1 283 081

PATENT SPECIFICATION

(11) 1 283 081

DRAWINGS ATTACHED



(21) Application No. 50391/69 (22) Filed 14 Oct. 1969
(31) Convention Application No. 776 628 (32) Filed 18 Nov. 1968 in
(33) United States of America (US)
(45) Complete Specification published 26 July 1972
(51) International Classification C23F 7/04
(52) Index at acceptance
C7U 3 7C

(72) Inventors BEVERLY BROWN FUQUA,
WILLIAM JOSEPH METRAILER,
MARNELL ALBIN SEGURA and EARL EDWIN TURNER

(54) QUENCHING AND PASSIVATION OF PARTICULATE METALS

(71) We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Active particles of reduced iron ores are made resistant to oxidation by treating them in a fluidized bed at elevated temperatures with mildly oxidizing gases.

This invention relates to the art of passivating reduced iron ore particles by forming protective films, surfaces or coatings on such particles.

Powdered iron, produced by reducing iron oxides with hydrogen-rich gases at relatively low temperatures, tends to be highly pyrophoric and will burn if exposed to air, even at relatively low temperatures. Iron ores that are reduced at relatively low hydrogen concentrations and high temperatures tend to be less pyrophoric on initial exposure but still possess a tendency, even after cooling, to be quite reactive. The metal becomes severely reoxidized, or back-oxidized, on continued exposure to an oxygen-containing gas, thus greatly decreasing its value. Moreover, when the reduced iron product is wetted, as by rain, the problem can become even more serious because hydrogen is liberated. The hydrogen can, under certain circumstances, ignite.

Two reactions are believed primarily responsible for the oxidation ond ignition of reduced iron product. The first, which is only slightly exothermic, involves the reaction between iron and water to produce iron oxides and hydrogen.

The second reaction, which is highly exothermic, is that between iron and oxygen to form iron oxides.

Fires may be started when reduced particulate iron is stored under circumstances such that the heat generated by the foregoing reactions cannot be rapidly dissipated. Eventually, the heat resulting from the hydrogen-generation reaction builds up until the temperature reaches a point where the air oxidation of iron becomes the controlling reaction. The latter reaction, being strongly exothermic may ignite the hydrogen. Combustion of hydrogen liberates still more heat, which sustains and increases the rate of the oxidation reaction. Under these conditions, the reactions can continue until all of the metallic iron has been back-oxidized.

Because of these and other difficulties, particulate reduced iron is generally compressed into dense briquettes, pellets or extrudates. This lessens the exposed area, reduces the amount of back-oxidation, and decreases the possibility of fires, though it by no means solves the problem unless very high densities are achieved. Often, various additives are incorporated with the particulate reduced iron at or prior to the time of compacting. The compacted product can also be surface coated to lessen the exposure to moisture and oxygen.

Attempts have been made to passivate particulate reduced iron product from direct iron-ore reduction processes and thus avoid the necessity of compacting the particles, but these attempts have not generally been successful. Where such efforts have been made, the powdered metal is heated in an inert, nonoxidizing, or reducing atmosphere. After sufficient cooling in such atmosphere, to lessen the detrimental effects of back-oxidation upon exposure to ambient air, the product is withdrawn.

It has long been felt desirable to develop more effective means for quenching and passivating hot, active powdered metals, particularly ferrous metals such as those produced in direct iron-ore reduction processes.

The primary objective of the present invention is to provide a method for passivat-

[Price 25p]

ing particulate ferrous metals. In particular, it is an object to obviate the foregoing and other disadvantages by providing a method for passivating particulate active ferrous metals and for quenching, cooling, and passivating such particulate metals by forming protective films on them. More particularly, it is an object to render particulate ferrous metals passive and resistant to back-oxidation so that they can be handled and stored. It is an object to provide a method for passivation of ferrous metals produced by direct reduction processes, especially fluidized iron-ore reduction processes.

These and other objects are achieved in accordance with the present invention which contemplates a new and improved process for passivating, or quenching and passivating, active metal particles of reduced iron ores by forming a bed of the particles, fluidizing the bed with a mildly oxidizing gas such as steam or oxygen diluted with steam or with inert gases such as nitrogen mixed with steam or oxygen, or both, and maintaining the fluidized bed at temperatures ranging from 90°F. to 650°F., preferably 150°F. to 450°F., for a time sufficient to reoxidize up to 3% of the metal in said particles to form a protective oxide coating on the particles. When the metal particles are introduced into the fluid bed at much higher temperatures, it is necessary to quench them to maintain bed temperatures within the desired range. This is achieved by contacting the bed with a spray of atomized water. Preferably, the sizes of the droplets of water range less than $^1/_8$ inch in diameter, and more preferably less than $^1/_{36}$ inch in diameter. When such water spray quenching is used, the temperature of the fluidized bed must be maintained at from 25°F. to 200°F., and preferably from 50°F. to 150°F., above the condensation temperature of the water under the conditions of operation.

Reduced iron products of a fluidizable particle size distribution ranging from 10 to 10,000 microns, averaging 50 to 400 microns, at temperatures ranging from 1000°F. to 1800°F., and preferably from 1300°F. to 1600°F., are injected directly into a fluidized bed of the product. The particles can be injected mechanically, e.g., using hoppers, screw feeders and the like, or pneumatically by entrainment in inert, mildly oxidizing, or even reducing, gases. (When reducing gases are used, the volume must be insufficient to render the overall fluid-bed gas composition non-oxidizing with respect to the metal surfaces of the particles.) At the normally desired operating pressures which range as high as 250 pounds per square inch, the bed is operated at temperatures ranging from 225°F. to 600°F., and preferably from 250°F. to 450°F. The particulate metal is quenched or cooled by the water spray without condensation on the surfaces.

Passivation of the particles is achieved by a thin film or surface coating of oxides believed to be substantially magnetite, i.e., Fe_3O_4, or magnetic oxide of iron. The thin film, which aids in protecting the particles against further back-oxidation, results from deliberate partial reoxidation ranging up to 3.0 percent, based on the total weight of the particles. Generally, excellent passivation is achieved when such partial reoxidation is carried out to the extent of 0.1 to 1.0%.

In general, fluidization is maintained by injecting a gas which is mildly oxidizing to the metal particle surfaces under conditions existing in the fluid bed. To avoid excessive reoxidation, the gas should contain no more than 12%, and preferably 1% to 8%, by volume, of free oxygen. If hot metal particles are added to the fluid bed directly from a high-temperature reduction process, the temperature rises and water is injected through an atomizer into the bottom of the bed to maintain the desired bed temperature. The vaporized droplets form steam which adds to the fluidizing gas.

The holding time of the reduced ore particles in the bed is sufficiently short to prevent excessive oxidation. Holding times range generally from 5 minutes to 1 hour, and preferably from 10 minutes to 40 minutes, depending upon the temperature and concentration of oxidizing constituents in the fluidizing gases.

In introducing the water into the fluidized bed for quenching of the particulate metal it is essential that the water be in liquid state, preferably in the form of relatively fine droplets. The droplets are generally formed and introduced as a fine spray, preferably by atomizing in a stream of gas, most preferably fluidizing gas.

Referring to the drawing, the combination contemplates a reactor 10 wherein oxidic iron ores are reduced by countercurrent contact with ascending reducing gases. A gas regeneration and recovery facility 20 is also shown, which provides for the recovery of spent reducing gas. A passivator 30 provides for the passivation, or cooling and passivation, of the particulate reduced iron product withdrawn from reactor 10.

In the iron-ore reduction portion of the process, oxidic iron ore, e.g., hematite, is charged into the top stage, i.e., stage 1, of reactor 10 via line 11. The iron oxides descend through, and are progressively reduced in the sequence of stages 1, 2, 3, 4, and 5, each of which contains one or more beds of fluidized ore at progressively decreasing degrees of oxidation. The individual beds or stages are operated at the same or at different elevated temperatures ranging generally from about 1000°F. to 1800°F.,

or more generally from about 1300°F. to 1600°F. In the first stage, the oxides are generally preheated. The oxides are thence reduced from ferric oxide to magnetic oxide of iron and in a subsequent stage, or stages, from magnetic oxide of iron to ferrous oxide. Finally, in the last stage, or stages, the ferrous oxide is reduced to metallic iron. In the final reduction stage, the reduced iron product is generally from about fifty to ninety-five percent metallized.

Reducing gas is introduced into reactor 10 counter-current to the flow of ore. Hot ascending reducing gas, consisting generally of carbon monoxide or hydrogen, or both, is introduced into the bottom of reactor 10 via line 12, the gas sequentially contacting fluidized beds in stages 5 through 1. Cyclone separators (not shown) are generally provided between the beds to remove entrained particles from the ascending fluidizing gas.

Spent gas is withdrawn from reactor 10 via line 13. The gas can be vented, but preferably most of the gas is regenerated by removal of the oxidized components, generally water and carbon dioxide. The gas is regenerated by passage through line 14 to the recovery facility 20 where water is precipitated and removed by cooling and the remaining gas is scrubbed, e.g., with basic compounds such as monoethanolamine, to remove carbon dioxide. The regenerated gas is then passed via lines 21 and 22, combined with fresh reducing gas from line 23, reheated via means not shown, and injected via line 12 into the bottom of reactor 10.

Particulate iron solids are withdrawn from the last stage of reactor 10, i.e., stage 5, via line 31. The particulate metal, of particle size averaging generally from about 50 to 400 microns, and as large as about 14 mesh (Tyler Series), is discharged into line 32, where it is entrained by a fluidizing gas stream and fed into the bottom of passivator 30.

Particulate metal solids are introduced at high temperatures into the lower part of fluidized bed 33 in passivator 30. The bed is in a generally turbulent fluidized state, and the solids are there contacted by an atomized spray of water introduced into the bottom of passivator 30 via lines 34, 35 and 36. Upon introduction into the fluid bed 33, the solids are instantly quenched and the water droplets are vaporized to form steam. The lower portion of the passivator 30 is characterized as preferably having a section having a length:diameter ratio ranging generally from about 2:1 to 6:1, and more preferably from about 3:1 to 4:1, to provide a relatively high velocity gas, ranging generally from about 1 foot per second to 5 feet per second, and preferably from about 2 feet per second to 3 feet per second, for creation of turbulence. The velocity of the gases through the upper portion of bed 33 ranges from about one-tenth to one-half this velocity, and preferably from about one-fourth to one-fifth this velocity.

The solids, after entry into the lower portion of quench passivator 30, are passed into the upper portion of fluidized bed 33. The passivated particulate product, after sufficient hold-up time, is removed from the upper portion of fluidized bed 33 via overflow line 37 as a passivated dry particulate product.

Effluent gases are removed from the quench passivator 30 via line 38 and introduced into the cyclone separator 39. Gases from the cyclone separator 39 are exhausted via line 40, and entrained solids are returned through line 41 to line 37 from whence they are recovered as product. Alternatively, solids from the cyclone can be recycled to the passivator, if additional passivation is required.

The following examples are illustrative of the effectiveness of preparing a passivated particulate product by the above-described process.

EXAMPLE 1

Particulate reduced iron ore, which is 95.0% metallized, is withdrawn from the final stage of reactor 10 at 1400°F., entrained in a gaseous mixture of nitrogen containing 4 volume % oxygen and injected into the bottom of passivator 30, which is maintained at essentially atmospheric pressure. The metal is there contacted by an atomized spray comprising 67 percent water and 33 percent nitrogen. The iron particles are quenched to fluid-bed temperatures of about 420°F. The water droplets are instantly vaporized to steam, which comprises about 30% of the total fluidizing gases. After a hold-up time of 16 minutes at 420°F., the dry particulate product is discharged from the fluidized bed of the passivator. It is then cooled to atmospheric temperature in nitrogen. The oxide coating on the product is sufficiently thin that metallization is reduced by only 0.3% to 94.7%.

To determine the degree of passivity of the particles, analyses are performed to measure the amount of hydrogen generated, upon immersion in water, and metallization loss upon exposure to the atmosphere for three days. The hydrogen generation measurements are calculated on the basis of standard cubic feet of hydrogen generated per hour per ton of reduced iron product, upon immersion in water, at 125°F. Analyses are also performed on an untreated or unquenched portion of the product taken directly from line 31 and cooled gradually in reducing gas to ambient temperature. Comparisons of the results are made. In accordance therewith, it is found that considerably

less hydrogen is liberated by the quenched passivated metal, which also loses much less metallization. This is shown by reference to the data given in the following table, wherein treatment "A" refers to the unpassivated product and treatment "B" refers to the passivated product.

Treatment	Metallization Loss	Hydrogen Generation
A	3—4%	11.1 SCFH/Ton
B	0.3%	0

EXAMPLE 2

Particulate iron of 88.0% metallization is withdrawn from the final stage of reactor 10, entrained in essentially pure nitrogen and injected into the bottom of passivator 30 at atmospheric pressure. Therein it is treated as in Example 1, except that it is held for 46 minutes in the fluid bed at 409°F. Comparison of unpassivated and passivated samples, "A" and "B", again show the excellent passivation achieved by the method of the present invention.

Treatment	Metallization Loss	Hydrogen Generation
A	3—4%	11.0 SCFH/Ton
B	0.4%	0.4

EXAMPLES 3 and 4

These examples illustrate the effectiveness of the present invention even when the water spray quench is not used.

Samples of reduced iron ore previously prepared and cooled in an inert atmosphere are introduced through a conventional lock hopper into passivator 30. The particles are heated and fluidized by a preheated fluidizing gas consisting of nitrogen and oxygen under conditions and for times indicated below. As the following table indicates, excellent passivation is achieved:

Example No.	3	4
Fluidizing Gas	$N_2+4.5\%O_2$	$N_2+8\%O_2$
Fluid Bed Temp.	357°F.	217°F.
Holding Time, Minutes	44	50
Product Metallization, %		
Before Passivation	94.8	96.0
After Passivation	94.4	96.0
Metallization Loss	0.4	(less than 0.1)
Hydrogen Generation, SCFH/Ton		
Before Passivation	17.6	7.9
After Passivation	0.0	0.0

In sharp contrast to the foregoing, when samples are treated in the passivator in precisely the same manner, but without any oxygen in the nitrogen, the resulting product is extremely active, generating hydrogen at essentially the same rate as untreated samples.

EXAMPLE 5

Reduced iron ore is prepared, and a portion of it is passivated essentially as in Example 4. The unpassivated portion is dumped into a conical shaped pile, exposed to the atmosphere, initially at a temperature of 120°F. The passivated portion is dumped at 210°F. into an adjacent pile virtually identical in size and shape. Both piles are penetrated at several points with thermocouple probes. Oxidation generates heat and causes increased temperatures in the unpassivated pile, while no increase is seen in the passivated pile, as shown below:

	Temperature, °F.		Metallization, %	
Pile	Initial	Maximum	Initial	After 3 Days
Unpassivated	120	240	96.1	92.9
Passivated	210	210	96.1	96.0

EXAMPLE 6

Reduced iron ore is prepared, and a portion of it is passivated as in Example 1. The unpassivated and passivated portions are subdivided into smaller portions of equal size, which are preheated with dry nitrogen to various initial temperatures and dumped into identical piles. The piles are equipped with thermocouples and temperatures are continuously recorded to observe the effect of back-oxidation. The results are given below:

Sample		Initial Temp.	Maximum Temp.
Unpassivated	...	90°F.	170°F.
		120°F.	240°F.
		220°F.	380°F.
Passivated	...	175°F.	175°F.
		230°F.	230°F.
		240°F.	240°F.

The advantages gained by the present process are apparent.

It is apparent that the invention is subject to various changes and modifications without departing from its scope.

WHAT WE CLAIM IS:—

1. A process for passivating active metal particles of reduced iron ore comprising:

forming a bed of the particles;

fluidizing the bed with a mildly oxidizing gas selected from the group consisting of steam, steam diluted with inert gas, oxygen diluted with inert gas, oxygen diluted with steam, and mixtures of these gases; and

maintaining the bed at temperatures ranging from 90°F. to 650°F. for a time sufficient to reoxidize up to 3.0% of the metal in said particles to form a protective oxide coating on the particles.

2. The process of claim 1 wherein said bed temperatures range from 150°F. to 450°F.

3. The process of claim 1 wherein said metal particles are continuously added to said bed at temperatures above 650°F. and are quenched to bed temperatures ranging from 225°F. to 600°F. by spraying liquid water into said bed.

4. The process of claim 3 wherein said particles are quenched to temperatures ranging from 250°F. to 450°F.

5. The process of claim 3 wherein said particles of reduced ore are introduced into said bed at temperatures ranging from 1000°F. to 1800°F. and comprise principally particles ranging from 10 to 10,000 microns, averaging 50 to 400 microns in size.

6. The process of claim 1 wherein from 0.1% to 1.0% of said metal is reoxidized.

7. The process of claim 1 wherein said mildly oxidizing gas contains up to 12 volume % free oxygen.

8. The process of claim 7 wherein said mildly oxidizing gas contains 1% to 8% free oxygen.

9. The process of claim 1 wherein said particles are maintained in said bed for holding times ranging from 5 minutes to 1 hour.

10. The process of claim 1 substantially as described and exemplified.

11. Active metal particles of reduced iron ore provided with a protective oxide coating when prepared by a process claimed in any of the preceding claims.

K. J. VERYARD,
15, Suffolk Street, S.W.1.
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1972.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.

Sample	Initial Temp.	Maximum Temp.
Unpassivated ...	90°F.	170°F.
	120°F.	240°F.
	220°F.	380°F.
Passivated ...	175°F.	175°F.
	230°F.	230°F.
	240°F.	240°F.

The advantages gained by the present process are apparent.

It is apparent that the invention is subject to various changes and modifications without departing from its scope.

WHAT WE CLAIM IS:—

1. A process for passivating active metal particles of reduced iron ore comprising:

forming a bed of the particles;

fluidizing the bed with a mildly oxidizing gas selected from the group consisting of steam, steam diluted with inert gas, oxygen diluted with inert gas, oxygen diluted with steam, and mixtures of these gases; and

maintaining the bed at temperatures ranging from 90°F. to 650°F. for a time sufficient to reoxidize up to 3.0% of the metal in said particles to form a protective oxide coating on the particles.

2. The process of claim 1 wherein said bed temperatures range from 150°F. to 450°F.

3. The process of claim 1 wherein said metal particles are continuously added to said bed at temperatures above 650°F. and are quenched to bed temperatures ranging from 225°F. to 600°F. by spraying liquid water into said bed.

4. The process of claim 3 wherein said particles are quenched to temperatures ranging from 250°F. to 450°F.

5. The process of claim 3 wherein said particles of reduced ore are introduced into said bed at temperatures ranging from 1000°F. to 1800°F. and comprise principally particles ranging from 10 to 10,000 microns, averaging 50 to 400 microns in size.

6. The process of claim 1 wherein from 0.1% to 1.0% of said metal is reoxidized.

7. The process of claim 1 wherein said mildly oxidizing gas contains up to 12 volume % free oxygen.

8. The process of claim 7 wherein said mildly oxidizing gas contains 1% to 8% free oxygen.

9. The process of claim 1 wherein said particles are maintained in said bed for holding times ranging from 5 minutes to 1 hour.

10. The process of claim 1 substantially as described and exemplified.

11. Active metal particles of reduced iron ore provided with a protective oxide coating when prepared by a process claimed in any of the preceding claims.

K. J. VERYARD,
15, Suffolk Street, S.W.1.
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1972.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.