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METHOD OF PROTECTING REDUCED IRON ORE BY COATING

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ABSTRACT OF THE DISCLOSURE

Reduced metals are protected for prolonged periods against back oxidation and water absorption by coating the metal with a composition comprising a bituminous material and from about 1 to about 40 wt. percent of an alkaline earth metal oxide, hydroxide or mixtures thereof to deposit thereon up to about 0.5 wt. percent of the bituminous material and the alkaline earth metal compound.

BACKGROUND OF THE INVENTION

This invention relates to a method for enhancing the storability of reactive reduced metal powders. More particularly, this invention relates to the art of protecting reduced iron ore containing materials against moisture absorption and concomitant loss of metallization as a result of back-oxidation upon prolonged storage of such materials in ambient atmospheres.

Reduced metals, powders and aggregates of reduced metal powders, such as reduced iron ore, have an acute tendency to chemically react and back-oxidize. As a result, prereduced iron ores present formidable problems in utilizing them in commercial quantities. For example, fine iron powder can catastrophically back-oxidize resulting in explosions and fires.

In order to commercially utilize highly reactive reduced metals, numerous techniques have been proposed to passivate them. For example, it has been suggested to protect reduced metallic iron ore from back-oxidation by incorporating or bonding to the metal surface a protective layer or coating of solid carbon. The carbon can also serve as a reducing agent for any residual oxides present in the ore.

Another method for rendering the surfaces of active metal iron passive and water repellent is described in U.S. application Ser. No. 845,936, filed July 23, 1969, and issued Jan. 19, 1971, as U.S. Patent No. 3,556,838. That application describes a method by which a liquid mixture containing certain kinds of olefins and silicones is applied to the surface of the active metal to form a film. After curing, the olefin-silicone mixture produces a discontinuous hydrophobic resinous deposit which renders the ore particles chemically passive and water repellent.

It has also been found that excellent passivation and water repellency of reduced iron ore can be achieved by contacting the reduced ore at high temperatures ranging from about 300° F. to about 700° F. with olefinic hydrocarbons composed generally of olefins, diolefins, polyolefins, dimers, trimers, tetramers and the like, of average carbon number ranging from about C_{20} to about C_{45}. Polymerization of the olefinic hydrocarbon on the metal surface results in a hydrophobic discontinuous film which renders the metallic surfaces passive.

Notwithstanding the success of the above-mentioned techniques in passivating highly reactive iron-metal powder to prevent explosions and spontaneous combustion, loss in metallization of the coated reduced ore upon prolonged storage nonetheless remains a significant problem.

The amount of hydrocarbon coating must be kept at a practical minium, not only from an economic point of view, but also because thick hydrocarbon coatings ignite and emit excessive amounts of smoke when the coated ore is added to a steelmaking furnace.

Additionally, high carbon content may necessitate further chemical adjustments in the steelmaking process.

Thus, the ore processor is faced with the dilemma that if the reduced ore is coated with a thin, discontinuous coating, metallization of the ore decreases upon prolonged storage. On the other hand, a thick continuous film on the ore is detrimental to the practical utilization of the ore in a steelmaking furnace. Consequently, there remains a need for an economical method of passivating reduced iron ores particularly against loss of metallization over extended periods which will overcome the deficiencies of the prior art.

SUMMARY OF THE INVENTION

This invention overcomes the deficiencies of the prior art and provides a practical and inexpensive method of protecting reduced ores for prolonged periods against back oxidation and water absorption. Accordingly, chemically active reduced iron ore is protected against excessive loss of metallization during outside exposure by coating the reduced ore with a bituminous material and an alkaline earth metal oxide, hydroxide or mixtures thereof.

In a particularly preferred embodiment of this invention a reduced iron ore is coated with an asphaltic material and from 10 to about 40 wt. percent of $Ca(OH)_2$ whereby the ore is protected upon exposure to the elements without excessive loss of metallization.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with this invention, reduced iron ores are protected against excess moisture absorption and loss of metallization by applying to the ores a coating of a bituminous material and an alkaline earth metal oxide, hydroxide or mixtures thereof.

By bituminous materials is meant mixtures of hydrocarbons of natural or pyrogeneous origin, or combinations of both, including asphalts such as petroleum, thermal and oxidized asphalts, and tars and derivatives, such as residua from coke ovens.

Preferred bituminous coating materials include asphalts of relatively high penetration index and liquid asphalts such as vacuum residuum.

This invention is based partly on the discovery that bitumens, and particularly asphalts, can be applied to reduced iron ore in amounts up to about .5 wt. percent and more without deleteriously affecting the steelmaking process when the coated reduced ore is subsequently added to the steelmaking furnace. Apparently the relatively high ratio of carbon-to-hydrogen in such materials lessens the tendency of smoking and combustion normally encountered with other hydrocarbon coated ores. Moreover, excellent passivation and water resistance is achieved when amounts less than about .5 wt. percent of the coating material is used.

Furthermore, the invention also is based on the discovery that alkaline earth metal oxides, hydroxides and mixtures thereof, greatly improve the storability of bitumen coated reduced ores. Apparently rust formation undercuts a neat bitumen coating, thereby exposing reduced ore which in turn is oxidized. The presence of alkaline earth metal oxides, hydroxides and mixtures thereof inhibit rust formation. While not wishing to be restricted to any particular theory, it is believed that rust formation is induced by acids, such as SO_2, deposited from the atmosphere on the reduced iron surface and that alkaline earth metal bases effectively neutralize these acids.

In any event, the use of alkaline earth metal bases according to this invention not only enhances the life of the protection afforded by the coating composition but also lowers the amount of bituminous base material that will be incorporated in the treated iron material. Consequently, this invention has the advantage of offering a degree of flexibility in forming coatings on active iron surfaces which will display a significantly increased storage life while being able to be adjusted to meet the needs of the ultimate user.

In a preferred embodiment of this invention, the alkaline earth metal is calcium or magnesium. Even more preferred, the alkaline earth metal hydroxide is lime. Thus, part of slag forming ingredients typically added to a steelmaking process are incorporated in the protected reduced ore.

Any type of active iron surface can be beneficially treated in accordance with the present invention. However, it is especially contemplated to use reduced iron ores of sizes conventionally produced for fluidized iron ore reduction processes. It is especially contemplated to use the instant invention for passivating briquettes, pellets and other porous compactions of reduced iron ore obtained from high pressure, high temperature briquetting or pelletizing processes. The passivating process of this invention is especially advantageous for use with porous compactions having porosities above about 10 to about 15% since it is at or above these levels that back oxidation and water absorption are especially acute.

As stated previously, bituminous materials suitable in practicing this invention include asphalts and tars, although asphalts are preferred. With regard to asphalts, any type of asphalt product is suitable for use in accordance with the present invention; for example, the asphalt can be a cutback, liquid, emulsified or oxidized type of asphalt. Preferably, the asphalt base utilized and practiced in this invention is either a high penetration asphalt or a liquid asphalt such as a residual oil or vacuum resid. Even more preferred the asphalt will have a penetration index of about 150 to 180 and the vacuum resid will have a wax content of about 15 to 20 wt. percent.

High penetration index asphalts and high wax containing vacuum resids are particularly effective since these types of materials completely coat and even enter small pores and fissures of the metal surface. Also, these asphalts have a relatively low viscosity at 300° to 400° F. while being semisolid at ambient temperatures. Finally, the asphalt coatings retain some plasticity on storage and consequently do not readily develop scratches or surface imperfections that lead to a deterioration in the coating.

In order to achieve relatively long term protection of reduced iron materials with coatings containing about .5 wt. percent, or less of bitumen material, it is essential that the coating composition used to treat the reduced iron also contain up to about 40 wt. percent of an alkaline earth hydroxide, oxide or mixtures thereof. Generally, about 1 to about 40 wt. percent of the alkaline earth hydroxide, oxide or mixtures thereof is employed. Calcium and magnesium are the preferred alkaline earth metals employed with from about 10 wt. percent to about 40 wt. percent of calcium hydroxide being preferred and 30 wt. percent of calcium hydroxide being particularly preferred.

Generally, a liquid hydrocarbon or chlorohydrocarbon can be used in the practice of the present invention to dilute the asphalt base material. Typically, no more than about 70 wt. percent of liquid hydrocarbon will be employed in the coating compositions of this invention; preferably, from about 30 wt. percent to about 60 wt. percent of diluent will be used. For best results, the liquid hydrocarbon diluent will be readily commercially available liquid hydrocarbons or chlorinated hydrocarbons, such as petrolatums, straight petroleum aliphatic solvents, naphtha, and methylene chloride and the like.

Preferably diluents are utilized when the bitumen base material is applied at ambient temperatures. If the coating composition and substrate are at elevated temperatures preferably a diluent is not incorporated with the bitumen materials and the briquette or solid material is merely "hot dipped."

In addition to the alkaline earth compounds, additives such as emulsifiers, water displacing agents, rust preventatives, antioxidants and the like may be incorporated in the basic coating composition.

In the application of the coatings of this invention, the alkaline-earth metal oxides, hydroxides and mixtures thereof are preferably added to the bitumen coating composition. Alternatively the alkaline earth compound may be applied directly to the reduced ore, for example, by rolling the metal with the dry powder additive or a slurry of the additive, and by spraying a solution or emulsion of the alkaline earth compound on the surface of hot briquettes.

Typically, the coating material is applied by spraying, brushing, dipping and the like. Preferably, reduced ore is contacted with the coating compositions of this invention while the latter is maintained at temperatures sufficient to induce some penetration of the coating composition into the capillary pores and crevices of the metal. Obviously, the temperature which will be sufficient to induce limited penetration of the coating composition into the capillary pores and crevices of the metal will depend to a certain extent upon the softening point of the asphalt base material employed, the type and amount of solvent and the amount and type of other additives utilized. Generally, however, the coating composition temperatures are of the order of from about 150° F. to about 700° F. although with greatly diluted solutions lower temperatures and even ambient temperatures are satisfactory.

Contact time is to some extent dependent upon the temperature of both the metal and the coating composition. However, contact time must be sufficient to deposit a continuous water barrier on the surface of the metal which is adequate to withstand the environmental factors and conditions. Suitably, the surface of the reduced ore is contacted with the bitumen-alkaline earth metal containing coating composition for about 1 to about 10 seconds and preferably for about 3 to about 5 seconds. After such contact, for about 5 to about 20 seconds are allowed for excess liquid to drain from the metal surfaces.

The invention will be better understood by reference to the illustrations and description of the examples which follow. In the following selected demonstrations and examples, reduced iron product is obtained by charging a raw natural hematite ore to the top or initial stage of a reactor containing a series of four fluidized beds. The ore is progressively reduced upon descent from one bed to the next of the series by treatment with ascending reducing gases at temperatures of about 1200° F. to about 1900° F. A particulate reduced iron product is withdrawn from the final stage of the reactor at about 1450° F. The withdrawn reduced powder is compacted in a rolled type press to form briquettes of size 3⅝ x 2¼ x 1⅝ inches. Reduced iron ore briquettes thus formed, generally ranging from about 80 to about 95% metallization, were employed in the test procedures outlined below.

Example 1

A comparative study of the effectiveness of petroleum based coatings was conducted by coating briquettes according to this invention with various bituminous materials including bituminous coatings containing lime and subsequently storing the briquettes in piles outside. Each pile was made up of approximately 15 tons of briquetted reduced iron ore. Uncoated briquettes were also stored outside in a comparable size pile to serve as a reference. Samples taken periodically from 6 to 12 inches within the pile were checked to determine the amount of water absorbed and the decrease in metallization of the reduced ore. The moisture absorbed by briquettes below the

surface of the pile is considered to be more representative of the moisture absorbed by the entire pile. The test was conducted for 39 days during which time the test piles were exposed to approximately five inches of rainfall. Additionally, each pile was sprayed with water at regular intervals as an accelerated weathering technique to provide the equivalent of five more inches of rain. Typical results of these tests are summarized in Table I below.

TABLE I.—COMPARATIVE OUTSIDE WEATHERING OF BRIQUETTES

Coating	Uncoated, percent	Asphalt, percent	Asphalt plus lime, percent
Moisture pick-up 6"–12" below surface	3.35	[1] 1.01	[1] 0.48
Metallization loss	[2] >1	[3] Negligible	[3] Negligible

[1] Represents an average from several piles.
[2] Surface samples showed loss of metallization up to 2%.
[3] Visual inspection indicating rusting proceeds at a considerably lower rate with lime in the coating than when only asphalt is used.

As the above data shows, uncoated reduced ore upon exposure to atmospheric conditions absorbs considerable moisture with concomitant loss in metallization. On the other hand, coated ore samples do not absorb moisture during early storage anywhere near as rapidly as uncoated materials. Indeed, experience has shown that briquette moisture adsorption of greater than about 0.5 wt. percent results in rapid back oxidation of stored briquettes. Consequently, the low moisture absorption for the asphalt plus lime coated briquettes shown in the above table is particularly significant.

Example 2

This example shows the beneficial effects that can be obtained when calcium hydroxide or calcium oxide are added to an asphalt coating material. In one test, reduced iron ore briquettes which had been cooled in air from 1250° F. to 600° F. were then dipped for three seconds in an asphalt having a penetration index of 150 to 180. A second test, a series of batches of briquettes had been similarly dipped in the same asphalt containing various amounts of calcium hydroxide. All the coatings were tested for initial water repellancy by submerging samples in water for five minutes and then measuring the amount of water absorbed. The results of these tests are shown in the Table II below.

TABLE II.—EFFECT OF LIME IN ASPHALT COATING

Wt. percent lime in coating	Initial H_2O pickup [1]	Avg. coating level [2] wt. percent
0	0.27	0.34
5	0.11	0.28
10	0.01	0.27
20	0.15	0.36
30	0.00	0.39
40	0.05	0.50

[1] 5 minute immersion test.
[2] Average of several samples.

As can be seen from the above data, utilization of calcium hydroxide in the coating bath results in a decrease in the average coating pickup while at the same time it enhances the initial water repellency. Optimum water repellency is achieved with asphalt coating materials containing 30 wt. percent of calcium hydroxide.

Finally, it can be seen from the test data given in Table III that weatherability of reduced ores coated in accordance with this invention upon prolonged exposure

to ambient atmospheres is particularly improved. The coated ores were prepared in the manner previously described.

TABLE III.—COMPARATIVE WEATHERING TEST DATA

Coating	Average coating level, wt. percent	Initial H_2O [1] pick-up, wt. percent	Days outside	Moisture,[2] wt. percent
Uncoated		3.21	39	3.35
30% lime, 70% asphalt	0.39	0.00	21	0.10
Do			90	0.34
30% lime, 70% vacuum resid [3]	0.35		21	0.07

[1] 5 minute immersion test.
[2] Weathering comparable to surface briquettes in a large pile.
[3] Contained 15% to 20% wax.

As can be seen from the data above, even after 90 days of storage outside relatively little water is absorbed by reduced ore coated in accordance with a preferred embodiment of this invention.

What is claimed is:

1. A method for protecting a reduced iron ore against a substantial loss of metallization upon prolonged storage outdoors and for providing a suitable material for utilization in steel-making furnaces, comprising contacting the surface of the reduced ore with a liquid mixture consisting essentially of a bituminous material and from about 1 to about 40 wt. percent of an alkaline earth metal compound selected from oxides, hydroxides, or mixtures thereof, said contacting being for a time sufficient to deposit up to about 0.5 wt. percent of said bituminous material and alkaline earth metal compound, whereby a reduced ore suitable for utilization in the steel-making furnace is protected against loss of metallization.

2. The method of claim 1 wherein the bituminous material is an asphalt product.

3. The method of claim 2 wherein the reduced ore is contacted with the liquid mixture for about 1 to about 10 seconds and then drained to provide a continuous coating on the surface of the ore.

4. The method of claim 2 wherein the asphalt is dissolved in a diluent.

5. The method of claim 2 wherein the asphalt is a vacuum resid which contains about 20% wax.

6. The method of claim 1 wherein the alkaline earth metal compound is calcium or magnesium.

7. The method of claim 1 wherein the alkaline earth metal compound is lime.

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