United States Patent

[11] 3,617,254

[72] Inventor **Louis George Imperato, Jr.**
Tenafly, N.J.

[21] Appl. No. **806,672**
[22] Filed **Mar. 12, 1969**
Continuation-in-part of Ser. No. 672,003, Oct. 2, 1967, Continuation-in-part Ser. No. 374,191, June 10, 1964, Pat. No. 3,382,063.
[45] Patented **Nov. 2, 1971**
[73] Assignee **Blocked Iron Corporation**
The portion of the term of the patent subsequent to May 7, 1985, has been disclaimed.

---

[54] **METHOD OF MAKING ORE AGGLOMERATES**
3 Claims, No Drawings

[52] **U.S. Cl.** **75/3**
[51] **Int. Cl.** **C21b 1/24**
[50] **Field of Search** 75/3

[56] **References Cited**

UNITED STATES PATENTS

2,805,141	9/1957	Apuli	75/3
2,844,457	7/1958	Amberg	75/3
3,235,371	2/1966	Volin et al.	75/3
3,382,063	5/1968	Imperato	75/3
3,437,474	4/1969	Imperato	75/3

Primary Examiner—Allen B. Curtis
Attorney—Buell, Blenko & Ziesenheim

ABSTRACT: A method is provided for producing lump metal ores by admixing the finely divided ore with an alkaline earth oxide or hydroxide and a carbonaceous material, forming the mixture into lumps and reacting it with carbon dioxide in the presence of moisture to form alkaline earth carbonates in situ in the lumps.

METHOD OF MAKING ORE AGGLOMERATES

This application is a continuation-in-part of my copending application Ser. No. 672,003, filed Oct. 2, 1967, which is a continuation-in-part of my application Ser. No. 374,191, filed June 10, 1964 now U.S. Pat. No. 3,382,063. **This invention relates to ore agglomerates and methods of making the same and particularly to high strength and at least partially self-reducing iron ore agglomerates and methods of making such agglomerates.**

The need for a satisfactory method of agglomerating iron and other ores, particularly oxide ores, has long been recognized. As the high purity, lumpy ores of the Mesabi and other ranges have been exhausted it has been necessary to turn to ore concentrates recovered from less pure ore deposits and to fine ores not heretofore considered suitable for steel making. In order to make these ores suitable for handling and use in steel-melting furnaces it has been necessary to agglomerate these ores into larger pieces. This has conventionally been done by pelletizing or briquetting the fine ores and sintering or fusing the pellets or briquettes to form the solidified agglomerates. Sintering requires extremely high temperatures and large capital outlays in temperature-resistant equipment.

I have invented an ore agglomerate and method of making such agglomerates which is much less expensive than these sintered agglomerates and is at least partially self-reducing.

In the preferred practice of my invention I admix ore fines with an oxide or hydroxide of an alkaline earth metal, a finely divided carbonaceous material of the group consisting of coal (both bituminous and anthracite), coke, graphite, charcoal, coke breeze and optionally with a small amount of a mineral acid salt of an alkali metal, or an alkaline earth metal and/or a small amount of an alkali hydroxide together with sufficient water to permit the formation of agglomerates such as pellets, briquettes or blocks. These agglomerates are then subjected to an atmosphere of carbon dioxide for a time sufficient to convert a major portion of the alkaline earth oxide or hydroxide to carbonate.

I have found that the moisture level for most effective operation of my process is below 10 percent by weight of the total admixture and preferably in the neighborhood of 5 percent or less.

Preferably the carbonaceous material used in my process is finely divided bituminous coal and i shall hereafter discuss the invention in terms of iron ores the bituminous coal. I prefer the size range of 4-mesh and under for the coal used and good results have been attained at both ends of the range as well as with mixtures of varying particle size coal. I have found that amounts between about 1 percent and 15 percent of coal by weight are most satisfactory for my purposes, although larger amounts to 25 percent have been satisfactorily used in practicing my process. I have found that the use of minus **100**-mesh coal makes it possible to ball or pelletize conventional "as received" specular hematite concentrate without the addition of reground hematite or without the addition of any other fine ore. Prior to my invention, it had been impossible to form balls or pelletize specular hematite by usual balling or pelletizing methods without regrinding or adding another fine ore. This has been one of the very real problems in the heat-indurated

types of pellets heretofore made and is a very distinct advantage to be gained by the practice of this invention. I have found that this can be accomplished within the range of coal concentration set out hereinabove, although I prefer to use about 10 percent minus **100**-mesh coal when forming specular hematite balls or pellets.

The amount of alkaline earth oxide or hydroxide, e.g. lime, preferably lies in the range from about 5 to 20 percent by weight of the admixture.

I prefer to add a small amount (up to about 2 percent)) of a solubilizing agent for calcium and magnesium, as disclosed in my patent U.S. Pat. No. 2,996,372 such as a sugar-containing material, e.g. blackstrap molasses, glucose, fructose, dextrose, syrups, or the like together with a small amount of a mineral acid salt of an alkali on alkaline earth metal such as calcium chloride in an amount less 1 about 10 percent. I may also add a small amount of an alkali metal oxide or hydroxide such as sodium hydroxide, preferably in the range of about 0.1 to about 1.5 percent.

The practice of my invention produces a resulting product which has high strength after being subjected to elevated temperatures, e.g. 1600°—1900° F., and which shows a high percentage of reduced iron after such heating indicating that the product is self-reducing. Both of these properties are highly sought after and difficult to achieve.

The practice of my invention can perhaps best be explained by reference to the following examples which show the significances of the practice of my invention.

EXAMPLE I

Pellets were made by admixing lime hydrated and specular hematite or taconite concentrates with coal. The resulting pellets were subjected to carbon dioxide sufficient to form recrystallized limestone in situ. The carbonated pellets were then divided into two parts, one heated to 1,600° F., and the other to 1,700° F. in an atmosphere containing carbon monoxide such as would be encountered in a blast furnace or like iron-handling furnace. The pellets were removed and analyzed for reduced iron. The results are tabulated in Table I.

TABLE I.—CARBONATE BONDED PELLET SUMMARY

	Percent reduction at—	
	1,600° F.	1,700° F.
Taconite concentrate:		
6 percent lime hydrate	38.7	44.8
6% lime hydrate+5% high volatile coal (−100 M)	49.1	81.5
Specular hematite concentrate:		
23.5% reground (−325 M) specular hematite+5% lime hydrate	39.3	45.6
23% reground specular hematite (−325 M)+5% lime hydrate+5% high volatile coal	{50.6 {39.8	74.1
As received specular hematite+5% lime hydrate+10% high volatile coal	49.1	87.1

EXAMPLE II

An additional series of pellets were made as in Example I and after removal from the heating furnace at 1,600° and 1,700° F., respectively, were screened to determine the amount above 4-mesh and the amount below **20**-mesh. They were then jarred for 15 minutes in a container and again screened. The test results appear in Table II.

TABLE II

	Screen test from furnace at—				Screen test after jarring at—			
	1,600° F.		1,700° F.		1,600° F.		1,700° F.	
	+4 M	−20 M	+4 M	−20 M	+4 M	−20 M	+4 M	−20 M
Taconite:								
6% lime hydrate	96.7	1.67	96.9	1.48			43.7	51.8
9% lime hydrate	99.9	0.1	99.87	0.13	77.82	21.96	78.28	21.62
12% lime hydrate	99.6	0.3	99.5	0.2	83.9	15.9	82.8	16.8
9% lime hydrate+10% high volatile coal (−8 M)	99.2	0.38	97.6	0.13	80.64	17.30	80.09	15.0
9% lime hydrate+8% high volatile coal (−8 M) and 2% low volatile coal (−8 M)	98.62	0.61	99.47	0.23	81.00	16.98	84.17	14.24
9% lime hydrate+8% high volatile coal (−8+150 M) and 2% low volatile coal (−8+150 M)	96.69	0.56	98.57	0.42	81.77	14.23	78.77	17.37
Specular hematite:								
25% reground (−325 M)+5% lime hydrate+15% high volatile coal (−100 M)	99.60	0.35	96.80	2.54	76.77	20.17	57.12	36.61
Venezuelan ore:								
Plus 4.76 lime hydrate	97.59	0.87			60.43	32.41		
6% lime hydrate+15% high volatile coal (−100 M)	98.0	1.0	95.4	2.0	85.70	11.79	84.75	12.82

EXAMPLE III

A series of tests were made on pellets produced by mixing together lime hydrate, specular hematite ore in both the "as received" and the "reground" forms as in Example I but substituting various other types of carbonaceous material for coal fines and omitting the molasses and chloride. The resulting pellets were subjected to an atmosphere of carbon dioxide as in Example I to form recrystallized limestone in situ. These hardened pellets were tested as were the pellets in Example II. The results of the tests appear in Table III.

TABLE III.—ROOM TEMPERATURE STRENGTH DATA

Pellet composition:
Specular hematite as received, percent, 17
Specular hematite reground, percent, 70
Lime hydrate, percent, 9
Carbonaceous materials, various, percent, 4

Carbonaceous materials, type	Compression test, lbs.	Tumble test, 0/0+¼" 280 rev.
Coke breeze	161	96
Anthracite	113	89
Graphite	119	89
Charcoal	173	96

EXAMPLE IV

Pellets made for Example III were then treated in the heated furnace as in Examples I and II. The test results appear in Table IV.

TABLE IV

Pellet composition:
Specular hematite as received, percent, 17
Specular hematite reground, percent, 70
Lime hydrate, percent, 9
Carbonaceous materials, various, percent, 4

	Screen test from furnace at—				Screen test after jarring at—			
	1600° F.		1,700° F.		1,600° F.		1,700° F.	
Carbonaceous materials, types	+4 M	−20 M	+4 M	−20 M	+4 M	−20 M	+4 M	−20 M
Coke breeze	99.6	0.30	----	----	74.8	23.5	----	----
Anthracite	99.8	0.19	----	----	73.0	26.2	----	----
Graphite	99.7	0.26	----	----	73.6	24.6	----	----
Charcoal	99.5	0.39	----	----	78.0	21.2	----	----
Heat-indurated taconite pellet	91.67	1.37	93.41	1.37	72.24	15.35	68.17	20.03

EXAMPLE V

Copper concentrates were mixed with dolomitic fines and coal fines to form three different compositions. These were pelletized and tested. The compositions are set out in Table V.

TABLE V

Test Sample, Identification and composition

Sample Number	Composition
I	95% by weight Copper Concentrate 5% Dolomitic Hydrate
II	93% by weight Copper Concentrate 22% percent Coal Fines 5% Dolomitic Hydrate
III	91% by weight Copper Concentrate 4% Coal Fines 5% Dolomitic Hydrate

The green ball physical characteristics of these pellets of copper concentrates are set out in Table VI.

TABLE VI

Green Ball Physical Characteristics

Sample Number	Pellet Moisture % By Weight, Dry Basis	Impact Resistance Measured as the Number of Drops from a Height of 18" Onto A Steel Plate Required to Fracture an Individually Dropped Ball (20 ball Average)
I	12.10	11
II	12.74	16
III	11.86	16

The pellets were dried prior to exposure and treatment with carbon dioxide to the levels of moisture set out in Table VII.

TABLE VII

Before exposure and treatment with carbon dioxide gas, the green wet pellets were dried to a moisture content indicated below:

Sample Number	Dried Pellet Moisture, % Dry Basis
I Run 1	4.72
Run 2	3.82
II Rub 1	4.17
Run 2	3.03
III Run 1	3.28
Run 2	4.26

TABLE VIII.—CARBONATED PELLET STRENGTH CHARACTERISTICS

Sample Number	Crushing strength [1] (20 ball avg.) −13/32"+25/64"	(20 ball avg.) −17/32"+½"	Abrasion resistance [2]
I Run 1	67	104	52.4
I Run 2	80	91	56.2
II Run 1	90	117	81.0
II Run 2	77	96	76.0
III Run 1	70	92	70.0
III Run 2	49	81	40.5

[1] Measured as the average total load in pounds required to fracture an individual pellet with the size consist indicated.
[2] Measured as the percent by Weight of +¼" material remaining in a five pound test sample of pellets which had previously been rotated in an ASTM coke tumbling drum for 200 revolutions.

A sample of pellets were heated in nitrogen from room temperature to 1,600° F. in approximately 60 minutes and the sample remained in the nitrogen atmosphere at 1,600° F. for an additional hour. The specimens were cooled in nitrogen to room temperature, removed from the furnace, and tested as follows:

Crushing Strength: Ten pellets were removed from the sample and the average load required to fracture an in-

dividual pellet was determined.

Abrasion Test: The remainder of the sample was placed on a 4-mesh sieve screen which was then put into a Ro-Tap shaker apparatus and jarred for 15 minutes. The percent by weight of the material remaining on the 4-mesh screen after jarring was determined.

The test results are set out in table IX

TABLE IX

Sample Number	Crushing Strength, in pounds	% +4M After Jarring
I RUN 2	5	31.7
II Run 1	101	51.9
III Run 1	27	48.5

It will be evident from the foregoing tables and examples that a high strength pellet capable of a high level of self-reduction can be achieved by the practice of my invention.

While I have described certain preferred practices and products according to my invention, it will be understood that this invention may be otherwise embodied within the scope of the following claims. 1. The method of producing a high strength, self-reducing lump ore from finely divided metal-containing materials comprising the steps of admixing the finely divided metal ore containing material with at least one of the group consisting of the oxides and hydroxides of alkaline earth metals and with a carbonaceous material from the group consisting of coal, coke, graphite, coke breeze and charcoal, forming the mixture into lumps and reacting the lumps with carbon dioxide in the presence of moisture to form alkaline earth carbonates in situ in the lumps.

2. The method as claimed in claim 1 wherein the carbonaceous material is coal having a fineness of 4-mesh and under.

3. The method as claimed in claim 1 wherein the metal ore is copper concentrates.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,617,254 Dated November 2, 1971

Inventor(s) Louis George Imperato, Jr.

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

Column 3, Example V, Table V, Sample Number II, "22% percent Coal Fines", should read -- 2% Coal Fines -- .

Signed and sealed this 24th day of October 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

RM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334