

UNITED STATES PATENT OFFICE

JOHN A. GANN AND MANLEY E. BROOKS, OF MIDLAND, MICHIGAN, ASSIGNORS TO THE
DOW CHEMICAL COMPANY, OF MIDLAND, MICHIGAN, A CORPORATION OF MICHIGAN

CASTING FREELY OXIDIZABLE METAL

No Drawing.

Application filed July 30, 1931. Serial No. 554,148.

The present invention relates to the casting of magnesium alloys and other freely oxidizable metals in water bound "green composition" molds, i. e. non-baked, which will not oxidize the molten metal when it comes in contact therewith. In ordinary casting practice where water bound green sand molds are used for the casting of readily oxidizable metals, such as magnesium and its alloys, not only is there a pronounced tendency for the metal to burn in the sprue, but the surface of the casting formed by contact with the complementary surface of the mold tends to become oxidized, pitted, or both, due to the formation of a powder (presumably an oxide or a nitride of metal). Where the casting poured in this manner is a relatively heavy section it either completely burns up or is badly damaged due presumably to the temperature of the metal cast remaining in the rapid oxidation range for a longer period of time than is the case with a thin section casting which chills promptly. Even if the impairment of the surface of such castings as can be made is not serious enough to prevent the cast article from being used or finished when removed from the mold, the casting has an unsightly appearance and a certain loss of metal is involved. It is to be noted, of course, that the cleaner the casting the more easily may the subsequent finishing operations be carried out.

It has heretofore been proposed to overcome these difficulties, specifically in casting magnesium and alloys containing same in dry sand molds, by dusting the mold prior to casting the metal with sulphur which is capable of giving off in contact with the molten metal a vapor which is more easily oxidizable than magnesium. This procedure, however, has the objection that it is obviously difficult to correctly gauge the amount of sulphur thus used and particularly if an excess is applied to the surface either of the mold proper or the mold core so much vapor may be generated that some of it becomes entrapped during the period in which the metal is solidifying, the result being blow holes or surface shrinks in the casting.

More recently it has been proposed to avoid the difficulties encountered in casting magnesium and its alloys by using a molding composition consisting of pulverized carbon, pulverized soapstone, magnesium oxide, and a light bodied mineral oil. We have found, however, that the use of magnesium oxide, which is commercially sold as a fine powder, is not only unnecessary but detrimental since it makes the mold less porous and thus tends to prevent the ready escape of gases generated during casting. This in itself is undesirable since it causes pitting, surface shrinks, and general surface injury to the casting. We have further found that the use of magnesium oxide in contact with hot magnesium and its alloys accelerates or promotes oxidation of the metal.

While working with pulverized carbon base molding compositions, we have discovered that not only can we omit the use of magnesium oxide to advantage, but that the relatively expensive mineral oil used as above noted can be omitted so that the use of any relatively expensive oil can be entirely avoided. Our improved composition consists of a mixture of pulverized carbon, a plasticizer, a relatively small amount of an oxidation inhibitor, and sufficient water to render the composition moldable.

Accordingly, among the objects of the present invention is the production of a water bound carbon base molding composition suitable for use in casting readily oxidizable metals such as magnesium and its alloys, the use of such composition further permitting the production of sound castings having a good surface appearance. Other objects and advantages will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, the invention, then, consists of the method and product hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail means and modes of carrying out the invention, such disclosed means and modes illustrating, however, but several of the various ways in which the principle of the invention may be used.

Where pulverized or finely divided carbon is used instead of sand for forming a mold, such mold will have a much higher heat conductivity than a similar sand mold. This increased heat conductivity causes the readily oxidizable metal being poured into the mold to chill promptly which not only decreases the period wherein rapid oxidation can take place, but produces a fine grain structure casting which exhibits superior properties as compared with a like casting made in sand. We have further found that where such carbon base mold is rendered moist or moldable by water instead of oil that the chilling effect is still further increased and accumulatively aids in producing a casting having exceptionally good properties. In this connection it is to be noted that carbon is chemically and physically not an equivalent to sand since it is not an oxide, it is combustible, and has a much higher heat conductivity than sand. We are aware that graphite, powdered coal, and lamp black have been used as facings and washes for molds used in the casting of iron and steel; however, the problem encountered there is in no way comparable with that encountered in the casting of an extremely readily oxidizable metal, such as magnesium and its alloys, which has to be handled and poured at a temperature wherein it readily ignites and burns.

Our improved molding composition, consisting of pulverized carbon, a plasticizer, and an oxidation inhibitor, moistened or made moldable with water, may be used to form a mold to produce a casting of any desired shape or size, e. g. a crank case for an internal combustion engine or like article and such mold, if desired, may have incorporated therein cores or metal parts, as is well known to the art.

If with the carbon base molding composition used in making such mold approximately 2 to 10 per cent of boric acid, ammonium compounds, sulphur, or a combination of these or other like oxidation inhibitors be intermixed, a very satisfactory result in the way of a casting is obtained upon pouring the metal into the mold in the usual manner, it being noted, of course, that ordinarily unless the casting section is very thin an amount of the above noted agents greater than the minimum noted should be used. For general casting service with such compositions, we have found that 4 per cent of boric acid, or 5 per cent ammonium chloride, or 5 per cent of sulphur admixed therewith, will produce castings of readily oxidizable metals that are substantially free from burning and exhibit, upon pickling or otherwise cleaning according to common practice, an exceptionally good surface finish. The use of our present invention is concerned broad-

ly with the treatment of a water bound or moistened "green" molding composition wherein pulverized or finely divided carbon is a major constituent. As a specific example of such a mixture may be noted the pulverized carbon, bentonite, oxidation inhibitor, water composition, wherein the proportions by weight of the ingredients will vary from 90 to 63 per cent for the carbon, 2 to 15 per cent for the bentonite, 2 to 10 per cent for the oxidation inhibitor, and 6 to 12 per cent for the water. As plasticizing material for use in our improved molding composition, we have found that bentonite (ground or otherwise finely divided), and clays as typified by Georgia white clay can be used in satisfactory manner. The amount used, of course, normally depends upon the bond strength and permeability desired when the composition is formed into a mold. While we have given percentage ranges and preferred amounts of oxidation inhibiting agents to be added to the pulverized carbon molding composition, we do not wish to be strictly limited to those specific ranges since we have found that as high as 20 per cent by weight of the oxidation inhibiting agent or agents can be used with satisfactory results. We have further noted that where sulphur is used according to the method described that as the percentage approaches 10 the casting produced takes on a dark appearance and that, however, when the percentage of sulphur is increased to 20 the dark appearance almost completely disappears. Even the dark castings, however, when pickled or cleaned according to common practice, exhibit an exceptionally good surface, which shows that the discoloration is not detrimental to the formation of good castings. The castings made with boric acid as the protective agent normally take on a beautiful iridescent color while the ammonium chloride protected castings normally assume a grayish appearance. These castings, however, when pickled or cleaned according to common practice exhibit sound castings having an exceptionally good surface. The following examples show in detail two preferred formulae of our improved molding composition.

Example 1

When using a freshly made mixture of pulverized carbon, bentonite, and an oxidation inhibitor, rendered "green" or moldable with water, we have found that very good castings can be made by using the following hand-mixed composition:—

10% water
10% bentonite
4% of oxidation inhibitor (boric acid, ammonium chloride, ammonium sulphate, sulphur, or a mixture of them)

76% carbon (pulverized coke) having the following sieve analysis—

Percent- age	Mesh
33	40-100
47	100-200
20	Through 200

Example 2

When the "green" carbon molding composition is thoroughly mixed such as mechanically in a Muller type of machine that efficiently brings the carbon and plasticizer into intimate contact, a relatively small percentage of plasticizer is necessary to form a satisfactory molding composition. A preferred composition when mixed in this manner is as follows:—

7% water

3% bentonite

4% oxidation inhibitor (boric acid, ammonium chloride, ammonium sulphate, sulphur, or a mixture of them)

86% carbon (pulverized coke) having the following sieve analysis—

Percent- age	Mesh
45	30-100
43	100-200
12	Through 200

In using the above compositions we have found that the castings produced present a very good surface which is substantially free from oxidation, pitting, and surface shrinks, and further we have found that the tensile properties, Brinell hardness, and fatigue endurance and toughness of such castings are above the average of like articles cast in sand according to current practice and are somewhat better than like articles cast in oil bound pulverized carbon composition molds.

Carbon base type of molding compositions utilizing bentonite or its equivalent as a plasticizer tend to dry out quite rapidly, making special handling or even frequent retempering of the molding heap necessary to keep the composition in satisfactory form for molding. We have found that the addition of a hygroscopic halogen salt to the molding composition in amount from 1 to 10 per cent overcomes or greatly mitigates this difficulty and moreover does not act as an active oxidation accelerator. Specifically, 4 per cent of calcium chloride is satisfactory for the purpose at hand.

In using our improved water bound molding composition for casting, a small amount of the oxidation inhibitor is driven off or otherwise lost due to the heat given off by the hot metal during the casting operation. There is, however, none of the relatively expensive oil present to be driven off and re-

quire replenishment. After the so poured casting has cooled to a point where it will not ignite or rapidly oxidize when exposed to air, it can be shaken out and the molding composition reconditioned by adding thereto sufficient of the oxidation inhibitor and water to overcome the losses and place the composition in shape for reuse, it being noted that the other ingredients of the composition will be substantially unaffected by casting conditions. The use of water for making our improved molding composition moldable is without the bad effects ordinarily encountered since the oxidation inhibitor in some way prevents the water or steam in the mold from giving up oxygen to oxidize the metal. While we have mentioned pulverized coke as the carbon material used in our improved molding composition, we do not wish to be limited to that material since we have found that pulverized gas carbon, coal, and other similar hard high carbon compounds can be used in like manner. The term "carbon" will, accordingly, be understood to broadly cover this class of materials unless otherwise specified. Further, we have found that the sieve analysis of the pulverized carbon may vary considerably from that specifically noted in the foregoing examples, the analysis used depending largely upon the permeability and bond strength desired.

The present application is a continuation in part of our copending application filed July 7, 1930, Serial No. 466,031.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the method and product herein disclosed provided the method and product stated by any of the following claims or the equivalent thereof be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. The process of casting a freely oxidizable metal which consists in forming a mold from pulverized carbon, a plasticizer and an oxidation inhibitor rendered moldable by the addition of water, and casting said metal in said mold.

2. In a process of casting a freely oxidizable metal to eliminate excessive burning thereof, the step which consists of pouring the molten freely oxidizable metal into a water bound carbonaceous mold containing a plasticizer and at least one of the materials boric acid, ammonium salt, sulphur.

3. In a method of casting a freely oxidizable metal such as magnesium and its alloys to eliminate excessive burning thereof, which comprises forming a water bound carbonaceous mold having boric acid in surface exposure, and casting the molten freely oxidizable metal in said mold in contact with such surfaces.

4. In a method of casting a freely oxidizable metal such as magnesium and its alloys to eliminate excessive burning thereof, which comprises forming a water bound carbonaceous mold having ammonium chloride in surface exposure, and casting the molten freely oxidizable metal in said mold in contact with such surfaces.
5. In a method of casting a freely oxidizable metal such as magnesium and its alloys to eliminate excessive burning thereof, which comprises forming a water bound carbonaceous mold having sulphur in surface exposure, and casting the molten freely oxidizable metal in said mold in contact with such surfaces.
6. A process of casting a freely oxidizable metal to eliminate excessive burning thereof, which comprises forming a water bound carbonaceous mold having incorporated in the mold cavity surfaces an oxidation inhibitor and a hygroscopic halogen salt, and pouring the molten freely oxidizable metal in said mold in contact with such surfaces.
7. A molding composition for casting readily oxidizable metals which comprises a mixture of pulverized carbon, a plasticizer, an oxidation inhibitor, and water.
8. A molding composition for casting readily oxidizable metals which comprises a water bound mixture of pulverized carbon, a plasticizer and at least one of the oxidation inhibitors, boric acid, ammonium salt, sulphur.
9. A molding composition for casting readily oxidizable metals which comprises a water bound mixture of pulverized carbon, a plasticizer and at least one of the oxidation inhibitors, boric acid, ammonium chloride, sulphur.
10. A molding composition for casting readily oxidizable metals which comprises a water bound mixture of pulverized carbon, a plasticizer and boric acid.
11. A molding composition for casting readily oxidizable metals which comprises a water bound mixture of pulverized carbon, a plasticizer and ammonium chloride.
12. A molding composition for casting readily oxidizable metals which comprises a water bound mixture of pulverized carbon, a plasticizer and sulphur.
13. A molding composition for casting readily oxidizable metals comprising a mixture of 63 to 90 per cent of pulverized carbon, 2 to 15 per cent of plasticizer, 2 to 10 per cent of oxidation inhibitor, and 6 to 12 per cent of water.
14. A molding composition for casting a readily oxidizable metal such as magnesium and its alloys which consists of a mixture of pulverized carbon (76%), finely divided bentonite (10%), boric acid (4%), and water (10%).
15. A molding composition for casting a readily oxidizable metal such as magnesium and its alloys which consists of a thorough mixture of pulverized carbon (86%), finely divided bentonite (3%), ammonium chloride (4%), and water (7%).
16. As an article of manufacture a mold for casting readily oxidizable metals, such mold being formed from a water bound moldable mixture containing chiefly pulverized carbon having admixed therewith finely divided bentonite, and an oxidation inhibitor.
17. As an article of manufacture a mold for casting readily oxidizable metals, such mold being formed from a mixture of pulverized carbon and finely divided bentonite moistened with water and having incorporated in the surface thereof an oxidation inhibitor.
18. As an article of manufacture a mold for casting readily oxidizable metals, such mold being formed from a mixture of pulverized carbon (76%), finely divided bentonite (10%), boric acid (4%), and water (10%).
19. A molding composition for casting readily oxidizable metals comprising a water-bound mixture of pulverized carbon, a plasticizer, $\frac{1}{10}$ per cent of a hygroscopic halogen salt, and $\frac{1}{20}$ per cent of an oxidation inhibitor.
20. A molding composition for casting readily oxidizable metals which consists of a water bound mixture of pulverized carbon, a plasticizer, calcium chloride, and at least one of the oxidation inhibitors boric acid, ammonium chloride, sulphur.

Signed by us this 28th day of July 1931.

JOHN A. GANN.

MANLEY E. BROOKS.

Certificate of Correction

Patent No. 1,886,252.

November 1, 1932.

JOHN A. GANN ET AL.

It is hereby certified that error appears in the printed specification of the above-numbered patent requiring correction as follows: Page 4, lines 12 and 13, claim 5, for the misspelled word "corbonaceous" read *carbonaceous*; line 18, claim 6, for "eleminate" read *eliminate*; line 92, claim 19, for " $\frac{1}{10}$ " read *1-10*, and line 93, for " $\frac{1}{20}$ " read *2-20*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 10th day of January, A. D. 1933.

[SEAL.]

M. J. MOORE,
Acting Commissioner of Patents.