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PATENT SPECIFICATION (11) 1 320 222

NO DRAWINGS

(21) Application No. 38451/70 (22) Filed 10 Aug. 1970 (19)

(44) Complete Specification published 13 June 1973

(51) International Classification C23F 7/04

(52) Index at acceptance
C7U 3 7C

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(54) METHOD OF PASSIVATING IRON

(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:—

This invention relates to passivating iron, especially very active forms of iron having large surface areas. More particularly, it relates to treating iron, especially porous aggregates of iron, to prevent hydrogen generation upon contact with water.

It is known to prepare finely divided iron particles having large surface areas. One process which makes large quantities of such particles is the fluidized iron ore reduction process wherein particulate iron ore is reduced substantially to metallic iron by direct contact with reducing gas such as hydrogen and/or carbon monoxide. The reduction is carried out at relatively high temperatures, e.g., above 1000°F. The powdered product from such processes is often used directly in particulate form or, alternately, it can be compacted into aggregates by such methods as rolling, extruding, pelletizing or briquetting. Unless extremely high temperatures and high compacting pressures are employed, aggregates tend to be highly porous, ranging generally from 5 to 35% porosity and having correspondingly high surface areas ranging from 5 to 20 square meters per gram.

Whether in the form of a powder or a porous aggregate, reduced iron ore having high surface areas and metallizations (as hereinafter defined) of 80 to 95% or higher often tends to be highly active when brought into contact with air or water. For example, the iron tends to back-oxidize rapidly, particularly at high temperatures, to convert metallic iron back to iron oxides. Even worse, upon contact with water, active iron will liberate or generate large quantities of hydrogen. This, among other things, also causes back-oxidation and can present serious safety hazards if the reduced iron products are not properly handled. For example, when a pile of active reduced iron briquettes is exposed to atmospheric air and moisture, the resulting reactions will produce intense heat and raise the temperature of the pile until the liberated hydrogen ignites and combusts with the oxygen in the air, producing a fire of extremely high temperature. Aside from the obvious safety hazard which is presented, the high temperatures also cause the briquettes to fuse together while simultaneously increasing the back-oxidation rate such that large quantities of reduced iron product may be converted to a mass of oxides. This, of course, is economically and operationally untenable.

Numerous methods have been proposed to prevent back-oxidation of reduced iron ore and to prevent hydrogen generation. One method is, of course, to eliminate large surface areas by making relatively nonporous aggregates. This is both economically and operationally unattractive since it requires compacting the reduced iron powder at extremely high temperatures and pressures. Another method is to coat the particles or aggregates of reduced ore to prevent their contact with air. Coatings of hydrocarbon materials such as asphalt, plastics or waxes have been proposed. These are often undesirable contaminants in the product and may also be expensive and inconvenient to apply. Moreover, when the reduced ore product is handled or transported, the coatings may tend to crack or rub off, thus exposing the active iron surfaces to the atmosphere. In such cases, when a fire is initiated, the hydrocarbon coatings merely add to the intensity of the flames.

Still another method for preventing back-oxidation and hydrogen generation is to blanket the active iron product in a dry, inert atmosphere such as nitrogen. This method

[Price 25p]

also can be expensive, if not commercially impractical, since in most cases it is desirable to store reduced iron ore outdoors.

It has now been found that the tendency of active iron to generate hydrogen upon contact with moisture and to back-oxidize on contact with air can be greatly reduced, or even eliminated, in accordance with the present invention.

This invention contemplates a process for producing passivated active or passivated potentially active forms of iron or reduced iron ore having surface areas exceeding 5 square metres per gram which comprises providing the (potentially) active iron or reduced ore at a temperature ranging from 1050 to 1600°F. and contacting the (potentially) active iron either with steam at a temperature in the range of 1200 to 1400°F over a time period of less than one minute, or with a free oxygen containing gas containing 2 to 18.5 mole % oxygen whereby to cool the iron to a temperature ranging from 800° to 1000°F. in a time ranging from one second to five minutes, preferably from one minute to four minutes, and thereafter further cooling the iron to a temperature below 400°F., preferably below 200°F., in a free oxygen-containing gaseous medium preferably containing 2 to 25 mole % oxygen (such as air), in a time period preferably of less than 45 minutes, the time period being so chosen that the metallization of the (potentially) active iron is lowered by an amount ranging up to 3%. Thus, it has been surprisingly found that passivation of active iron, and resistance to back-oxidation of reduced ore, can be achieved by deliberately partially oxidising the iron under carefully controlled conditions.

Potentially active iron can, of course, be provided by reducing oxides of iron at temperatures in the 1050° to 1600°F. range, and then passivated in accordance with this invention (either before cooling, or after first cooling and then reheating to 1050 to 1600°F.).

The maximum contact time with the said free oxygen containing gas, during which the iron is cooled down to 800° to 1000°F, should be sufficiently short so that together with the step of further cooling the iron to below 400°F not more than 3% of the metallic iron in the product is oxidized back to iron oxides. Preferably. the average metallization of the reduced iron will be lowered during this contacting and cooling step by 0.1% to 2% due to oxidation, lesser oxidation being usually insufficient to passivate the product. Metallization as used herein is defined as the weight percentage of total iron in the reduced ore product which is present as metallic iron, i.e.,

$$\frac{\text{(metallic Fe} \times 100\%)}{\text{(Total Fe present as metallic Fe and Oxides, and other materials)}}$$

The precise time required for contact with the free oxygen containing gas and for the cooling step to provide a satisfactory passivated iron product will depend on a number of factors, including gas flow rates and temperature, the size and form of the iron or reduced ore particles and the oxygen concentration in the free oxygen containing gas and in the cooling gas. High gas rates will, of course, provide more oxygen contacting and greater cooling than lower gas rates for a given cooling time. Similarly, ambient temperature cooling gases will obviously cool the iron more rapidly than will heated gases. Also, small particulate forms of iron are oxidized and cooled much more readily than aggregates such as pellets or briquettes. The oxygen concentration in the cooling gas will greatly effect the desired cooling time since high concentration of oxygen will back-oxidize a reduced ore in a correspondingly shorter time than will gases having a low oxygen concentration. It is undesirable, in any event, to use a free oxygen containing gas comprising more than 18.5 mole % oxygen in the first step of the process of the invention since higher concentrations result in severe product back-oxidation, even with very short contact times.

In the second cooling step of the process of the invention, rapid cooling or quenching is preferred to minimize further oxidation. It is important also that the iron or reduced ore should not be allowed to contact liquid water in the quenching step, as this can destroy the passivity of the product. In a preferred embodiment of the invention, air at ambient temperature is used as the oxygen-containing cooling gas in the final cooling step.

In the alternative procedure of this invention wherein the freshly formed reduced iron ore is contacted at a temperature of from 1200° to 1450°F with steam for a period of less than one minute, it is preferred that the steam contacting period should be not less than ten seconds and not more than one minute. When this procedure is employed, the subsequent cooling rate and oxygen concentration of the gas used for cooling in the final cooling step is no longer critical and results in considerable savings in equipment and operating costs. Metallization loss is similar to that mentioned above for the procedure in which the iron is contacted with the free oxygen containing gas.

Particularly suitable forms of iron product are aggregates, such as briquettes, having a porosity ranging from 5 to 30% and a metal-

lization ranging from 80 to 99+%. Briquettes in this range of metallization and porosity are inclined to be highly active in liberating hydrogen from water and are highly susceptible to back-oxidation in the absence of a passivating treatment.

The following examples and demonstrations will serve to illustrate the high degree of passivity that can be imparted to reduced iron ore products having large and active surface areas by treating them in accordance with this invention.

Active particulate reduced iron ore is produced in a fluidized iron ore reduction process and has a particle size ranging generally from 1 to 5000 mircons, averaging about 250 microns, from a surface area averaging about 11 square metres per gram, and a metallization of 94%. A portion of the particulate powder is compacted by conventional means into low porosity "D"-shaped briquettes measuring 3¾ inches by 1½ inches by $^9/_{16}$ inch and having a porosity of about 8%. The surface area of the briquettes is about 9 square metres per gram.

A second portion of the particulate reduced ore powder is formed into high porosity briquettes having a porosity of about 32%, but otherwise being identical in size and form to the low porosity briquettes.

Samples of each of the low porosity and high porosity briquettes are immersed in water at 125°F., and the liberated hydrogen is measured as an indication of the product activity. Other samples are tested for susceptibility to back-oxidation in an atmosphere of pure oxidation at 75°F. The results of these measurements are shown below in Table I.

TABLE I

Sample	H_2 Generation	O_2 Consumption(1)
Low Porosity Briquettes	1.0 SCFH/Ton	2.0 SCFH/Ton
High Porosity Briquettes	8.5 SCFH/Ton	18.0 SCFH/Ton

(1) Average O_2 consumption over a 6-hour period.

Samples of each of the above forms of product are then heated in a nitrogen atmosphere to 1400°F. and cooled to surface temperatures of about 900°F. in about 3 minutes by blowing ambient temperature gas containing 85 mole % nitrogen and 15 mole % oxygen through a bed of the sample material. After cooling to 900°F. the product is then cooled in atmospheric air to 200°F. in about 30 minutes. Samples are then analyzed and tested for metallization, hydrogen generation rate and oxygen consumption rate. The results are shown below in Table II.

TABLE II

Sample	% Metallization	H_2 Generation	O_2 Consumption
Low Porosity Briquettes	93	0.4 SCFH/Ton	1.0 SCFH/Ton
High Porosity Briquettes	91.5	1.0 SCFH/Ton	4.0 SCFH/Ton

By comparing the H_2 generation and oxygen consumption rates for the untreated samples in Table I with the samples of Table II, one can appreciate the astonishing reduction in activity of the iron product treated according to this invention. The data also show that only a very small metallization loss occurs for samples treated according to the invention. In sharp contrast to the foregoing, when air is used in the first cooling step, excessive metallization losses of 10% or more are encountered. It is also found that when the second cooling step is accomplished by water or steam quenching or cooling in hydrogen or nitrogen, little or no passivity is achieved.

The durability of the passivation treatment according to this invention is further illustrated by comparing the results of long-term atmospheric storage tests on untreated and treated high-porosity briquettes as shown below in Table III.

TABLE III

Days of Storage	% Metallization	
	Untreated Briquettes	Treated Briquettes
0	94.0	91.5
10	84.0	91.0
20	80.0	90.5
30	77.0	90.0
40	74.5	89.5
50	73.0	88.5
60	71.0	87.0

As the data indicate, there is 16% greater loss of metallization in the untreated briquettes than in the briquettes treated in accordance with this invention.

In a test of the alternate passivation technique, i.e., contact with steam, high (<30%) porosity briquettes were treated with steam at a briquette temperature of 1250°F. followed by cooling in air without regard to controlling cooling rate or oxygen content of the coolant. The following results were obtained:

TABLE IV

	H_2 Generation SCFH/Hr./Ton		
	No Passivation	Controlled Air Cooling	Steamed 15 Seconds No Critical Air Cooling
High Porosity Briquettes	17.0	7.9	6.5

The invention is not intended to be limited by the above examples, which are illustrative, the scope of the invention being defined by the appended claims.

WHAT WE CLAIM IS:—

1. A process for producing passivated active, or passivated potentially active, forms of iron having a surface area exceeding 5 square metres per gram in which the (potentially) active form of iron is provided at a temperature in the range of from 1050—1600°F and is contacted either with steam or with a free oxygen containing gas having an oxygen content of from 2 to 18.5 mole % oxygen, the active iron either being at a temperature in the range of 1200 to 1450°F over a time period of less than one minute when the contact is with steam, or being cooled to a temperature in the range of from 800 to 1000°F over a time period ranging from one second to five minutes when the contact is with the free oxygen containing gas, and further cooling the thus contacted iron to a temperature below 400°F in a free oxygen-containing gaseous medium over a time period so chosen that the metallization of the (potentially) active iron is lowered by an amount ranging up to 3%.

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2. A process according to claim 1 in which, when the contact of the (potentially) active form of iron is with steam, the period of contact ranges from 10 seconds to one minute.

3. A process according to claim 1 in which, when the contact of the (potentially) active form of iron is with said free oxygen containing gas, the further cooling of the said contacted iron is effected in a gas containing from 2 to 25 mole % of oxygen during a time period of less than 45 minutes.

4. A process according to claim 3 in which the cooling of the (potentially) active iron with said free oxygen containing gas is effected over a time period of from one minute to four minutes.

5. A process according to any preceding claim in which the further cooling of the said contacted iron in the free oxygen-containing gaseous medium is to a temperature of less than 200°F.

6. A process according to any preceding claim in which the further cooling of the said contacted iron is effected with air.

7. A process according to claim 6 in which the said air is at ambient temperature.

8. A process according to any preceding claim in which the metallization of the (potentially) active iron is lowered by from 0.1 to 2%.

9. A process according to any preceding claim in which the (potentially) active form of iron is obtained from the fluidized reduction of particulate iron ore.

10. A process according to claim 9 in which the (potentially) active form of iron is provided at temperatures in the range of from 1050 to 1600°F by reducing oxides of iron at temperatures in the range of 1050 to 1600°F.

11. A process according to any of claims 1 to 8 in which the active form of iron is provided by heating active iron from a lower temperature.

12. A process according to claim 11 in which the active iron which is heated is in the form of briquettes obtained by compacting active iron particles.

13. A process for producing passivated active or passivated potentially active forms of iron according to claim 1 and substantially as described.

14. Passivated active forms of iron when produced by a process in accordance with any preceding claim.

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Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1973.
Published at The Patent Office, 25 Southampton Buildings, London WC2A 1AY
from which copies may be obtained.

