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PATENT REQUEST: STANDARD PATENT

I/We, the Applicant(s)/Nominated Person(s) specified below, request I/We be granted a patent for the invention disclosed in the accompanying standard complete specification.

[70,71] Applicant(s)/Nominated Person(s):

Minteq International Inc., incorporaed in Delaware, of 235 East 42nd Street, New York, New York, 10017, UNITED STATES OF AMERICA

[54] Invention Title:

Dry Refractory Composition

[72] Inventor(s):

John Damiano, Julie A. Hebron, Wilfred A. Martinez

[74] Address for service in Australia:

Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia (Code SF)

Divisional Application Details

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Person by whom made: Quigley Company, Inc. (now changed to Minteq International Inc.)

DATED this TWENTY NINTH day of MARCH 1995

Minteq International Inc.

By: J. Spruson

Registered Patent Attorney

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NOTICE OF ENTITLEMENT

I, John Gordon Hinde, of Spruson & Ferguson, St Martins Tower, 31 Market Street, Sydney, New South Wales, 2000, Australia, being the patent attorney for the Applicant(s)/Nominated Person(s) in respect of an application entitled:

Dry Refractory Composition

state the following:-

The Applicant(s)/Nominated Person(s) has/have entitlement from the actual inventor(s) as follows:-

The Applicant(s)/Nominated Person(s) is/are the assignee(s) of the actual inventor(s).

The Applicant(s)/Nominated Person(s) is/are the applicant(s)/patentee(s) of the original application(s)/patent(s).

DATED this 29th day of March 1995

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John Gordon Hinde

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(71) Applicant(s)
MINTEQ INTERNATIONAL INC.

(72) Inventor(s)
JOHN DAMIANO; JULIE A. HEBRON; WILFRED A. MARTINEZ

(74) Attorney or Agent
SPRUSON & FERGUSON , GPO Box 3898, SYDNEY NSW 2001

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(57) Claim

1. A refractory composition for application as a dry refractory, based on a refractory aggregate material selected from magnesia, alumina, calcia, silica, zirconia or combinations thereof; and characterised by including from 1.0 to 5.0wt% of a phenolic resin low temperature bonding agent; and from 0.5 to 10.0wt% of at least one intermediate temperature bonding agent selected from a phosphate-containing compound having a sodium content of less than 40.0wt%, or a mixture of an alkali metal silicate compound and a metal powder, such that at least one of said phosphate-containing compound and said silicate containing compound is present and no one said intermediate temperature bonding agent is present in the composition at more than 10.0wt%; and from 0.0 to 5.0wt% clay; with the balance of the composition to total 100.0wt% being said refractory aggregate material.

10. A refractory composition for application as a dry refractory comprising: from 2.5 to 3.5wt% phenol formaldehyde; from 2.5 to 3.5wt% monosodium phosphate; from 2.5 to 3.5wt% of a 50/50wt% mixture of anhydrous sodium silicate and a ferrosilicon alloy metal powder; and from 0.0 to 5.0wt% clay wherein the balance of the composition is a refractory aggregate material selected from the group consisting of magnesia, alumina, calcia, silica and combinations thereof.

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12. A dry method for applying a monolithic refractory lining to the inner surface of a vessel such as a tundish or the like, in hot practice, characterised by the steps of: a) placing a cast-forming device for form shaping a dry refractory composition into said vessel in such a way as to leave a gap between said vessel and said cast-forming device; b) pouring into said gap an amount of a refractory composition sufficient to cover the inner surfaces of said vessel, said refractory composition containing from 1.0 to 5.0wt% of a low temperature bonding agent; from 0.5 to 10.0wt% of at least one intermediate temperature bonding agent; and from 0.0 to 5.0wt% clay; with the balance totaling 100wt% being a refractory aggregate material; c) curing the refractory composition by raising the temperature in the vessel from 150°C to 540°C to cause interparticle bond formation between particles of the refractory aggregate initiated by the low temperature bonding agent; d) removing the cast-forming device to leave a monolithic casting of the refractory material on the inner surface of the vessel; and e) preheating the refractory composition by raising the temperature in the vessel from 540°C to 1370°C to further cause interparticle bond formation between particles of the refractory aggregate initiated by the intermediate temperature bonding agent.

Dry Refractory Composition

This invention relates to refractory compositions, particularly those which are installed without the need for water. The invention further relates to refractory compositions which are useful for forming the wearable, disposable monolithic lining which coats the permanent lining of either a tundish used in continuous molten metal casting processes or a ladle used in molten metal casting processes. The invention still further relates to refractory compositions which can be applied dry either with or without the aid of vibration.

A tundish is a large intermediate holding vessel for molten metal used in continuous casting processes, such as the continuous casting of steel. The tundish is, in effect, an intermediate process reservoir which receives a large quantity of molten metal from conveying ladles exiting a furnace in which actual smelting of the ores or refining of molten metal occurs, and which then transfers the molten metal to a casting system. A system of inlet and outlet nozzles controls the flow of molten metal into and out of the tundish.

The tundish itself is generally a steel vessel which is lined with several layers of a refractory composition. A permanent lining, generally of refractory brick, serves as an inner lining to protect the vessel. The permanent lining, in turn, is coated with a wearable and disposable lining, generally of a refractory composition which has been applied to the permanent lining by gunning, spraying, trowelling, or dry vibration. The disposable lining is in direct contact with the molten metal in the tundish and protects the permanent lining from exposure to the molten metal.

In general, there are two types of monolithic refractory compositions which are used as disposable tundish linings, those which require the addition of a liquid phase, usually water, in order to apply the composition to the permanent lining and those which do not require a liquid phase for the application of the composition to the permanent lining. Those compositions which require a liquid are applied by either gunning, spraying, or trowelling. Those compositions which do not require a liquid are called "dry vibratables".

A dry vibratable is generally installed by one of two methods, one which uses a former to control the application thickness and the other which does not require the use of a former. The former is shaped to the contour of the inner dimensions of the vessel. This method allows for the even application of a desired thickness of monolithic refractory (dry vibratable) in large or complex vessels. The method for application which does not require a former, namely, the so called "no-former" method, involves preheating the vessel from about 650°C to about 1100°C. Once preheated, the vessel is completely filled with the dry monolithic refractory. The refractory is allowed to cure in the vessel for about 1-5 minutes. After this time has elapsed, a working lining of finite thickness is formed and the uncured refractory is reclaimed for reuse. This method allows the control

of application thickness by time allowed for curing. This method is useful for lining small or uncomplicated vessels.

In the continuous casting process of steel making, there are two general tundish practices, cold practice and hot practice. Cold practice means that the tundish is at ambient temperature when steel is conveyed from the ladle into the tundish. Hot practice involves preheating the tundish to temperatures ranging from about 650° to about 1370°C. Thus, the steel is conveyed from the ladle to a "hot" tundish. The use of hot practice in steel making hes resulted in higher quality steel being produced from the continuous casting process. The higher quality from the hot practice has been related to, among other things, reduced chilling effects, reduced gas evolution and reduced turbulence in the preheated tundish due to reduced gas evolution from the preheated refractory lining.

Traditionally, only the gunnable, sprayable, or trowellable monolithic refractories have been used as disposable linings for hot practice tundishes. Dry vibratable refractories were not used in this application because their bonding system was not sufficient at preheat temperatures. The traditional dry vibratable bond system is comprised of two parts, a low temperature bonding agent, usually an organic resin, and a high temperature bond system, usually a silicate. In order to facilitate pre-heating, an intermediate temperature bonding agent was needed. This has been accomplished in the present invention by replacing the silicate with either a phosphate or silicate/metal powder bonding system which gives the refractory the necessary strength at both intermediate and high temperatures. The strength at these temperatures is necessary to ensure that the dry vibratable monolithic refractory remains in place to act as the tundish working lining.

We have discovered that the properties of a refractory material suitable for use as the material of a disposable lining for a tundish are significantly improved in a composition wherein the principal component is a refractory aggregate such as magnesia, alumina, calcia, silica or combinations of the above materials, together with from about 1.0 to about 5.0wt% of a low temperature bonding agent such as a phenolic resin, and from about 0.0 to about 5.0wt% clay, by the addition of an intermediate bonding agent comprised of either a phosphate, monosodium phosphate or sodium hexametaphosphate, or a combination of an alkali metal silicate and a metal powder in a 1:1 weight ratio, such as anhydrous sodium silicate and ferrosilicon metal alloy powders.

Refractory compositions prepared according to the present invention have been found to have excellent preheat capabilities. The material is applied as a dry vibratable. When applied as a protective lining to a tundish on top of the permanent lining, materials of the present invention demonstrate excellent strength at preheat temperatures (650°C-1370°C) which enhances steel quality by virtue of the increased lining temperature and reduces chilling effects on molten steel poured into the tundish. Moreover, since the materials of the present invention require no water for application, the risk of steam explosions in the tundish is eliminated. The present material also exhibits excellent

deskullability properties which reduces the turn-around time for reuse of the tundish. The present material has a high durability and causes little or no marring of the tundish permanent lining surface to which it is applied.

In accordance with the present invention, a dry vibratable refractory composition for use as a disposable liner for a tundish or the like includes, as a principal component, a refractory aggregate material selected from the group consisting of magnesia, alumina, calcia, silica, zirconia and combinations thereof; from about 1.0 to about 5.0wt% of an organic resin as a low temperature bonding agent, in particular a phenolic resin; from about 0.5 to about 10.0wt% of at least one intermediate temperature bonding agent comprised of either a phosphate, in particular, a sodium phosphate containing less than 40.0wt% ~~soda~~ sodium, or monoammonium phosphate; or a combination of an alkali metal silicate and a metal alloy powder, preferably in a 1:1 weight ratio. In the latter such combination, the silicate is selected from the group consisting of anhydrous sodium silicate and hydrated sodium silicate, and the metal is selected from the group consisting of a ferrosilicon, preferably having an iron content of from about 20.0 to about 30.0wt% and a silicon content of from about 80.0 to about 70.0wt%, and most preferably an iron content of 25.0wt% and a silicon content of 75.0wt%; aluminium/silicon alloy, preferably having an aluminium content of from about 70.0 to about 90.0wt% and a silicon content of from about 30.0 to about 10.0wt%, and most preferably an aluminium content of 80.0wt% and a silicon content of 20.0wt%; and magnesium/aluminium alloy, preferably having a magnesium content of from about 40.0 to about 60.0wt% and an aluminium content of from about 60.0 to about 40.0wt%, and most preferably a magnesium content of 50.0wt% and an aluminium content of 50.0wt%; and from about 0.0 to about 5.0wt% clay selected from the group consisting of ball clay, kaolin clay, bentonite and mixtures thereof, to enhance surface quality. The balance of the composition, adding to 100.0wt%, is the refractory aggregate base material.

The metal alloy powders are most effective when they have a particle size in the range of from about 1 to about 500μm.

The preferred phenolic resin low temperature bonding agents in the compositions of the present invention are phenol formaldehyde polymers having a hexamine content of from about 1.0 to about 10.0wt%, and an average molecular weight of from about 4000 to 10 000.

The overall range of refractory compositions encompassed by this invention is:

Component	Weight Percent
Refractory Material	Balance
Low Temperature Bonding Agent	1.0 - 5.0
Intermediate Temperature Bonding Agent	0.5 - 10.0
Clay	0.0 - 5 0

In order to be able to preheat the composition described, it has been found that the intermediate temperature bond agent must be present in the composition in

the proper amount. The presence of this additive supplies strength to the refractory lining after the low temperature bond agent has lost its strength enhancing capabilities at higher temperatures. The intermediate bond agent forms interparticle bonds at temperatures lower than the usual preheat temperatures. This results in a strong material at the preheat temperatures which will retain its shape and position to afford protection to the permanent lining. It has been found that without the addition of the intermediate bond agent the refractory crumbles and spalls when exposed to preheat temperatures. This spalling is caused by lack of sufficient intermolecular bonds in the refractory at the preheat temperatures.

It has been found that the addition of about 0.0 to about 5.0wt% of clay enhances the surface quality of the cured refractory lining and aids in increasing the intermediate temperature bond strength. The surface quality aspect is predominantly an aesthetic effect and is not greatly reduced if the clay is not added. It has been found that if a sufficient quantity of the intermediate temperature bond agent is supplied to the composition, the clay can be omitted without detracting from the preheat strength of the composition.

The refractory compositions of the present invention have been found to be highly effective for application as a monolithic lining to the inner surface of a vessel such as a tundish or a ladle used in molten metal casting processes, especially steel making, in hot practice, by utilising a dry method which comprises the steps of placing a cast-forming device for form shaping a dry refractory composition into the vessel in such a way as to leave a gap between the vessel and the cast-forming device; pouring into the gap an amount of a refractory composition sufficient to cover the inner surfaces of the vessel; the refractory composition containing from about 1.0 to about 5.0wt% of a low temperature bonding agent; from 0.5 to about 10.0wt% of at least one intermediate temperature bonding agent; and from 0.0 to about 5.0wt% clay; with the balance totaling 100wt% being a refractory aggregate material; curing the refractory composition by raising the temperature in the vessel from about 150°C to about 540°C to cause interparticle bond formation between particles of the refractory aggregate initiated by the low temperature bonding agent; removing the cast-forming device to leave a monolithic casting of the refractory material on the inner surface of the vessel; and preheating the refractory composition by raising the temperature in the vessel from about 540°C to about 1370°C to further cause interparticle bond formation between particles of the refractory aggregate initiated by the intermediate temperature bonding agent.

Examples

The present invention can be more fully understood in light of the following non-limiting examples.

Refractory compositions according to the present invention were prepared utilising the following materials:

Refractory - Dead burned magnesia (MgO);

Low temperature bond agent - phenolic resin;

Intermediate temperature bond - Type #1, a phosphate of a composition which contains less than 40.0wt% sodium oxide; and type #2, a combination of an alkali metal silicate and a powdered metal alloy present in a 1:1 weight ratio;

Clay - air floated ball clay.

Example 1

Preparation of Samples - Curing

The ingredients were first dry mixed thoroughly in a planetary paddle type electric mixer for from 1-5 minutes. The mixture was poured into a steel mould to make standard 17.8cm × 2.5cm × 2.5cm bars. The bars were leveled to produce a smooth surface The bars are heated to 175°C for 90 minutes.

Example 2

Example Formulations

	Weight Percent		
Component	IA	IIA	IIIA
Magnesia/Silica/Alumina	Balance	Balance	Balance
Air Floated Ball Clay	1.0	1.0	0.0
Phenolic Resin	3.0	4.0	2.5
Monosodium Phosphate	2.5	-	
Sodium Hexametaphosphate	-	2.0	-
Monoammonium Phosphate	-	-	6.0

All compositions prepared according to method in Example 1.

Example 3

Example Formulations

	Weight Percent		
Component	IB	IIB	IIIB
Magnesia/Silica/Alumina	Balance	Balance	Balance
Air Floated Ball Clay	1.0	0.0	2.0
Phenolic Resin	3.0	3.0	4.0
Anhydrous Sodium Silicate	1.5	-	2.0
Hydrated Sodium Silicate	-	2.0	-
Ferrosilicon powder, -150mesh	1.5	-	-
Aluminium/Silicon powder	-	2.0	2.0

All compositions prepared according to method in Example 1.

Example 4

Laboratory Evaluation of Refractory Compositions for Strength at Preheat Temperatures

The samples prepared according to Example 1 were cut into thirds lengthwise. These samples were fired to either 540°C, 815°C, or 1100°C and soaked at temperature for 1 hour. At the end of the soak period, the samples were abraded with a metal rod and qualitatively rated for strength. A rating scale-was established as follows:

Rating	Criteria
0	Sample does not retain shape at temperature
1	Sample retains shape but crumbles upon abrasion
2	Abrasion results in ½" deep cut in sample
3	Abrasion results in ½" deep cut in sample
4	Abrasion results in 1/8" deep cut in sample
5	Abrasion does leave cut in sample

Ratings of 3, 4 and 5 are judged as viable compositions for application in tundish.

Example 5

Compositions from Examples 2 and 3 were tested according to the procedure in Example 4. Results are shown in Table 1.

Table 1

	Rating		
Composition	540°C	815°C	1100°C
IA	3	4	5
IIA	2.5	3	4
IIIA	3	4	4
IB	3.5	4	5
IIB	3	3.5	4
IIIB	3.5	4	4.5

Example 6

Field Evaluation of Composition IA

Composition IA was evaluated in actual tundish application. Preheat temperature was from about 1150°C to about 1425°C. Composition IA was sequenced on continuous caster. Material deskulled cleanly and easily. No damage or marring of the permanent lining of the tundish occurred.

Example 7

Field Evaluation of Composition IIA

Composition IIA was evaluated in actual tundish application. Preheat temperature was from about 815°C to about 980°C. Composition IIA survived preheat and was sequenced on continuous caster. The material deskulled cleanly and easily. The tundish permanent lining showed no signs of wear.

Example 8

Field Evaluation of Composition IIIA

Composition IIIA was evaluated as disposable ladle lining in a foundry casting ladle. The material was installed using a no-former method The material installation was successful and the ladle was preheated to about 1370°C. Five heats of steel were cast through the ladle. The lining deskulled cleanly and easily. The castings showed a reduced non-metallic inclusion count as compared to castings which were made from a ladle that was not lined with a refractory lining of composition IIIA.

The claims defining the invention are as follows:

1. A refractory composition for application as a dry refractory, based on a refractory aggregate material selected from magnesia, alumina, calcia, silica, zirconia or combinations thereof; and characterised by including from 1.0 to 5.0wt% of a phenolic resin low temperature bonding agent; and from 0.5 to 10.0wt% of at least one intermediate temperature bonding agent selected from a phosphate-containing compound having a sodium content of less than 40.0wt%, or a mixture of an alkali metal silicate compound and a metal powder, such that at least one of said phosphate-containing compound and said silicate containing compound is present and no one said intermediate temperature bonding agent is present in the composition at more than 10.0wt%; and from 0.0 to 5.0wt% clay; with the balance of the composition to total 100.0wt% being said refractory aggregate material.

2. The refractory composition according to claim 1, wherein the phenolic resin is a phenol formaldehyde polymer.

3. The refractory composition according to claim 2, wherein the phenol formaldehyde polymer is further characterised by a hexamine content of from 1.0 to 10.0wt%, and an average molecular weight of from 4000 to 10 000.

4. The refractory composition according to any one of claims 1 to 3, wherein the phosphate-containing compound is monosodium phosphate, sodium hexametaphosphate, or monoammonium phosphate; the alkali metal silicate is anhydrous sodium silicate or hydrated sodium silicate, and the metal powder is ferrosilicon alloy, aluminium/silicon alloy or magnesium/aluminium alloy.

5. The refractory composition according to claim 4, wherein the ferrosilicon alloy has an iron content of from 20.0 to 30.0wt% and a silicon content of from 80.0 to 70.0wt%; the aluminium/silicon alloy metal powder has an aluminium content of from 70.0 to 90.0wt% and a silicon content of from 30.0 to 10.0wt%; and the magnesium/aluminium metal powder has a magnesium content of from 40.0 to 60.0wt% and an aluminium content of from 60.0 to 40.0wt%.

6. The refractory composition according to any one of claims 1 to 5, further characterised by the alkali metal silicate and the metal powder being present in the mixture in equal weight amounts, and the metal powder having a particle size in the range of from 1μm to 500μm.

7. The refractory composition according to any one of claims 1 to 6, further characterised by containing from 0.0 to 5.0wt% of ball clay, kaolin clay, bentonite, or mixtures thereof.

8. The refractory composition according to any one of claims 1 to 7, wherein the low temperature bonding agent initiates interparticle bond formation between particles of the refractory material in the temperature range of from 150°C to 540°C; and the intermediate temperature bonding agent initiates interparticle

bond formation between particles of the refractory material in the temperature range of from 540°C to 1370°C.

9. The refractory composition according to any one of claims 1 to 8, further characterised by being vibratable.

10. A refractory composition for application as a dry refractory comprising: from 2.5 to 3.5wt% phenol formaldehyde; from 2.5 to 3.5wt% monosodium phosphate; from 2.5 to 3.5wt% of a 50/50wt% mixture of anhydrous sodium silicate and a ferrosilicon alloy metal powder; and from 0.0 to 5.0wt% clay wherein the balance of the composition is a refractory aggregate material selected from the group consisting of magnesia, alumina, calcia, silica and combinations thereof.

11. A refractory composition for application as a dry refractory, substantially as hereinbefore described with reference to any one of the examples.

12. A dry method for applying a monolithic refractory lining to the inner surface of a vessel such as a tundish or the like, in hot practice, characterised by the steps of: a) placing a cast-forming device for form shaping a dry refractory composition into said vessel in such a way as to leave a gap between said vessel and said cast-forming device; b) pouring into said gap an amount of a refractory composition sufficient to cover the inner surfaces of said vessel, said refractory composition containing from 1.0 to 5.0wt% of a low temperature bonding agent; from 0.5 to 10.0wt% of at least one intermediate temperature bonding agent; and from 0.0 to 5.0wt% clay; with the balance totaling 100wt% being a refractory aggregate material; c) curing the refractory composition by raising the temperature in the vessel from 150°C to 540°C to cause interparticle bond formation between particles of the refractory aggregate initiated by the low temperature bonding agent; d) removing the cast-forming device to leave a monolithic casting of the refractory material on the inner surface of the vessel; and e) preheating the refractory composition by raising the temperature in the vessel from 540°C to 1370°C to further cause interparticle bond formation between particles of the refractory aggregate initiated by the intermediate temperature bonding agent.

13. A dry method for applying a monolithic refractory lining to the inner surface of a vessel such as a tundish or the like, in hot practice, substantially as hereinbefore described with reference to any one of the examples.

Dated 26 March, 1997
Minteq International Inc.

Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON

Dry Refractory Composition

Abstract

A refractory composition, particularly for application as a dry vibratable refractory for forming the wearable, disposable monolithic lining coating the permanent lining of a tundish or a ladle used in molten metal casting processes is disclosed. The composition contains a refractory aggregate, a low temperature bonding agent, at least one intermediate temperature bonding agent, and, optionally, clay. The use of both a low and intermediate temperature bonding agent enables installation of the refractory in hot practice.