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# BRIQUETTED RIMMING AGENTS AND METHOD OF MAKING SAME

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This application, relating as indicated to a briquetted rimming agent, is particularly directed to a novel briquette incorporating a fluoride rimming activating agent of calcium fluoride, sodium fluoride or sodium aluminum fluoride and, under certain conditions, combinations of these.

In general, in connection with the rim activators and with the making of steel, it has been customary to use certain alloy addition agents, sometimes in briquetted form, and it has also been customary to use fluoride activators, particularly fluorspar, i. e., calcium fluoride, sodium fluoride and sodium aluminum fluoride. Many problems have come up in connection with the use of these fluorides. For best action the powder should be relatively fine and non-crystalline. However, the packaging of this is troublesome and when added to a ladle of molten steel or ingot in this form, it is difficult to get into solution in the molten steel. When the bag approaches the molten metal, the convection of hot air billows the powdered chemical upwards into the crane cab creating a safety hazard. Bagged sodium fluoride breaks or burns from sparks flying from the mold. Sodium fluoride then sifts through a whole barrel of bags and the pouring crew personnel get this toxic material on their hands. The briquette of this invention by being coated and being a solid eliminates this safety hazard.

This briquetted rimming agent comprises a green briquette, generally a 1 oz. or 4 oz. briquette, which is a combination of a particular binder, such as a synthetic shellac, briquetted at a pressure of 1,000–8,000 p. s. i., coated with a water glass solution combined with a wetting agent, and sintered at 100–500° F., or generally 400–500° F.

This produces a very convenient form which is absolutely anhydrous and non-hygroscopic. The addition of water even in minute particles can be a source of explosion. These briquettes will not absorb moisture in transit to the steel mill or when stored under humid or moist conditions. They are firm and will not spall or crack readily. They have delayed reaction on entering the molten metal, so that they will sink and get the fluoride well into the melt before it dissolves and distributes itself through the metal in the mold.

An object of this invention is to produce a new and improved briquetted rimming agent and method of making same.

A further object of this invention is to produce a highly active form of a fluoride with a synthetic binder, held together in a mass and coated with a water-proof material that is a non-contaminate and anyhdrous.

A further object of this invention is to produce a new briquetted rimming agent with improved properties, characterized by a slightly delayed solubility in the molten steel.

To the accomplishment of the foregoing and related ends, said invention then consists of the means hereinafter fully described and particularly pointed out in the claims; the following description setting forth in detail



but one approved method of carrying out the invention, such disclosed method, however, constituting but one of the various ways in which the principles of the invention may be used.

In the prior art various fluoride addition agents have been used, as, for example, in Tanczyn Patent No. 2,510,154, which teaches a lithium fluoride agent to stainless steel, and in Harris Patent No. 1,920,465, which teaches an alkali fluoride and an alkaline earth oxide for desulphurization. Other patents teach that it was common in the open hearth furnace to add calcium fluoride (fluorspar), in order to keep the slag fairly fluid.

In this general field, the following prior art patents were also noted:

British Patent No. 509,422 which teaches the addition of aluminum and calcium or sodium fluoride to the steel ingot in the ladle to produce a rimmed steel. This reduces defects of blow-holes. This patent also teaches a method of making steel, i. e., rimmed steel ingots, by adding both aluminum and either calcium or sodium fluoride to the steel with the aluminum;

British Patent No. 423,489 (fluorides as fluxes to chrome steels) relates to the casting of steel alloys, including aluminum not exceeding 5 percent and chromium not exceeding 8 percent. Aluminum oxidizes readily and makes a sticky slag, and it is almost impossible to pour the metal. This patent also relates to fluorides which in general will dissolve or react with aluminum oxide to form a flux or slag. These fluorides are sodium, potassium, calcium, barium and the double fluorides of aluminum and sodium, i. e., Cryolite. All of the alkali and alkaline earth groups are suitable fluxes or solvents for the oxide. When aluminum is under 2 percent by weight of the metal, one-quarter lb. of the double fluoride of sodium and aluminum per hundred pounds of metal is sufficient. The invention here then is directed to the casting of a ferrous alloy containing less than 2 percent by weight of aluminum and up to 8 percent chromium, which includes adding to the ladle Cryolite, one-quarter lb. per one hundred lbs. of metal to act as a flux for the aluminum oxide;

Haserick Patent No. 121,245 (U. S.) which teaches a briquette of iron, bound together by clay with the use of pressure;

Vance Patent No. 2,405,278 (U. S.) which consists of a steel making addition of ferro alloy fragments, with a binder of three to five percent of tar or pitch;

Turnbull Patent No. 1,869,925 (U. S.) which teaches an alloying material to ferro silicon or ferro manganese, with a container of Portland cement, including reinforcing materials that may be added to steels;

Olivo Patent No. 2,540,173 (U. S.) which teaches a briquette of carbonaceous material, calcium silicide and an inorganic binder;

Stohr Patent No. 2,497,745 (U. S.) which teaches a silicon carbide briquette, together with binders and other materials;

Mican Patent No. 2,205,043 (U. S.) which teaches water glass as a binder for comminuted oxides for the production of steel;

Frauenknecht Patent No. 2,068,793 (U. S.) which teaches carbon additions to steel which are rendered incombustible with water glass, i. e., sodium silicate, and are held together by an organic adhesive;

Brown Patent No. 2,111,521 (U. S.) which teaches sodium silicate as a binder for silicon carbide;

Crosser Patent No. 1,568,271 (U. S.) which teaches a briquetted deoxidizer such as ferro silicon, ferro manganese and the like, together with a large volume of binder, as, for example, clay, i. e., they use 50 to 80 percent by volume of binder—ceramic or clay;

Jordan Patent No. 2,232,242 (U. S.) which teaches the use of fluorspar bearing metallurgical flux made from fluorspar and petroleum coke with water, formed in pellets and sintered;

Kern Patent No. 2,620,267 (U. S.) which teaches a slag forming agent for a ladle or ingot consisting of a mixture of fine fluorspar, lime and cement, forming a binder with water glass, sodium silicate and ferric chloride and briquetting to 4,000 lbs./sq. inch;

Hyde Patent No. 2,184,078 (U. S.) which consists of a pellet of fluorspar, together with about 5 percent of Mason's hydrate and 10 percent of fuel, such as coke, and sintered in a bath;

Abbott Patent No. 2,220,383 (U. S.) which teaches the addition of casine and bentonite clay, pelleting and drying;

Abbott Patent No. 2,220,384 (U. S.) which teaches a briquette and a method of making same, with tall oil;

Abbott Patent No. 2,220,385 (U. S.) which teaches a flux and the method of making same, comprising adding to fluorspar sulphite liquor and bentonite clay, and heating to 200–400° F.;

Vahrenkamp Patent No. 2,459,203 (U. S.) which consists of mixing a small amount of bentonite and water and fluorite, and calcining the pellets at about 1,000° C.;

Davies Patent No. 1,848,323 (U. S.) which teaches a metallurgical flux of potassium chlorite, borax, sodium fluoride and manganese dioxide;

Smith Patent No. 1,744,418 (U. S.) which consists of incorporating in a steel a mixture of lead oxide and sodium fluoride which agglomerates the inclusions; and

Robinson Patent No. 1,997,602 (U. S.) which teaches a process of treating molten iron with sal soda, saltpeter and fluorspar, including some charcoal.

The following prior art patents may also be of interest:

| | |
|---|---|
| 1,562,655 | 128,365 |
| 1,672,446 | 464,815 |
| 1,727,088 | 958,700 |
| 1,748,217 | 1,038,370 |
| 2,044,908 | 1,536,033 |
| 156,009 | 1,539,314 |
| 572,969 | 1,739,839 |
| 1,910,444 | 1,741,544 |
| 2,215,078 | 1,920,246 |
| 2,279,033 | 1,982,541 |

Notwithstanding the teachings of the above-noted patents, an improved way has not been found of adding a rim activator to the ladle or ingot for the purpose of rimming steel.

In general, this invention consists of a fine powder of sodium fluoride in one modification, calcium fluoride in another modification and sodium aluminum fluoride in a third modification, which is mixed with a binder of "Vinsol," an adhesive manufactured by Hercules Powder, or "Corex," a synthetic shellac. This is used from 1 to 10 percent of the compound, but more specifically 3 to 5 percent. Under 3 percent of a binder produces a briquette which breaks too easily. The briquette is formed under a pressure of from 1,000–8,500 lbs./sq. inch. Lower pressures produce a briquette which dissolves too rapidly and breaks too easily. Higher pressures do just the reverse. I generally, however, prefer to use 3,500–6,500 p. s. i.

Of particular importance is the screen analysis of the fluoride powder, and I prefer those which offer most surface of grains to molten metal when dissolved, yet have maximum binding or briquetting qualities.

These green briquettes are coated on the outside and dipped for 11 to 15 minutes in a sodium silicate solution, i. e., water glass consisting of 3 to 5 percent sodium silicate, with a smaller quantity of a wetting agent, such as "Pluoronics," and 1 percent of "Corex." These are baked for 15 minutes at 100–500° F., preferably 400–500° F. These briquettes when cooled are absolutely anhydrous and non-hygroscopic. They dissolve in from 13 to 30 seconds in molten steel and distribute evenly the fluoride material through the mixture. This material has been fully tested, both with sodium and calcium fluorides and sodium aluminum fluoride in the preferred ranges. The following table gives examples of these materials:

| | Excessive Breakage, Not Desired | | Desired | | Not Desired, Melts Too Slowly | |
|---|---|---|---|---|---|---|
| Binder | 3% | 3% | 3% | 5% | 5% | 5% |
| Compression, p. s. i. | 1,000 | 1,100 | 3,500 | 5,000 | 6,500 | 8,500 |
| Solution time, sec. | 17 | 19 | 24 | 19 | 38 | 44 |

In connection with this invention the following is a detailed description of the method and components:

*Binders*

(1) Use a naturally occurring thermoplastic resin recovered from the refining of FF wood rosin, as, for example,

(*a*) "Corex"—manufactured by Crosby Chemicals, Inc.

(*b*) "Vinsol"—manufactured by Hercules Powder Co.

(2) These materials melt at approximately 350° F.

(*a*) This melting point enables holding a powdered material in solid form for a short period in a molten metal bath and then gives fast dispersion of the grains of powder as the heat of the bath permeates the briquette.

(3) These materials give green strength from compression, which holds the briquette in form to be baked.

(4) When baked these materials give excellent dry strength to the briquette which allows shipping and handling without breakage.

(5) These materials fill the interstitial spaces between the grains of powder and prevent the entrance of moisture. They also form a protective glaze to the briquette which prevents powder from rubbing off on workers' hands.

(6) The amount of binder giving the best results was from 1 to 10 percent of the compound, depending on the percentage of various fluorides used in the compound. 3 to 5 percent generally proved the ideal range.

*Material sizes*

(1) It was found that the grain size of fluoride powders to be briquetted were of prime importance in producing a strong briquette with solubility facile enough to prevent the material from freezing in the molten metal. The following specifications of raw materials were found to give maximum bonding qualities, maximum fluorine release, and maximum dispersion when immersed in molten bath.

| | Percent |
|---|---|
| (*a*) Sodium fluoride: | |
| on 65 mesh screen (W. S. Tyler test screen) | 3–4 |
| 65–100 mesh screen (W. S. Tyler test screen) | 5–6 |
| 100–200 mesh screen (W. S. Tyler test screen) | 25–30 |
| 200–325 mesh screen (W. S. Tyler test screen) | 30–40 |
| Thor 325 mesh screen (W. S. Tyler test screen) | 25–35 |
| (*b*) Cryolite (synthetic): | |
| On 20 mesh (W. S. Tyler test screen) | 16+or−10 |
| 20–48 mesh (W. S. Tyler test screen) | 21+or−10 |
| 48–100 mesh (W. S. Tyler test screen) | 13+or−10 |
| 100–200 mesh (W. S. Tyler test screen) | 10+or−10 |
| Thor 200 mesh (W. S. Tyler test screen) | 40+or−10 |
| (*c*) Calcium fluoride: | |
| Thor 20 mesh (W. S. Tyler screen) | 100 |
| Thor 325 mesh (W. S. Tyler test screen) | 22 |
| (*d*) Greenland mined Cryolite: | |
| Thor 325 mesh (W. S. Tyler test screen) | 92 |
| On 250 mesh (W. S. Tyler test screen) | 5 |
| Fluorine content | 54.3 |

Material of finer or coarser mesh either crumbled in the green state, or laminated after compresison. Other mesh materials had proper green strength, but then crumbled or laminated after or during baking.

*Density*

(1) It was found, after testing, that density of the briquette had a very important effect on solution time. To reach the proper density, compression under pressure of from 1,000 to 8,500 p. s. i. proved to be necessary. I generally, however, prefer to use 3,500–5,000. Lower pressure produces a briquette which powders or spalls excessively. Pressures over 8,500 p. s. i. give a dense briquette which goes into solution too slowly, and presents the hazard of freezing in the molten bath.

(2) A table giving test examples of various density briquettes and their solution times is given above.

*Baking time of briquette*

(1) The briquette must be baked at a specific, even rate for a specific time in order that the interspersed binder be semimelted throughout the whole body of the briquette. If the briquette is not thoroughly baked, it will crumble or break. If it is overbaked, a refractory ash or crust forms on the surface of the briquette which prevents its giving into solution and causes freezing of a solid mass of the compound in the molten bath as it solidifies.

It was found that the proper temperature and lengths of baking time was from 100–500° F. for a period of from 11 to 15 minutes. If a quicker, hotter bake was given, the binder sintered and formed the refractory cover described above.

*Safety coating of briquette*

(1) These briquettes were given a protective coating of a 5 percent sodium silicate solution, i. e., water glass, for two reasons:

(*a*) So that any toxic materials incorporated in the briquetted compound would not rub off in handling.

(*b*) So that the briquette would be anhydrous and thus the hazard of explosion caused by incorporated moisture being injected below the surface of a molten bath of metal would be eliminated.

(2) The coating is given by dipping the green briquette in a solution of 5 percent silicate of soda, 1 percent synthetic shellac (Corex) and ½ percent of a wetting agent, such as "Pluoronics."

(*a*) The wetting agent aids in getting the silicate of soda and "Corex" to penetrate approximately ¼ inch into the surface of the briquette so that all interstitial spaces are well filled and exterior grains of powder well coated to prevent intrusion of moisture or "rubbing off" of toxic or non-toxic powder.

*Size of briquette*

It was found to be advantageous to have a specific weight of powder in the briquettes. By manufacturing them to be even divisable parts of a pound, ease of control of amount of additions was obtained.

(1) 4 oz. briquettes were found to be the maximum safe size of a briquette to insure perfect solvability. When larger briquettes were used, sporadic freezing of the briquette in the metal occurred.

(2) In bottom pour ingots, 1 oz. briquettes were found to be the maximum safe size to insure perfect solvability of the briquette, and to prevent clogging or freezing in the runners.

(3) In "big end up" molds, used in making rimmed steel, 1 oz. briquettes were found to be the maximum safe size.

*Fluorine release*

It was found that the size sodium fluoride described above gave the maximum fluorine release, i. e., from 36.4 percent. Regular granules gave 24.6 percent.



When other mesh sizes were used, lesser amounts of released fluorine were obtained. The maximum fluorine release was obtained from mined Greenland Cryolite, 44.5 percent. The exact mechanism of this release is not entirely understood. It probably is related to particle size and distribution.

*Conclusion*

(1) Briquettes made with "Corex" or "Vinsol," a thermoplastic resin recovered from refining of FF wood rosin, was the best binder for manufacturing the briquette.

(*a*) The amount of binder, 1 to 10 percent, gives proper "green and dry" strength, holds briquette in solid form to introduce it well into molten bath and then disperses it thoroughly and quickly through bath.

(2) The proper size powder or powders contained in the compounds are essential to manufacturing strong, efficient briquettes.

(3) The density of briquette determines speed of going into solution and strength of briquette to withstand shipping and handling without powdering, crumbling or breaking.

(4) Baking the briquette twice determines strength and solvability of briquette. Too fast a bake at high temperatures causes a refractory coating which prevents briquette from going into solution. Bake from 11 to 15 minutes at from 100–500° F.

(5) Safety coating of briquette done by dipping in 5 percent solution of silicate of soda, ½ percent of "Pluoronics" or a similar wetting agent and 1 percent of "Corex." This forms a protective coating approximately ¼ inch deep which prevents components of briquette from rubbing off, and makes the briquette anhydrous, eliminating the hazard of explosion caused by entrapped moisture being injected beneath the surface of molten metal.

(6) The size of the briquette may be 1 oz. or 4 ozs. The maximum sizes prevent freezing in molten metal as it solidifies.

Although the present invention has been described in connection with a few preferred embodiments thereof, variations and modifications may be resorted to by those skilled in the art without departing from the principles of the invention. All of these variations and modifications are considered to be within the true spirit and scope of the present invention as disclosed in the foregoing description and defined by the appended claims.

I claim:

1. An anhydrous briquetted rimming agent of a fluoride member of the group consisting of calcium fluoride, sodium fluoride, sodium aluminum fluoride and mixtures of these powders, which consists of the powder bound together with 3 to 5 percent of a binder of a member of the group consisting of synthetic shellac and synthetic resin, said powder and binder being compressed to 3,500 to 6,500 p. s. i., coated on the exterior side with sodium silicate and a wetting agent, and heated to 100–500° F. for about 15 minutes.

2. The briquette of claim 1 using calcium fluoride.

3. The briquette of claim 1 using sodium fluoride.

4. The briquette of claim 1 using sodium aluminum fluoride.

5. A method of making an anhydrous rimming agent briquette which comprises taking a fluoride of the group consisting of calcium fluoride, sodium fluoride, sodium aluminum fluoride and mixtures thereof, mixing it with a binder of the group consisting of shellac and resin from 3 to 5 percent of the powder, briquetting it at 1,000 to 8,500 p. s. i., coating with 5 percent sodium silicate solution and sintering the briquette at 100–500° F. for about 15 minutes.

6. The briquette of claim 1 in which 3 to 5 percent of synthetic shellac is the binder.

7. The method of claim 5 in which sodium fluoride is the agent.

8. The method of claim 5 in which the briquette is sintered at 400–500° F.

9. The method of claim 5 in which the powder is compressed at 3,500 to 6,500 p. s. i.

10. A method of making an anhydrous rimming agent briquette which comprises taking a sodium fluoride powder, mixing it with 3 to 5 percent of synthetic shellac, compressing it to 3,500 to 6,500 p. s. i., coating it with sodium silicate and sintering it at 400–500° F., whereby the binder melting at 300–400° F. gives a slight delay in dissolving in the molten steel.

11. An anhydrous briquetted rimming agent of a member of the group consisting of calcium fluoride, sodium fluoride, sodium aluminum fluoride and mixtures thereof, which consists of the powder bound together with 3 to 5 percent of a binder of the group consisting of synthetic shellac and synthetic resin, said powder and binder being compressed at 3,500 to 6,500 p. s. i., and given an outer case coating of sodium silicate, synthetic shellac and a wetting agent and heated to 100–500° F. for about 15 minutes.

12. The anhydrous briquetted rimming agent of claim 2 in which 100 percent of the powder passes through 20 mesh and 22 percent through 325 mesh.



13. The briquetted rimming agent of claim 3 in which the distribution of the particle sizes of sodium fluoride is as follows: on 65 mesh screen, 3–4 percent; on 65–100 mesh screen, 5–6 percent; on 100–200 mesh screen, 25–30 percent; on 200–325 mesh screen, 30–4 percent; and through 325 mesh screen, 25–35 percent.

14. The briquetted rimming agent of claim 4 in which synthetic sodium aluminum fluoride is used with the following particle sizes: on 20 mesh, 16 percent, plus or minus 10 percent; on 20–48 mesh, 21 percent, plus or minus 10 percent; on 48–100 mesh, 13 percent, plus or minus 10 percent; on 100–200 mesh, 10 percent, plus or minus 10 percent; and through 200 mesh, 40 percent, plus or minus 10 percent.

15. The briquetted rimming agent of claim 4 in which Greenland mined Cryolite is used of the particle size distribution of 92 percent through 325 mesh and 5 percent on 250 mesh, whereby a fluorine release content of 54.3 percent is produced.

No references cited.