# United States Patent [19]

**Gamble**

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[54] **PROTECTIVE COATING FOR MATERIALS EXPOSED TO MOLTEN ALUMINUM AND ITS ALLOYS**


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**Related U.S. Application Data**

[62] Division of Ser. No. 188,611, Oct. 12, 1971, Pat. No. 3,754,949.

[52] **U.S. Cl.** ..... **117/169 R,** 117/123 B, 117/127

[51] **Int. Cl.** ..... **C04b 35/02,** C04b 35/10

[58] **Field of Search** ..... 117/169 R, 127, 123 B; 106/56, 62, 63, 65, 67



[56] **References Cited**

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[57] **ABSTRACT**

A protectively coated structural part for contact with molten metal and a process for protecting articles to be in contact with molten metal. The structural part is coated to a thickness of at least 0.002 inch with a coating composition of a mixture of finely divided powders consisting essentially of:

A. 30 to 70 percent by weight of a refractory material consisting essentially of tri-calcium phosphate,

B. 10 to 30 percent by weight of aluminum oxide,

C. 2 to 8 percent by weight of a smoothing agent,

D. 3 to 10 percent by weight of raw Kaolin clay, and

E. 12 to 45 percent magnesium orthoborate.


**9 Claims, No Drawings**

# PROTECTIVE COATING FOR MATERIALS EXPOSED TO MOLTEN ALUMINUM AND ITS ALLOYS

This is a division, of application Ser. No. 188,611, filed Oct. 12, 1971, now U.S. Pat. No. 3,754,949.

## BACKGROUND OF THE INVENTION

The present invention relates to protective coatings. More particularly, the present invention resides in protective coatings for metals and ceramics used in contact with molten metals.

In molten metal handling applications it is desirable to use certain materials for structural parts due to their desirable properties. In the melting and casting of aluminum and aluminum alloys, for example, it is highly desirable to utilize heat resistant carbon steels, stainless steels, or cobalt alloy structural parts, such as molten metal flow distributors, spouts, filtering screens, thermocouple protection tubes and hand tools. These materials provide savings in initial cost of structural parts, savings in reduced downtime and replacement of parts, as well as permitting the design of parts used in continuous contact with molten metals.

The properties of many heat resistant, high strength metals and alloys could be used to great advantage in nonferrous foundry equipment except for the inevitable early failure of such metals under attack and dissolution by the molten alloys being processed. For example, molten aluminum invariably attacks these materials causing rapid deterioration and short life.

If these structural materials could be protected from molten metal attack by a relatively inexpensive inorganic coating of attack resistant material, their properties of ductility, thermal and mechanical shock resistance and ease of fabrication could be used to good advantage in molten metal handling and casting equipment.

The attainment of such a protective coating for use under these extreme conditions presents numerous problems. For example, one must find a coating resistant to attack by the molten metal and particularly molten aluminum alloys. One must find a coating which will be firmly bonded to the metal part and maintain its integrity for substantially the life of the metal part. One must find a coating which has these characteristics and maintains them in use despite strenuous conditions such as thermal cycling and so forth.

Another of the major difficulties in the application of a coating to high temperature metals is that of obtaining a thermal expansion fit between the coating and the metal base. Metals have high coefficients of thermal expansion whereas most nonmetallic compounds and materials have low coefficients. If the thermal expansion differential between coating and base is not minimized, the coating will tend to separate and spall off with repeated immersion of the coated part in molten metal followed by cooling to room temperature.

It is, therefore, a principal object of the present invention to provide a protective coating for metals and ceramics used in contact with molten metals and particularly aluminum and its alloys.

It is an additional object of the present invention to provide a coating as aforesaid which can be readily and firmly bonded to metal parts and maintain its integrity for substantially the life of the part throughout a wide variety of strenuous conditions.



It is an additional object of the present invention to provide an inorganic coating as aforesaid which will withstand repeated use in molten aluminum and aluminum base alloys on cycling from molten metal temperatures to room temperature without loss by spalling, peeling or flaking off.

Further objects and advantages of the present invention will be apparent from a consideration of the following specification.

In accordance with the present invention it has now been found that the foregoing objects and advantages may be readily attained.

## SUMMARY OF THE INVENTION

The protective coating composition of the present invention comprises from 30 to 70 percent by weight of a refractory material consisting essentially of tricalcium phosphate, from 10 to 30 percent by weight aluminum oxide, from 2 to 8 percent calcined clay, from 3 to 10 percent raw air floated Kaolin clay, and from 12 to 45 percent magnesium orthoborate. From 7 to 25 percent boric acid plus from 5 to 20 percent light magnesium oxide may be employed in place of the magnesium orthoborate and which converts to magnesium orthoborate upon the addition of water.

In accordance with the present invention it has been found that the foregoing coating protects a substrate of the aforementioned materials from virtually any attack by molten aluminum and aluminum alloys for long periods of time. The coating adheres tenaciously, is thermally shock proof, non-wetting and easily cleaned after use. When applied to oxide and other refractory crucibles and ceramic bodies, it also exhibits the property of inhibiting penetration of molten metal and oxides, thus extending life and minimizing contamination of the melt.

It is particularly advantageous that the foregoing objects of the present invention are readily accomplished in accordance with the present invention. An additional advantage of the present invention is the ability of the coating composition to reduce to a substantial extent the rate of oxygen uptake by the underlying metal to which it is applied despite the exposure of the coated metal to high temperature oxidizing atmospheres.

A further advantage of the present invention is that the coating material does not hydrate when in use and consequently the danger of a molten aluminum steam explosion is eliminated.

## DETAILED DESCRIPTION

The protective coating composition of the present invention comprises from 30 to 70 percent by weight of a refractory material consisting essentially of tricalcium phosphate from 10 to 30 percent by weight aluminum oxide, from 2 to 8 percent of a smoothing agent, from 3 to 10 percent raw air floated Kaolin clay, and from 12 to 45 percent magnesium orthorborate.

The refractory tri-calcium phosphate material such as for example, commercial bond ash, acts as a filler of high refractoriness, and is nonreactive with molten nonferrous metals. The refractory material is resistant to attack by molten metal such as aluminum and aluminum base alloys and is compatible with the magnesium orthoborate bonding agent. The preferred range is 30 to 45 percent by weight and optimally about 32 to 40 percent by weight.

The coating composition of the present invention utilizes a finely divided aluminum oxide, such as produced by the Bayer process, in an amount from 10 to 30 percent by weight.

The preferred amount of this constituent is from 12 to 30 percent by weight.

The protective coating composition of the present invention utilizes finely divided powders.

The powder particle size is such that 97 percent will pass through a 200 mesh U.S. standard sieve.

In addition to the foregoing constituents, the coating composition of the present invention contains from 12 to 45 percent of magnesium orthoborate as the refractory bonding agent or binder. The bonding agent or binder is refractory, i.e., it must withstand high temperatures up to 2500°F. In addition, the refractory binder may contain, for example, small amounts of organic bonding agents.

The refractory bonding agent is nonhydratable and is utilized in an amount from 12 to 45 percent by weight and preferably from 22 to 32 percent by weight.

If desired, in lieu of employing magnesium orthoborate in the initial make-up of the composition, one may employ 7 to 25 percent boric acid and from 5 to 20 percent light magnesium oxide which produces nonhydratable magnesium orthoborate upon the addition of water to the mixture. It is preferred to employ from 14 to 20 percent by weight of boric acid and from 8 to 12 percent magnesium oxide. It is necessary however that the weight ratio of the boric acid to the light magnesium oxide not exceed 1.03 maximum to insure the formation of the magnesium orthoborate rather than other hydratable borates. An excess of light magnesium oxide may be employed if desired within this limitation which increases the applicability of the coating mixture due to the presence of unreacted magnesium oxide with the boric acid. The unreacted magnesium oxide after the addition of water is normally in an amount of up to 15 percent, based upon the total nonaqueous components, and preferably from about one to 15 percent.

Naturally, one may also employ varying mixtures of magnesium orthoborate, boric acid and magnesium oxide so long as the total amount of magnesium orthoborate produced by the addition of water is within the range of 12 to 45 percent by weight.

In addition to the foregoing constituents, one also employs from 3 to 10 percent by weight of raw air floated Kaolin clay, such as raw Georgia Kaolin, as a suspending or thickening agent with the preferred range from 3 to 5 percent. However, one may use any thixotropic or gelling agent, preferably refractory in nature, such as Bentonite and the Montomorillinites. The purpose of these compounds is to keep the ingredients of the coating composition in suspension upon the addition of water. Otherwise, the ingredients would tend to settle on standing. In addition, the suspending or thickening agent tends to improve the applicability of the coating composition by painting, that is, it makes a smoother suspension.

An additional requisite component is a smoothing agent such as calcined Kaolin clay in an amount from 2 to 8 percent by weight and preferably from 3 to 5 percent by weight. This material also improves ease of application.

To apply the coating composition water is added to the aforementioned nonaqueous components to prepare a suspension. One should utilize sufficient water to prepare a suspension containing from about 50 to 67 percent water, and preferably about 55 to 67 percent water, to provide the proper consistency for brushing the material on the part to be coated. If spray coating is desired from about 67 to 75 percent water is preferred. The aqueous suspension is applied to the structural part in a thickness of at least 0.002 inch, normally from 0.002 to 0.006 inch, and preferably from 0.003 to 0.005 inch.

In utilizing the coating composition of the present invention one may premix all of the dry solid, or nonaqueous, ingredients of the coating and this mixture may then be stored for any desired period of time without degradation and loss in properties. The coating composition is then prepared for application and use when needed by the addition of the proper amount of water and thorough mixing.

Graphite in an amount of from 4 to 30 percent by weight may also be included, if desired, in order to increase the applicability of the coating composition as, for example, by painting. The graphite may also be premixed, as aforementioned, with the other nonaqueous ingredients if desired.

The present invention will be more readily apparent from a consideration of the following illustrative examples:

## EXAMPLE I

The following dry coating ingredients were prepared by mixing the following finely divided powders in a suitable blender until uniformly mixed:

| | |
|---|---|
| tri-calcium phosphate (commercial bone ash, −325 mesh particle size, 97% $Ca_3(PO_4)_2$min.) | 32.0% by weight |
| Aluminum oxide powder −200 mesh | 14.4% by weight |
| Calcined Kaolin clay −325 mesh | 3.2% by weight |
| Kaolin clay, air floated, water washed, −325 mesh | 3.2% by weight |
| Boric acid powder, fine | 17.6% by weight |
| Magnesium oxide, light | 9.6% by weight |
| Graphite | 20% by weight |

The above powders were intimately mixed and then tempered with clean water to prepare an aqueous slurry containing 60 percent by weight water. This slurry was brushed on degreased nodular cast iron specimens and air dried. After air drying for about 5 minutes, the coated samples were oven dried at 300°F to remove all remaining moisture.

The coated metal part was then immersed in molten 5A grade commercially pure aluminum at 1380°F, removed and reinserted over a four hour period at frequent intervals. After each removal the coated specimens were easily cleaned of any adhering aluminum film and the substrate found unattacked in each case and at the conclusion of the test.

## EXAMPLE II

The following dry coating ingredients were prepared by mixing the following finely divided powders in a suitable blender until uniformly mixed:

| | |
|---|---|
| tricalcium phosphate (commercial bone ash, −325 mesh particle size, 97% $Ca_3(PO_4)_2$min.) | 49% by weight |
| Aluminum oxide powder −200 mesh | 21% by weight |
| Calcined Kaolin clay −325 mesh | 4% by weight |
| Kaolin clay, air floated, water washed, −325 mesh | 4% by weight |

-Continued

| | |
|---|---|
| Boric acid powder, fine | 10% by weight |
| Magnesium oxide, light | 12% by weight |

The above powders were intimately mixed and then tempered with clean water to prepare an aqueous slurry containing 60 percent by weight water. This slurry was brushed on degreased nodular cast iron specimens and air dried. After air drying for about 5 minutes, the coated samples were oven dried at 300°C to remove all remaining moisture.

The coated metal part was then immersed in molten 6061 aluminum alloy at 1380°F, removed and reinserted over a four hour period at frequent intervals. After each removal the coated specimens were easily cleaned of any adhering aluminum film and the substrate found unattacked in each case and at the conclusion of the test.

## EXAMPLE III

The following dry coating ingredients were prepared by mixing the following finely divided powders in a suitable blender until uniformly mixed:

| | |
|---|---|
| tri-calcium phosphate (commercial bone ash, −325 mesh particle size, 97% $Ca_3(PO_4)_2$min.) | 40% by weight |
| Aluminum oxide powder −200 mesh | 18% by weight |
| Calcined Kaolin clay −325 mesh | 4% by weight |
| Kaolin clay, air floated, water washed, −325 mesh | 4% by weight |
| Boric acid powder, fine | 22% by weight |
| Magnesium oxide, light | 12% by weight |

This combination of fine powders was thoroughly dry mixed and then tempered with clean water to prepare an aqueous slurry containing 55 percent by weight water. This slurry was brushed on a cast iron specimen and then the specimen placed in an oven at 300°C to dry immediately. There was no special preparation of the cast iron specimen other than degreasing.

The dry coated specimen was attached to a light weight refractory support and floated with the coated specimen fully submerged in molten 6061 aluminum alloy at 1380°F. The specimen was removed at approximately 1½ hour intervals and cleaned of most of the adhering aluminum film by shaking. After each removal the specimen was returned to the molten bath until a total of more than 30 hours of immersion time was accumulated on the specimen. Final examination showed no attack whatsoever had taken place on the cast iron base material.

## EXAMPLE IV

The following dry coating ingredients were prepared by mixing the following finely divided powders in a suitable blender until uniformly mixed.

| | |
|---|---|
| tri-calcium phosphate (commercial bone ash, −325 mesh particle size, 97% $Ca_3(PO_4)_2$min.) | 33% by weight |
| Aluminum oxide powder −200 mesh | 14% by weight |
| Calcined Kaolin clay −325 mesh | 3.5% by weight |
| Kaolin clay, air floated, water washed, −325 mesh | 3.5% by weight |
| Boric acid powder, fine | 18% by weight |
| Magnesium oxide, light | 10% by weight |
| Graphite | 18% by weight |

The above powders were thoroughly dry mixed and blended for uniformity. To the powder mixture was added clean water to prepare an aqueous slurry containing 55 percent by weight water.

When thoroughly tempered with water the slurry was brushed on specimens of hot rolled steel measuring three-fourths in. wide, 6 in. long and one-eighth in. in thickness which had been degreased. Whatever scale was present and firmly adherent was allowed to remain prior to coating with the above mix.

The specimens were hung in a fixture and placed in a testing fixture which cycled them up and down in a melt of 6061 aluminum alloy over a three-fourth inch amplitude at 6 times per minute with about half the specimen in the molten alloy at all times. This test continued for 4 hours with the melt temperature maintained at 1400°F.

At the conclusion of the test the coated specimens showed no attack or dissolution of the substrate while an uncoated specimen had dissolved completely over the length (approximately 3 inch) that had been immersed in the molten test bath.

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:

**1.** A protectively coated structural part for contact with molten metal, said structural part coated to a thickness of at least 0.002 inch with a coating composition of a mixture of finely divided powders consisting essentially of:

A. 30 to 70 percent by weight of a refractory material consisting essentially of tri-calcium phosphate,

B. 10 to 30 percent by weight of aluminum oxide,

C. 2 to 8 percent by weight of a smoothing agent,

D. 3 to 10 percent by weight of raw Kaolin clay, and

E. 12 to 45 percent magnesium orthoborate.

**2.** A protectively coated structural part according to claim **1** wherein said coating includes from 4 to 30 percent by weight graphite.

**3.** A protectively coated structural part according to claim **1** wherein at least 97 percent of said ingredients A., B., C., and D. will pass through a 200 mesh sieve.

**4.** A protectively coated structural part according to claim **1** wherein said magnesium orthoborate component is provided by the addition of from 7 to 25 percent boric acid, from 5 to 20 percent light magnesium oxide and water which produces nonhydratable magnesium orthoborate and up to 15 percent of unreacted magnesium oxide.

**5.** A process for protecting articles to be in contact with molten metal comprising:

I. preparing an aqueous slurry containing a mixture of finely divided powders consisting essentially of

A. 30 to 70 percent by weight of a refractory material consisting essentially of tri-calcium phosphate,

B. 10 to 30 percent by weight of aluminum oxide,

C. 2 to 8 percent by weight of a smoothing agent,

D. 3 to 10 percent by weight of raw Kaolin clay, and

E. 12 to 45 percent magnesium orthoborate;

II. applying said slurry to the article to be protected to a thickness of at least 0.002 inch; and

III. drying the slurry coated article to remove the moisture.

**6.** A process according to claim **5** wherein said slurry is a suspension of said powders containing from 50 to 75 percent water.

**7.** A process according to claim **6** wherein said mixture includes from 4 to 30 percent graphite.

**8.** A process according to claim **6** wherein said magnesium orthoborate component is provided by the addition of from 7 to 25 percent boric acid, 5 to 20 percent light magnesium oxide and water which produces nonhydratable magnesium orthoborate and up to 15 percent of unreacted magnesium oxide.

**9.** A process according to claim **8** wherein said boric acid-magnesium oxide mixture contains from 1 to 15 percent unreacted magnesium oxide.

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# UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 3,850,684 Dated November 26, 1974

Inventor(s) Elton S. Gamble

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

Page 1, in the heading, after the word "Assignee:" insert ---Swiss Aluminium Limited, Chippis, Switzerland---.

Signed and sealed this 18th day of March 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

FORM PO-1050 (10-69)

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