

1

2

3,437,474

**METHOD OF MAKING ORE AGGLOMERATES**  
 Louis George Imperato, Tenafly, N.J., assignor to Blocked  
 Iron Corporation, a corporation of New York  
 No Drawing, Continuation-in-part of application Ser. No. 5  
 374,191, June 10, 1964. This application Oct. 2, 1967,  
 Ser. No. 672,003

The portion of the term of the patent subsequent to  
 May 7, 1985, has been disclaimed  
 Int. Cl. B22b 1/24; B21b 1/28  
 U.S. Cl. 75-3

8 Claims

## ABSTRACT OF THE DISCLOSURE

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 di-  
 oxide in the presence of moisture to form alkaline earth  
 carbonates in situ in the lumps.

This application is a continuation in part of my co-  
 pending application Ser. No. 374,191, filed June 10, 1964,  
 now Patent No. 3,382,063.

This invention relates to ore agglomerates and methods  
 of making the same and particularly to a 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 neces-  
 sary 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 mak-  
 ing 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 con-  
 vert a major portion of the alkaline earth oxide or hydrox-  
 ide to carbonate.

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

Preferably the carbonaceous material used in my pro-  
 cess is finely divided bituminous coal and I shall hereafter  
 discuss the invention in terms of iron ores and 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%

to 15% of coal by weight are most satisfactory for my  
 purposes, although larger amounts up to 25% 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 hema-  
 tite concentrate without the addition of reground hema-  
 tite 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 in-  
 vention. I have found that this can be accomplished with-  
 in the range of coal concentration set out hereinabove,  
 although I prefer to use about 10% 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%  
 by weight of the admixture.

I prefer to add a small amount (up to about 2%) of  
 a solubilizing agent for calcium and magnesium, as dis-  
 closed in my Patent No. 2,996,372, such as a sugar con-  
 taining material, e.g. blackstrap molasses, glucose, fruc-  
 tose, dextrose, syrups, or the like together with a small  
 amount of a mineral acid salt of an alkali or alkaline  
 earth metal such as calcium chloride in an amount less  
 than about 1%. 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%.

The practice of my invention produces a resulting prod-  
 uct which has high strength after being subjected to ele-  
 vated temperatures, e.g. 1600°-1900° F., and which shows  
 a high percentage of reduced iron after such heating indi-  
 cating 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 ex-  
 plained by reference to the following examples which  
 show the significances of the practice of my invention.

### EXAMPLE I

A series of test were made on pellets produced by ball-  
 ing specular hematite "as received" and reground with  
 high volatile coal and low volatile coal and mixtures of  
 the two types of coal, with lime and with 0.5% blackstrap  
 molasses and 0.4% calcium chloride. The coal was used  
 "as received" in which condition its size was minus 4 mesh  
 and reground to 100 mesh (100 M). The lime was a mono  
 hydrated dolomitic lime powder known in the trade as  
 Ohio Super spray hydrate.

A series of tests to determine the green ball strength and  
 characteristics were performed as follows:

#### Drop test

A representative sample of twenty carefully sized  
 -1 $\frac{1}{32}$ " +1 $\frac{1}{32}$ " green wet balls are dropped individually  
 from a height of eighteen inches onto a steel plate and the  
 number of consecutive drops required for failure is used  
 to determine an arithmetical average.

#### Green ball compression test

An identical sample as just previously described is used  
 and a compressive load is applied to individual balls and  
 the load required to fracture is used to determine the  
 arithmetical average.

The resulting data appear in Table I.

TABLE I.—GREEN BALL STRENGTHS

Coal, type	Coal, percent	Specular Hematite conc. as rec'd, percent	Specular Hematite conc. re-ground, percent	Lime, percent	Drop test, drops to failure	Compression, lbs. to failure
None.....		71.00	24.00	5.00	6	2.2
High volatile coal, as rec'd.....	9.48	64.10	21.30	5.12	13	3.3
High volatile coal, as rec'd -100 M.....	4.75	67.60	22.54	5.12	14	3.3
Do.....	9.48	64.10	21.30	5.12	16	4.1
Do.....	18.96	56.96	18.96	5.12	24	3.4
Do.....	25.00	52.42	17.46	5.12	40	3.2
Low volatile coal, as rec'd.....	9.48	64.10	21.30	5.12	16	3.1
Low volatile coal, as rec'd -100 M.....	9.48	64.10	21.30	5.12	13	4.1
High volatile coal, -100 M.....	11.00	83.88	None	5.12	13	3.1
High volatile coal, -100 M.....	8.00	85.00	None	7.00	19	3.6

## EXAMPLE II

The pellets of Example I were treated with carbon dioxide at room temperature to harden and convert the lime to carbonate in situ. These hardened pellets were tested as follows:

## Tumble test

A five pound charge of the completed pellets are tumbled in an A.S.T.M. coke tumbler and the residue remaining on a  $+1/4$ " screen after 280 revolutions is recorded as a percentage of the original five pounds and noted as the tumble strength index.

## Compression test

A representative sample of twenty  $-13/32$ "  $+12/32$ " pellets are drawn and a compressive load is applied to individual pellets and the load required to fracture is used to determine the arithmetical average.

The results of these tests are tabulated in Table II.

TABLE II.—ROOM TEMPERATURE STRENGTH DATA

Coal, percent	Coals, type	Specular Hematite conc., percent		Taconite, percent	Lime Hydrate, percent	Compression test, lbs.	Tumble test, 0/0- $+1/4$ " 280 Rev.
		Rec'd	Reground				
4.74	High volatile -100 M.....	67.60	22.54	-----	5.12	320	99
9.48	do.....	64.10	21.30	-----	5.12	225	99
18.96	do.....	56.92	18.96	-----	5.12	105	96
25.00	do.....	52.42	17.46	-----	5.12	50	96
9.48	Low volatile -100 M.....	64.10	21.30	-----	5.12	170	99
9.48	High volatile, as rec'd.....	64.10	21.30	-----	5.12	250	99
9.48	Low volatile, as rec'd.....	64.10	21.30	-----	5.12	225	98
10.00	High volatile -100 M.....	84.00	0	-----	6.00	260	98
0	-----	-----	-----	93.70	6.30	343	96
0	-----	-----	-----	80.90	9.10	445	-----
5	High volatile -100 M.....	-----	-----	90.00	5.00	205	-----
5	do.....	-----	-----	89.00	6.00	255	99
5	do.....	-----	-----	88.00	7.00	323	-----
9.48	50/50 -100 high volatile/ -100 low volatile.....	64.10	21.30	-----	5.12	205	99
9.48	50/50 as rec'd. high volatile and low volatile.....	64.10	21.30	-----	5.12	240	98

## EXAMPLE III

The carbonated pellets of Example II were tested at elevated temperatures and in reducing atmospheres as follows and compared to a commercial taconite heat indurated pellet.

## Reduction test

Pellets which had been heated in the above described crucible test are placed in a magnetic field and the degree of attraction is recorded as a qualitative observation.

The results appear in Table III.

TABLE III.—CRUCIBLE TEST DATA

Coal percent-type	Specular Hematite conc., percent		Taconite, percent	Lime hydrate, percent	Crucible test, load to failure, lbs.							
	Rec'd	Reground			After time in minutes							
					0	15	30	45	60	90	210	
None.....	72	23	-----	5.00	410	23	14	9	8	11	12	
4.74 -high volatile -100 M.....	67.6	22.54	-----	5.12	320	30	30	29	29	29	27	
Heat indurated taconite pellet.....	-----	-----	-----	-----	500	23	15	16	19	12	18	
9.48 -high volatile as rec'd.....	64.1	21.3	-----	5.12	250	27	27	24	22	22	19	
9.48 -high volatile -100 M.....	64.1	21.3	-----	5.12	225	30	30	30	30	29	21	
Do.....	34.2	51.20	-----	5.12	180	30	30	30	30	30	27	
9.48 -low volatile as rec'd.....	64.1	21.3	-----	5.12	-----	30	25	21	20	20	17	
18.96 -high volatile -100 M.....	56.96	18.96	-----	5.12	105	30	23	23	17	15	10	
11.00 -high volatile -100 M.....	83.88	-----	-----	5.12	160	30	28	23	20	19	12	
13.00 -high volatile -100 M.....	81.88	-----	-----	5.12	135	30	30	29	25	22	16	
None.....	70.0	23.5	-----	6.50	500	30	26	23	16	19	17	
10.00 -high volatile -100 M.....	84.0	-----	-----	6.00	170	30	30	30	30	28	18	
Do.....	83.0	-----	-----	7.00	178	30	30	30	30	28	22	
None.....	57.00	38.00	-----	1.50	11	5	8	8	8	9	0	
9.48.....	51.2	34.2	-----	1.5, 1.2	5	5	3	2	2	3	3	
None.....	60	40	-----	None	10	2	2	2	2	2	2	

† Non-carbonated.

‡ Non-carbonated, 0.75 bentonite.

15

20

25

30

**5**  
**EXAMPLE IV**

Pellets were made as in Example II by carbonation substituting taconite concentrates for the specular hematite. These pellets were subject to the same tests as Example III and the data tabulated in Table IV.

5

**6**  
**EXAMPLE VII**

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

TABLE IV

Coal percent-type	Specular hematite conc., percent		Taconite, percent	Lime hydrate, percent	Crucible test—load to failure, lbs.							
	Rec'd	Reground			After time in minutes							
					0	15	30	45	60	90	210	
None.....			93.7	6.3	343	30	30	30	30	30	30	30
5.00 —high volatile —100 M.....			88.0	7.0	323	50	40	30	30	30	30	30
None.....			93.28	16.72	10	18	25	28	20	13	19	18
9.48 —high volatile —100 M.....			83.80	16.72	7	8	7	9	7	6	8	8

<sup>1</sup> Non-carbonated.

**EXAMPLE V**

Pellets were made by admixing lime hydrate, coal and or as in Example I. 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 1600° F. and the other to 1700° 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 V.

25

30

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 VII.

TABLE V.—CARBONATE BONDED PELLET SUMMARY

Taconite Concentrate	Percent Reduction	
	1,600° F.	1,700° F.
6% Lime Hydrate.....	38.7	44.8
6% Lime Hydrate Plus 5% High Volatile Coal (—100 M).....	49.1	81.5
Specular Hematite Concentrate		
23.5% Reground (—325 M) Specular Hematite Plus 5% Lime Hydrate.....	39.3	45.6
23% Reground Specular Hematite (—325 M).....	50.6	74.1
Plus 5% Lime Hydrate Plus 5% High Volatile Coal.....	39.8	-----
As Received Specular Hematite Plus 5% Lime Hydrate Plus 10% High Volatile Coal.....	49.1	87.1

**EXAMPLE VI**

An additional series of pellets were made as in Example V and after removal from the heating furnace at 1600° F. and 1700° 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 VI.

50

55

TABLE VII.—ROOM TEMPERATURE STRENGTH DATA

Pellet Composition: Specular Hematite as received, 17%; Specular Hematite reground, 70%; Lime Hydrate, 9%; Carbonaceous Materials, various, 4%.

Carbonaceous Materials, type	Compression test, lbs.	Tumble Test, 9/0+1/4" 280 Rev.
Coke Breeze.....	161	96
Anthracite.....	113	89
Graphite.....	119	89
Charcoal.....	173	96

TABLE VI

Taconite	Screen Test From Furnace				Screen Test After Jarring			
	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
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 plus 10% High Volatile Coal (minus 8 M).....	99.2	0.38	97.6	0.13	80.64	17.30	80.09	15.0
9% Lime Hydrate plus 8% High Volatile Coal (minus 8 M) and 2% Low Volatile Coal (minus 8 M).....	98.62	0.61	99.47	0.23	81.00	16.98	84.17	14.24
9% Lime Hydrate plus 8% High Volatile Coal (minus 8 plus 150 M) and 2% Low Volatile Coal (minus 8 plus 150 M).....	96.69	0.56	98.57	0.42	81.77	14.23	78.77	17.37
Specular Hematite:								
25% Reground (minus 325 M) plus 5% Lime Hydrate plus 15% High Volatile Coal (minus 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 (minus 100 M).....	98.0	1.0	95.4	2.0	85.70	11.79	84.75	12.82

7  
EXAMPLE VIII

Pellets made for Example VII were then treated in the heated furnace as in Examples V and VI. The test results appear in Table VIII.

TABLE VIII

Pellet Composition: Specular Hematite as received, 17%; Specular Hematite reground, 70%; Lime Hydrate, 9%; Carbonaceous Materials, various, 4%.

Carbonaceous Materials, types	Screen Test From Furnace				Screen Test After Jarring			
	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
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

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.

I claim:

1. The method of producing a high strength, self reducing lump ore from finely divided iron containing materials comprising the steps of admixing the finely divided iron 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 up to about 2% by weight of the total mixture of a solubilizing agent for alkaline earth metals is added.

3. The method as claimed in claim 1 wherein a mineral acid salt from the group consisting of alkali and alkaline earth metals is added in an amount up to about 1% on the weight of the admixture.

4. 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 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, adding thereto up to about 2% of a solubilizing agent for magnesium and calcium, up

to about 1% of mineral acid salt of a member from the group consisting of alkali metals and alkaline earth metals and about 0.1% to about 1.5% of a member from the group consisting of alkali metal oxides and hydroxides,

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.

5. The method as claimed in claim 4 wherein the moisture level in the mixture is less than about 10% by weight on the total admixture.

6. The method of producing a high strength, self reducing lump ore from finely divided iron containing materials comprising the steps of admixing the finely divided iron containing material with about 5% to 20% of at least one of the group consisting of the oxides and hydroxides of alkaline earth metals and with between about 1% to 25% of a carbonaceous material from the the group consisting of coal, coke, coke breeze, graphite 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.

7. The method as claimed in claim 6 wherein up to about 2% of a solubilizing agent for calcium and magnesium is incorporated into the admixture.

8. The method of producing a high strength lump iron ore as claimed in claim 6 wherein the mixture contains up to about 10% moisture.

#### References Cited

##### UNITED STATES PATENTS

145,462	12/1873	Taylor	-----	75—3
2,823,109	2/1058	Sudo	-----	75—3
2,996,372	8/1961	Imperato	-----	75—3
3,205,063	9/1965	Franklin et al.	-----	75—3

L. DEWAYNE RUTLEDGE, *Primary Examiner*.

ERNEST L. WEISE, *Assistant Examiner*.