled and transported from the point of production to the point of use. In practice, it has been found that up to 5% of the weight of the carbonized briquettes may be lost in the can. However, this high figure is peculiar to the weakest product from commercial production. For that product of normal strength, an abrasion figure of 0.5% is much more realistic. The test developed is called the Vibration Test and is performed in the following manner. One hundred grams of the nearest whole number of carbonized briquettes are charged to a 5" diameter 10 mesh laboratory sieve with a 2½" high wall. The sieve is attached to a vibrator such as the "Vita-Surge" SPN 74207, which moves the screen at 60 cycle frequency between ¼ and ¼" in horizontal direction. The test is run for 30 minutes when the fines generated are totaled and weighed. These composite fines are screened through a 325 mesh sieve (44 microns), and the amount passing the sieve expressed as weight percent of the charged briquettes is called the dust index.

**EXAMPLE 4**

One hundred fifty grams of 2" x 2" x 1" briquettes were treated with 100 p.p.m. of stannous chloride out of a 10% solution. These briquettes were cured and carbonized as with other examples described herein. On testing for dust index, these briquettes did not abrade, and no particles smaller than 44 microns (325 mesh sieve size) were formed. The control counterpart showed a dust index of 0.25% by weight.

**EXAMPLE 5**

Approximately 200 pounds of 2" x 2" x 1" pillow briquettes, made from a Polish coal of high rank, via the method of U.S. Patent 3,184,293, were cured in the presence of the metallic tin contained in the coating of approximately 250 square feet of tin-coated steel (six 1-gallon can lids) for 120 minutes at 450 to 500°F. In a continuous pilot unit with capacity of 200 pounds per hour. The operation of this unit is such that heated air passes through the weight of briquettes charged in a basket that is moving in an insulated section of an oven held at the reaction temperature. The tin-coated lids described hereafter were placed in a vertical position across the width of the oven at 4°F from each wall and 4" between each lid. Rows of three lids on each side of the basket were used. After carbonizing as taught in U.S. Patent 3,184,293, these briquettes had deposited on their surface a hard, dense gray coating of glanz carbon. When tested in the ASTM Modified Tumbler Test, using 7 pounds of charge in a 6" long x 36" diameter cylinder and rotating for 700 revolutions at 28 minutes, the amount abraded that passed the ¼" square mesh sieve was 18.2% by weight of the charge. When the tumbler was opened, a very small dust cloud appeared that lasted less than 2 seconds.

The untreated control counterpart had a comparable dust index on this modified tumbler test of 21% by weight of the charge and produced a dust cloud of about 20 cubic feet which persisted for almost 60 seconds. The can lids used in curing were partially coated with hard brittle pitch. The quality of the carbonized briquettes in both cases was excellent, with crushing resistance for the control sample of 1,200 pounds and for those cured in the presence of tin at 1,450 pounds. No chemical evidence of tin on the briquette surface could be detected.

**EXAMPLE 6**

Ten cured briquettes were treated with stannous chloride as in Example 4, and were then cooked at 1750°F. The briquettes were covered with a silvery-gray glanz carbon coating, and had much improved qualities. Obviously, the examples can be multiplied indefinitely without departing from the scope of the invention as defined in the claims.

**We claim:**

1. The method of treating uncured form coke briquettes which are otherwise unsuitable to produce dusting on abrasion to substantially reduce the dusting by producing a hard dense glanz carbon coating which substantially fills the —5 micron pores adjacent the surface of the briquettes and forms a coating over the larger pores, which comprises heating the briquettes to at least curing temperatures in the presence, adjacent the surface of the briquettes, of catalytic quantities of an element of the group consisting of tin and zinc.
2. The method of claim 1, in which the briquettes are reactive form coke, and the glanz carbon coating is produced during the curing operation.

3. The method of claim 1, in which the briquettes are reactive form coke, and the glanz carbon coating is produced during the coking operation.

4. The method of claim 1, in which the catalytic element is tin.

5. The method of claim 1, in which the catalytic metal is derived from pieces of metal placed in the hot-gas stream contacting the briquettes.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,725,019 Dated April 3, 1973

Inventor(s) Anthony P. Zampirri, et al

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 5 "Zampirri" should read --Zampirri--.

Column 1, line 23 "lumps or irregular" should read --lumps of irregular--.

Column 1, line 56 "particles" should read --briquettes--.*

Column 1, line 57 "particles" should read --briquettes--.*

Column 3, line 55 "product" should read --produce--.

Column 4, line 48 "briquette" should read --briquettes--.

Column 5, line 63 "stimulate" should read --simulate--.

Signed and sealed this 20th day of November 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGTMeyer
Acting Commissioner of Patents