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3,711,318

**METHOD OF CONTROLLING ULTRAFINES FROM
REACTIVE FORM COKE**

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2 Claims

ABSTRACT OF THE DISCLOSURE

Reactive form coke, made as described in Work et al., U.S. Pats. 3,140,241 and 3,140,242, issued July 7, 1964, is treated with an aqueous dispersion of a film former to deposit on and adjacent the surface thereof from about 0.05 to about 3 weight percent of a solid which adheres to the surface and deposits in the surface pores, and acts both to reduce abrasion and to cause material abraded from the surface to be larger in size than the ultrafine (20-micron and smaller) particles which are produced in the absence of the coating, thereby controlling the airborne-dust problem which otherwise makes handling of the reactive form coke extremely difficult.

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 of 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 difficulties in 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 test 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 1/4" standard sieve after tumbling. In normal operations, any coke that degraded in handling to a size that will pass through the 1/4" 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 noncoking coals. One such material is described and claimed in the Work et al., U.S. Pat. 3,184,293 issued, May 18, 1965; it is produced by the methods described in Work et al., U.S. Pats. 3,140,241 and 3,140,242 issued, July 7, 1964. The product made in accordance with these patents comprises briquettes made by briquetting reactive coal calcinate particles with oxidized coal tar, 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

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the unloading are 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.

OBJECT OF THIS INVENTION

This invention aims to provide a means of overcoming the problem of airborne dust associated with long rail shipments and handling of products produced by the methods described in U.S. Pats. 3,140,241 and 3,140,242, without interfering with its utility in blast furnaces and for other uses.

STATEMENT OF THE INVENTION

In accordance with this invention, we accomplish this result by treating briquettes produced by the above methods, i.e. "reactive form coke"—with an amount of an aqueous dispersion of a solid film former to produce a film, on the surface and in the pore immediately adjacent the surface, which contains from about 0.05 to about 3%, and preferably from about 0.5 to 3%, based on original reactive form coke weight, of the solid film former. This treatment does not affect the operability of the reactive form coke in the blast furnace, but it reduces abrasion and it results in drastically changing the particle size distribution of the material abraded from the briquettes during prolonged shipment and handling, so that the dusting problem on unloading and handling is substantially eliminated. In fact, where in-transit screening to remove the material abraded from the coke is used on by-product coke lumps and the untreated reactive form coke, treating reactive form coke in accordance with this invention, eliminates the need for in-transit screening, greatly facilitates the coke handling operations and tends to lower production costs.

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 3,140,242. Briefly, in accordance with these patents, a reactive calcinate is made 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-producing 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 nonvolatiles, 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 coked 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 produces the series 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 ultrafines 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 this was due

to the fact that the cell walls of the coke were much thinner in reactive form coke than in conventional coke, so that any abrasion that occurred produced a substantially higher percentage of ultrafines than conventional coke.

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.

We have found that the problem is most effectively solved by uniformly coating the reactive form coke with an aqueous dispersion of a film-forming solid to produce a film on the surface of the reactive form coke which does not penetrate substantially beyond the pores immediately adjacent the surfaces of the product, and which adds about 0.05 to 3% of solids to the weight of the reactive form coke. The reactive form coke is preferably treated while it is still hot, so that the water in the coating is largely driven off by the heat. However, cold treatment is also effective, except that the water added is not completely removed by air evaporation.

At least about 0.05% of any film-forming solid we have used is necessary to get the desired results; more than 3.0% will ordinarily cause difficulty with one or more desirable properties of the reactive form coke, for example they may tend to stick together when piled in large heaps. However, it is very difficult to reproduce laboratory results on a large scale with very low concentrations of added material, since the cost entailed in careful spraying is high. Experience indicates that in plant operations about 0.5% of add-on is about the low point which will produce reasonably even coverage.

From our experimental work, it would appear that the added film-forming solids work in three principal ways. Since they are distributed on and immediately adjacent to the surface of the briquettes, even 0.05% by weight will add considerably to the wall thickness and particularly to the wall weight of the outside layers of the briquettes, which are what is abraded off, so that the abraded dust consists of larger and heavier particles. Further, the additives function as cements for the ultrafine particles, thus again reducing the amount of ultrafines. Finally, the films are more resistant to abrasion than the reactive form coke itself, resulting in less total fines.

It is essential that the film former be added in water. When organic solvents are used, there is a tendency for the film formers to be carried into the reactive form coke well below the surface, so that the desired concentration on and adjacent to the surface is not obtained; more film former is needed to control dusting, resulting in too great a change in the reactive form coke properties. Moreover, solvent is trapped inside the reactive form coke, and must be driven out in a heating step. Melts of the film formers avoid these difficulties, but do not distribute themselves in sufficiently thin films, nor do they penetrate the surface pores sufficiently. The aqueous dispersions do form the desirably thin films, and penetrate the surface just enough to anchor the films and thicken the surface walls. But the aqueous dispersions just penetrate the surface pores; the high surface tension of the water apparently prevents undesirable deeper penetration.

We have successfully used aqueous dispersion of a variety of cheap film formers, including sodium silicate, blackstrap molasses, and a variety of terpene resins. The cheapest and most interesting products are the very dark to black coal and petroleum derived hard pitches, and asphalts which are solid at ordinary ambient temperature.

It should be noted that most of these cheap materials make rather brittle films which are not in themselves abrasion-resistant. Surprisingly, when deposited on the reactive form coke, they are as effective as tougher, more expensive products which are themselves abrasion-resistant.

Since the standard abrasion test method of the indicated ASTM D-294-64 does not measure the airborne dust problem, it was necessary to find methods which more nearly simulated the problem created in long rail shipments and subsequent handling. Experimental rail shipments of full cars of coke of approximately 1,000 miles indicated that the dust problem was serious with a variety of reactive form cokes made from different coals, and that the amount of dust varied depending on the basic coal treated and the care exercised in the plant. Tests were designed by comparing the fines generated therein with those obtained in such long rail shipments, using a variety of materials which generated from about ½ to 3% of fines in the actual shipments. The preferred test developed in our work is called by us the Vibration Test. The test consists of charging approximately 100 grams (to the nearest whole briquette) of carbonized briquettes to a 5" diameter, 10 mesh sieve with a 2" 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 a horizontal direction. The test is run for 30 minutes, when the fines generated are screened through a 325 mesh sieve (44 microns) screen and the material passing through the screen is weighed. This test can be used for all sizes of briquettes by changing the screen, and the time can be varied as desired to simulate any changes in the actual haulage and handling conditions. The specific conditions were picked to get the same results as those obtained in actual large scale tests.

It was noted that the percentages of ultrafines (20 microns and less) derived from untreated reactive form coke approximated 50% of the -325 mesh material derived from treated samples were substantially lower.

SPECIFIC EXAMPLES OF THE INVENTION

In the following specific examples of the invention, which are given by way of illustration and not by way of limitation, each test was run by splitting a representative sample consisting of a number of briquettes of reactive form coke into groups. One group was then tested without treatment; the other group or groups was coated and then tested in identical fashion, so that the comparisons are always between treated and untreated samples of the same product.

EXAMPLE 1—SILICATE TREATMENT

A group of briquettes was selected from a reactive form coke which produced 0.66% of -325 mesh fines when subjected to the Vibration Test.

One hundred grams of sample (to the nearest whole briquette) were treated by spraying onto the surface thereof a dilute (0.4%) sodium silicate solution (ratio of SiO_2 to Na_2O —1 to 1) to add 1% sodium silicate to the briquette surfaces. The samples were allowed to air-dry for a week to eliminate almost all of the moisture, and then subjected to the same abrasion test. The amount of -325 mesh fines was reduced from the original 0.66% to 0.10%, and the percentage of ultrafines was very small.

A similar test, adding 0.5% sodium silicate, resulted in 0.12% fines -325 mesh.

EXAMPLE 2—PETROLEUM RESIN EMULSION

The same base sample as used in Example 1 was used except that 100-gram samples were treated with a dilute (5%) aqueous emulsion of a hard petroleum resin, to deposit varying small amounts of resin on the surface, and the samples were air-dried for two weeks. The Vibration Test was used, with the following results:

Percent additive:	Percent fines, -325 mesh
None	0.66
0.05	0.07
0.1	0.06
0.5	0.002
1.0	Trace

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EXAMPLE 3—PETROLEUM ASPHALT EMULSION

Example 2 was repeated, using a 5% petroleum asphalt emulsion at 0.1, 0.5 and 1.0% solid added levels. Results were:

Percent additive:	Percent fines, —325 mesh
0.1 -----	0.07
0.5 -----	0.04
1.0 -----	0.002

EXAMPLE 4—COAL TAR PITCH EMULSION

A 5% coal tar pitch emulsion was used on a sample of reactive form coke which produced 0.32% fines by the Vibration Test. A 0.5% coating reduced the fines to 0.02% —325 mesh.

EXAMPLE 5—BLACKSTRAP MOLASSES

Blackstrap molasses was reduced to 3% solids, and sprayed on a sample of the reactive form coke of Example 1, to get 3% added solids. After drying for two weeks, the product produced 0.1% of —325 mesh fines.

These examples can obviously be multiplied, without departing from the scope of the invention as defined in the claims.

We claim:

1. The method of controlling the dusting tendencies of reactive form coke briquettes which will rub against each other to form very fine dust of —325 mesh size which is easily air-borne, which comprises coating and reinforcing the surface layers thereof by applying thereto an amount of an aqueous dispersion of a solid film former

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to produce a film, on the surface and in the pores immediately adjacent thereto, which contains from 0.05 to 3%, based on the original weight, of the solid film-former, the solid film-former lacking abrasion resistance of itself but having abrasion resistance when applied to the reactive form coke briquettes, whereby the dust resulting from abrasion is increased in size and the amount of —325 dust is substantially reduced.

2. The method of claim 1, in which the amount of film-former is 0.5 to 3%.

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44—6; 117—100 B, 165, 168, 169

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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

Column 2, line 1 "are" should read --area--.

Column 2, line 65 "series" should read --serious--.

Column 4, line 34 "derived from treated samples were substantially lower." should read --, whereas the percentages of ultrafines in the smaller amounts of -325 mesh material derived from treated samples were substantially lower.--

Signed and sealed this 1st day of October 1974.

(SEAL)
Attest:

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