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**NOTICE OF ENTITLEMENT**

AUSTRALIAN PATENT  
APPLICATION NO. 37369/93

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of 235 E. 42nd Street, New York, New York, U.S.A.

being authorized by the Applicant(s)/Nominated Person(s) in respect of an application entitled:

Sprayable Refractory Composition

state the following:-

1. The Applicant(s)/Nominated Person(s) has/have, for the following reasons, gained entitlement from the actual inventor(s):-

The Applicant/Nominated Person is the assignee of the inventors.

2. The Applicant(s)/Nominated Person(s) is entitled to rely on the basic application listed in the Declaration under Article 8 of the PCT as follows:

The Applicant/Nominated Person is the assignee of the actual inventors.

3. The basic application(s) listed in the Declaration under Article 8 of the PCT is the application first made in a Convention Country in respect of the invention.

- ~~4. The Applicant(s)/Nominated Person(s) is/are~~

DATED this 20th day of July, 1991

SPECIALTY REFRACTORIES INC.

BY: \_\_\_\_\_  
(Signature)

\_\_\_\_\_  
(Name & Title)



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SPRAYABLE REFRACTORY COMPOSITION

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(56) Prior Art Documents  
EP 425139  
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(57) Claim

1. An alkali oxide-free refractory composition for use as a disposable lining comprising:

a refractory aggregate;

an alkali free phosphate compound in an amount sufficient to impart stiffening properties to the composition, in combination with a set retarding agent which is added in an amount sufficient to prolong the setting time of the composition when mixed with water;

at least one density reducing material in an amount sufficient to reduce the density of the composition;

a low temperature binder; and

a plasticizer in an amount sufficient to enhance the ability of the composition to adhere to vertical surfaces after mixing with water.

16. An alkali oxide free refractory composition for use as a disposable lining comprising:

from 0.1 to 2 weight percent of a stiffening agent of monocalcium phosphate;

from 0.1 to 2 weight percent of a set retarding agent of powdered citric acid;

from 0.1 to 5 weight percent of paper fibers present as a density reducing material;

from 0.1 to 1 weight percent of styrofoam beads present as a density reducing material;

from 0.1 to 5 weight percent of a clay present as a plasticizer;

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from 0.1 to 2 weight percent of calcium lignosulfonate as a low temperature binder;  
and

at least 83 weight percent of a refractory aggregate of a source of magnesia having at least 85% MgO and at least 1 to 5 weight percent olivine and less than 0.1 weight percent of alkali oxides; wherein the stiffening agent and set retarding agent are present in a weight ratio of about 1:1.

17. A vessel for handling molten metal comprising:

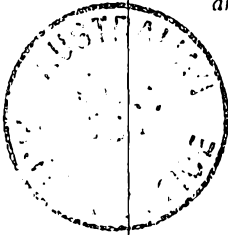
means for holding molten metal therein;

a relatively permanent refractory lining disposed within the holding means for protecting the holding means against the effects of the molten metal; and

a disposable refractory lining disposed upon at least a portion of the permanent refractory lining and comprising the composition of any one of Claims 1 to 16.



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<p>(21) International Application Number: PCT/US93/01862 (22) International Filing Date: 3 March 1993 (03.03.93) (30) Priority data: 847,560 6 March 1992 (06.03.92) US (71) Applicant: <del>SPECIALTY REFRACTORIES INC. (US/</del> <del>US); 235 East 42nd Street, New York, NY 10017-5755</del> <del>(US).</del> (72) Inventors: RUMPELTIN, Charles, R. ; 10 Pheasant Ct., Flanders, NJ 07836 (US). DODY, Julie, Annette ; 3569 New Hampshire Avenue, Easton, PA 18042 (US). <i>(73) Minteq International Inc</i> <i>405 Lexington Avenue</i> <i>New York New York 10174-1901</i> <i>USA</i></p>	<p>(74) Agents: RICHARDS, John et al.; Ladas &amp; Parry, 26 West 61 Street, New York, NY 10023 (US). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, RO, RU, SD, SE, SK, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG). <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i></p>	
<p>(54) Title: SPRAYABLE REFRACTORY COMPOSITION</p> <p>(57) Abstract</p> <p>The present invention discloses an alkali oxide free low density refractory material especially adapted for use as a disposable liner material for molten metal containing vessels. This material includes about 0.1 to about 2 weight percent of a stiffening agent, about 0.1 to about 2 weight percent of a set retarding agent, about 0.1 to 6 weight percent of density reducing materials, about 0.1 to about 5 weight percent of a plasticizer, up to about 2 weight percent of a low temperature binder, and the balance of a refractory aggregate which is preferably MgO. The stiffening agent and set retarding agent are used in substantially the same amounts to provide the disclosed refractory material with increased resistance to slumping while, at the same time, allowing spraying apparatus residence times of up to one half hour without clogging. The composition includes less than about 0.1 weight percent of alkali oxides, so that reaction and fusion of the disposable liner with a permanent liner is avoided thereby allowing increased ease in mechanical removal of the disposable liner. Also, the invention relates to methods for applying the disposable lining by spraying and an apparatus for holding molten metal which includes a steel shell, a relatively permanent refractory lining disposed therein and a disposable lining disposed upon at least a portion of the permanent refractory lining.</p>		



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### SPRAYABLE REFRACTORY COMPOSITION

#### Technical Field

The present invention relates to substantially alkali-free refractory compositions which are preferably mixed with water and sprayed onto a permanent lining of a tundish to form a disposable lining thereon.

#### Background of the Invention

Tundishes and ladles are intermediate containment vessels utilized in processing metals and metal alloys. These vessels contain a permanent refractory lining material which has high heat resistance. A material such as 50 to 70%  $Al_2O_3$  brick is often used to form the permanent refractory lining. Although permanent liner materials are highly temperature resistant, contact with molten metal and numerous cycles of heating and cooling during molten metal processing can degrade and necessitate frequent replacement of the permanent liner. Therefore, disposable liners formed of dry vibratable, trowellable, gunnable or sprayable refractory materials are formed upon the permanent liner of a tundish or other molten metal processing vessel permanent liner.

The disposable liner acts as a thermal or chemical barrier which protects the permanent

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liner and simultaneously maintains the temperature of the molten metal. After a tundish or ladle has been utilized for numerous cycles, the disposable liner is replaced. Since  
5 the disposable liner has a different thermal coefficient of expansion as compared to the permanent liner, "deskulling" or removal of the disposable liner should be easily accomplished. However, refractory compositions of the past  
10 utilized to form such disposable liners have often included alkali oxides such as, for example,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ . Heat penetration of the tundish or ladle can cause a reaction which occurs at the interface of the disposable and  
15 permanent linings. At this interface, the oxides may react with the permanent liner thereby causing fusion of the two liners. Therefore, deskulling of the disposable liner becomes difficult, and portions of the permanent  
20 liner which fuse to the disposable liner can be removed during this operation. Furthermore, contamination of the permanent liner increases the thermal coefficient of expansion of the layer adjacent the disposable liner. The  
25 differences in expansion between this layer and the remainder of the permanent liner can result in sheet spalling of the permanent liner, thus leading to premature failure.

Basic refractory materials are  
30 commonly used as disposable lining materials. The term "basic" refers to the chemical behavior of these materials rather than the complexity of their composition. Basic refractory materials include magnesia, doloma, olivine, calcia or  
35 mixtures thereof.

In addition to the refractory aggregate, such conventional refractory

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compositions may also include various binders, density reducing materials and plasticizers. Furthermore, water is generally added to the composition in order to facilitate application  
5 by trowelling, gunning or spraying.

Sprayable refractory materials generally contain from about 20 to 30 weight percent water, thus enabling them to be pumped through a hose and to be sprayed when mixed with  
10 compressed air in a spray gun. Sprayable liners are well adapted for use in casting vessels such as hot tops, ladles, tundishes, troughs and pipes.

It has heretofore been observed that  
15 sprayable refractory materials can suffer from slumping, i.e., a condition in which a recently applied refractory material lacks the necessary adhesion to remain fixed to the surface to which it is applied.

20 Therefore, it would be highly advantageous to provide a sprayable refractory material for use as a disposable lining which provides satisfactory thermal insulation, ease of removal from the permanent liner and which  
25 provides a uniform layer without significant slumping of wet material. It would be further advantageous to provide a sprayable material which achieves the above advantages while also providing a density of less than about 100  
30 pounds per cubic foot ("p.c.f.") while allowing a spray gun residence time of up to about 30-40 minutes without blockages. Moreover, if these materials could be essentially free of alkali oxides, the problem of contamination and/or  
35 premature deterioration of the permanent lining could be reduced.

### Summary of the Invention

In accordance with the present invention, a substantially alkali oxide free refractory material is provided which can be applied as a disposable refractory lining which has satisfactory chemical and high temperature resistance and provides ease of removal after cooling.

In particular, the present invention provides a low density, substantially alkali oxide free refractory composition which contains less than about 0.1 weight percent alkali oxides. Furthermore, the composition resists slumping when applied by spraying while simultaneously providing a residence time of up to about 30 to 40 minutes without blocking the spray apparatus. The dried density of the composition is below 100 p.c.f. and typically between about 80 to 95 p.c.f. Also, the alkali containing components of the composition total not more than about 0.1% of the overall composition. Therefore, disposable linings formed from the refractory compositions of the present invention help to enhance the longevity of the permanent linings within the casting vessel.

The preceding advantages are obtained in a refractory composition that includes a stiffening agent, a set retarding agent, one or more density reducing materials, a plasticizer, a low temperature binder and a refractory aggregate. Also, the stiffening agent and set retarder can be added in predetermined weight ratios to achieve optimal performance during spray application of the composition.

Thus, according to a first embodiment of the present invention there is provided an alkali oxide-free refractory composition for use as a disposable lining comprising:

a refractory aggregate;

an alkali free phosphate compound in an amount sufficient to impart stiffening properties to the composition, in combination with a set retarding agent which is added in an amount sufficient to prolong the setting time of the composition when mixed with water;

at least one density reducing material in an amount sufficient to reduce the density of the composition;

a low temperature binder; and

a plasticizer in an amount sufficient to enhance the ability of the composition to adhere to vertical surfaces after mixing with water.

According to a second embodiment of the present invention there is provided an alkali oxide-free refractory composition for use as a disposable lining comprising:

from 0.1 to 2 weight percent of a stiffening agent comprising an alkali free phosphate compound;

from 0.1 to 2 weight percent of a set retarding agent;

from 0.1 to 6 weight percent of a density reducing material;

from 0.1 to 5 weight percent of a plasticizer;  
 a low temperature binder; and  
 at least 85 weight percent of a refractory aggregate.

According to a third embodiment of the present invention there is provided an alkali oxide-free refractory composition for use as a disposable lining comprising:

from 0.1 to 2 weight percent of a stiffening agent of an alkali free phosphate compound;

from 0.1 to 2 weight percent of a set retarding agent;  
 from 0.1 to 5 weight percent of a first density reducing material;  
 from 0.1 to 1 weight percent of a second density reducing material;  
 from 0.1 to 5 weight percent of a plasticizer;  
 from 0.1 to 2 weight percent of a low temperature binder; and  
 at least 83 weight percent of a refractory aggregate.

According to a fourth embodiment of the present invention there is provided an alkali oxide free refractory composition for use as a disposable lining comprising:

from 0.1 to 2 weight percent of a stiffening agent of monocalcium phosphate;  
 from 0.1 to 2 weight percent of a set retarding agent of powdered citric acid;  
 from 0.1 to 5 weight percent of paper fibers present as a density reducing material;  
 from 0.1 to 1 weight percent of styrofoam beads present as a density reducing material;

from 0.1 to 5 weight percent of a clay present as a plasticizer;  
 from 0.1 to 2 weight percent of calcium lignosulfonate as a low temperature binder;

and

at least 83 weight percent of a refractory aggregate of a source of magnesia having at least 85% MgO and at least 1 to 5 weight percent olivine and less than 0.1 weight percent of alkali oxides; wherein the stiffening agent and set retarding agent are present in a weight ratio of about 1:1.

According to a fifth embodiment of the present invention there is provided a vessel for handling molten metal comprising:

means for holding molten metal therein;

a relatively permanent refractory lining disposed within the holding means for protecting the holding means against the effects of the molten metal; and

a disposable refractory lining disposed upon at least a portion of the permanent refractory lining and comprising the composition of any one of Claims 1 to 16.

According to a sixth embodiment of the present invention there is provided a method for installing a disposable refractory lining which comprises:

forming the composition of any one of Claims 1 to 16;

mixing the composition with a sufficient amount of water to form a sprayable mixture;

and

spraying the mixture onto an inner surface of a molten metal holding vessel to form a disposable lining therein.

According to a seventh embodiment of the present invention there is provided a method for installing a disposable refractory lining which comprises:

modifying the properties of a refractory composition which contains an alkali oxide free refractory aggregate, an alkali free phosphate compound in an amount sufficient to impart stiffening properties to the composition, a low temperature binder and a plasticizer by increasing its stiffening property, retarding or prolonging the setting time of the composition when mixed with water;

reducing the density of the composition, and enhancing the ability of the composition to adhere to vertical surfaces after mixing with water to form a refractory composition;

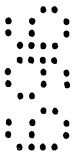
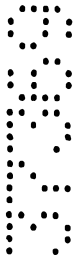
mixing the composition with a sufficient amount of water to form a sprayable mixture;

and

spraying the mixture onto an inner surface of a molten metal holding vessel to form a disposable lining therein.

### Detailed Description of the Invention

In the description which follows, all



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references to percentage or % refer to percent by weight unless otherwise noted.

The present invention is directed to refractory compositions which include, as a principle component, any one of various refractory aggregates such as magnesia, doloma, olivine, calcia, alumina, silica and combinations thereof. For disposable casting vessel or tundish linings, the preferred refractory aggregate would be a basic refractory, and most preferably, one based on magnesia or other sources of MgO.

The magnesia aggregate should contain at least about 50 to 95% MgO. Thus, any source of MgO providing a water insoluble particulate refractory grain may be selected, such as dead burned magnesia, sea water magnesia, periclase or the like. In formulating an alkali oxide free composition, the remaining percentage of the refractory aggregate should not contain any significant amount of alkali oxide components.

The refractory aggregate constitutes about 83% or more of the overall composition, and preferably above about 90%. When magnesia is used as the aggregate, a portion may be substituted with olivine, if desired. Thus, the MgO content of the overall composition supplied by the refractory aggregate can vary from about 38% to 99%, while olivine can be used in an amount of up to 45%.

A plasticizer is added to enhance the ability of the composition to adhere to the surfaces to which it is applied. The plasticizer is utilized in an amount of about 0.1 to about 5%. It is preferred that the plasticizer be a clay selected from bentonite, kaolin clay and ball clay. However, it is

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especially preferred to select bentonite clay as the plasticizer.

To control the density of the composition, at least one density reducing material is added in an amount of between about 5 0.1 and about 6%. Any of a wide variety of density reducing materials may be utilized, including inorganic or organic fibers, expanded inorganic or organic materials, or other 10 lightweight fillers. Paper fibers (either coarse or fine), ceramic or glass fibers, rockwool, expanded clay, and polystyrene beads are typical components that can be added.

Advantageously, the density reducing material is a combination of a cellulose fiber 15 and expanded polystyrene beads. It is preferred that the organic fiber be coarse paper fibers, fine paper fibers or mixtures thereof. These fibers generally would have fiber lengths of 20 from about 0.1 to about 1.5 mm. The use of these fibers enables the refractory composition of the present invention to provide a dried density of less than about 100 pounds per cubic foot.

25 Along with the paper fibers, fine perlite, expanded polystyrene beads, expanded fire clay and mixtures thereof are added to further reduce the density of the composition. It is most preferred to select expanded 30 polystyrene beads having an average particle diameter of from about 0.5 to about 2 mm, a bulk density of about 1 to 2 lb/ft<sup>3</sup>, a melting temperature of from about 400 to 500°F, and a vaporization temperature of about 500 to 600°F. 35 Further details on these beads can be found in U.S. Patent 5,073,525, the content of which is expressly incorporated herein by reference

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thereto. These beads, in combination with the paper fibers, provide the refractory composition with a dried density of as low as about 80 pounds per cubic foot.

5           The composition also contains about 0.1 to about 2 % of a stiffening agent and about 0.1 to about 2 % of a set retarding agent. The stiffening agent is added to impart initial gelling properties to the composition when it is  
10 mixed with water. For spray application, an amount of water in the range of about 20 to 30% is typically added to provide a pumpable viscosity. Preferably, the stiffening agent is an alkali-free phosphate compound, such as an  
15 alkaline earth phosphate, an aluminum phosphate, encapsulated phosphoric acid, ammonium phosphate or an organic phosphate compound. Of these compounds, monocalcium phosphate is the most advantageous. The stiffening agent also imparts  
20 high temperature strength to the composition.

          The set retarding agent is added to control the gelling properties of the stiffening agent, thus imparting a practical residence time to the composition. The set retarding agent is  
25 added in an amount of about 0.1 to about 2% and is preferably an organic acid. Any di- or tri-basic carboxylic acid may be used, with citric, tartaric, oxalic or malic acid being representative. Of these, powdered citric acid  
30 has been found to be the most advantageous.

          These agents also may be further adjusted within the previously described ranges to control the viscosity of the refractory composition while being pumped through a spray  
35 apparatus. Optimum performance during application of the composition is achieved by controlling the weight ratio of stiffening agent

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to set retarding agent. A ratio of about 3:1 to  
1:3 is suitable, with between about 1.5:1 to  
1:1.5 being preferred. The most advantageous  
ratio is about 1:1. At this level, these agents  
5 co-act to prevent slumping of the refractory  
material during the period of time immediately  
following spraying and prior to drying.

The set retarding agent prevents the  
refractory composition from prematurely reaching  
10 too high a viscosity which would effectively  
restrict flow through the spray apparatus. It  
is preferred that the set retardant agent be  
used in an amount which provides a refractory  
material residence time within the spray  
15 apparatus of up to about 30 to 40 minutes  
without causing blockages in the apparatus.  
Therefore, the composition allows spraying to  
resume after a 30-40 minute work stoppage  
without the necessity of debriding spray head or  
20 hoses connected thereto. A 1:1 weight ratio of  
powdered citric acid and monocalcium phosphate  
is most preferred for imparting the desired  
residence time and anti-slumping characteristics  
to the composition.

25 The refractory composition of the  
present invention may further comprise from  
about 0.1 to 2% of a secondary binder. It has  
been found that the addition of this binder  
contributes to refractory strength while also  
30 improving air entrainment to the composition to  
further reduce its density. It is preferred  
that this binder be an alkaline earth  
lignosulfonate such as, for example, calcium  
lignosulfonate.

35

#### EXAMPLES

The following non-limiting examples  
further illustrate the preferred embodiments of

the present invention.

Example 1

The following test formulations were prepared by dry blending the components to a homogeneous batch, combining the batch with 25% water, and mixing the combination to substantially uniformly distribute the water throughout the batch. As shown in Table 1, varying amounts of stiffening and set retarding agents were used and their effects on the gelling properties of the composition were evaluated.

Table 1

Material	1	2	A	B	C	D	E
MgO	92.7	92.7	92.7	92.2	92	92.2	92.2
Olivine	2	2	2	2	2	2	2
Bentonite	2	2	2	2	2	2	2
Calcium Ligno-sulfonate	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Mono-calcium Phosphate	-	1	0.5	0.75	0.85	0.5	1
Powdered Citric Acid	1	-	0.5	0.75	0.85	1	0.5
Coarse Paper Fibers	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Expanded Poly-styrene Beads (Type #2)	0.6	0.6	0.6	0.6	0.6	0.6	0.6

The results are shown below in Table 2.

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Table 2

	Sample	Qualitative Observations
5	Sample 1	Very little stiffening
	Sample 2	Very little stiffening
10	Sample A	Stiffened somewhat overnight
	Sample B	Stiffened somewhat overnight (a little more than A)
15	Sample C	Stiffened in about one hour
	Sample D	Some stiffening in about 4 hours
20	Sample E	Some stiffening in about 4 hours

Sample C, having 0.85 percent of monocalcium phosphate and 0.85 percent citric acid, exhibited a preferable stiffening time which would enhance slump resistance and residence time.

Example 2

It has been found that a density of less than 90 p.c.f. may be attained by incorporating an ultra lightweight aggregate comprising expanded polystyrene beads (type #2) and coarse paper fibers into the refractory composition.

Table 3 below lists five test formulations which were prepared as described above in Example 1 except that the water content is stated in the Table. Varying amounts of expanded polystyrene beads were used to evaluate the effects on the dried density of the composition as well as the dispersibility of the beads in the dry composition.

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Table 3

Material	F	G	H	I
Mgo	92	92.25	91.3	92
Olivine	2	2	2	2
Bentonite	2	2	2	2
Calcium Lignosulfonate	0.5	0.5	0.5	0.5
Monocalcium Phosphate	1	1	1	1
Powdered Citric Acid	1	1	1	1
Coarse Paper Fibers	1	1	1.5	1
Expanded Polystyrene Beads	0.5	0.25	0.7	0.6
Water %	24.9	22.0	26.0	25.0
Density (pcf)	84.0	100.4	83.8	85.0

As indicated above, samples F, H and I exhibit dried densities which are well below 90 p.c.f. Sample I met the criteria of dried density (less than 90 p.c.f.) while also exhibiting good dispersibility of the beads in the dry powder prior to mixing with the water.

### Example 3

The formulation of sample I of Example 2 was used in a number of spray application field tests. The composition was tested as a disposable tundish liner at several locations. The composition met the requirements for spray application, i.e. spray rates, residence time, slump resistance, etc. The resulting lining also met performance requirements in the areas of drying, preheating, molten metal and slag resistance, durability and sequencing

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requirements. The desulfurability of the lining was found to be good in all locations and improved over those which use conventional alkali oxide containing refractory compositions.

5           While it is apparent that the invention herein disclosed is well calculated to fulfill the objects above stated, it will be appreciated that numerous modifications and  
10           embodiments may be devised by those skilled in the art. It is intended that the appended claims cover all such modifications and  
          embodiments as fall within the true spirit and scope of the present invention.

**The claims defining the invention are as follows:**

1. An alkali oxide-free refractory composition for use as a disposable lining comprising:

a refractory aggregate;

an alkali free phosphate compound in an amount sufficient to impart stiffening properties to the composition, in combination with a set retarding agent which is added in an amount sufficient to prolong the setting time of the composition when mixed with water;

at least one density reducing material in an amount sufficient to reduce the density of the composition;

a low temperature binder; and

a plasticizer in an amount sufficient to enhance the ability of the composition to adhere to vertical surfaces after mixing with water.

2. An alkali oxide-free refractory composition for use as a disposable lining comprising:

from 0.1 to 2 weight percent of a stiffening agent comprising an alkali free phosphate compound;

from 0.1 to 2 weight percent of a set retarding agent;

from 0.1 to 6 weight percent of a density reducing material;

from 0.1 to 5 weight percent of a plasticizer;

a low temperature binder; and

at least 85 weight percent of a refractory aggregate.

3. An alkali oxide-free refractory composition for use as a disposable lining comprising:

from 0.1 to 2 weight percent of a stiffening agent of an alkali free phosphate compound;

from 0.1 to 2 weight percent of a set retarding agent;

from 0.1 to 5 weight percent of a first density reducing material;

from 0.1 to 1 weight percent of a second density reducing material;

from 0.1 to 5 weight percent of a plasticizer;

from 0.1 to 2 weight percent of a low temperature binder; and

at least 83 weight percent of a refractory aggregate.

4. The composition of any one of the preceding claims, wherein the stiffening agent and set retarding agent are present in a weight ratio of between 3:1 and 1:3.

5. The composition of Claim 4, wherein the aggregate is a source of magnesia having at least about 85% MgO and the composition contains less than 0.1 weight percent of alkali oxides.

6. A composition according to any one of the preceding claims, wherein the stiffening agent is an alkaline earth phosphate, an aluminum phosphate, encapsulated phosphoric acid, ammonium phosphate or an organic phosphate compound, and the set retarding agent is an organic acid or mixtures thereof.

7. The composition of any one of the preceding claims, wherein the set retarding agent is citric, tartaric, oxalic or malic acid or mixtures thereof.

8. The composition of any one of the preceding claims, wherein the density reducing material is an inorganic fiber, an organic fiber, an expanded inorganic material, an expanded organic material or mixtures thereof.

9. The composition of Claim 8, wherein the density reducing material is a cellulose fiber, expanded clay, styrofoam beads or mixtures thereof.

10. The composition of any one of the preceding claims, wherein the plasticizer is bentonite clay, a kaolin clay or ball clay.

11. The composition of any one of the preceding claims, wherein the aggregate is magnesia, alumina, calcia, silica or mixtures thereof.

12. The composition of Claim 3, wherein the stiffening agent is monocalcium phosphate and the set retarding agent is powdered citric acid.

13. The composition of Claim 3, wherein the stiffening agent and set retarding agent are present in a weight ratio of between 1.5:1 and 1:1.5.

14. The composition of Claim 3, wherein the first density reducing material is an organic fiber and the second density reducing material is an expanded inorganic or organic material.

15. The composition of Claim 3, where the low temperature binder is an organic binder of a starch, cereal or natural or synthetic resin.

16. An alkali oxide free refractory composition for use as a disposable lining comprising:

from 0.1 to 2 weight percent of a stiffening agent of monocalcium phosphate;

from 0.1 to 2 weight percent of a set retarding agent of powdered citric acid;

from 0.1 to 5 weight percent of paper fibers present as a density reducing material;

from 0.1 to 1 weight percent of styrofoam beads present as a density reducing material;

from 0.1 to 5 weight percent of a clay present as a plasticizer;

from 0.1 to 2 weight percent of calcium lignosulfonate as a low temperature binder;

and

at least 83 weight percent of a refractory aggregate of a source of magnesia having at least 85% MgO and at least 1 to 5 weight percent olivine and less than 0.1 weight percent of

alkali oxides; wherein the stiffening agent and set retarding agent are present in a weight ratio of about 1:1.

17. A vessel for handling molten metal comprising:  
means for holding molten metal therein;

a relatively permanent refractory lining disposed within the holding means for protecting the holding means against the effects of the molten metal; and

a disposable refractory lining disposed upon at least a portion of the permanent refractory lining and comprising the composition of any one of Claims 1 to 16.

18. A method for installing a disposable refractory lining which comprises:  
forming the composition of any one of Claims 1 to 16;

mixing the composition with a sufficient amount of water to form a sprayable mixture;  
and

spraying the mixture onto an inner surface of a molten metal holding vessel to form a disposable lining therein.

19. A method for installing a disposable refractory lining which comprises:

modifying the properties of a refractory composition which contains an alkali oxide free refractory aggregate, an alkali free phosphate compound in an amount sufficient to impart stiffening properties to the composition, a low temperature binder and a plasticizer by increasing its stiffening property, retarding or prolonging the setting time of the composition when mixed with water;

reducing the density of the composition, and enhancing the ability of the composition to adhere to vertical surfaces after mixing with water to form a refractory composition;

mixing the composition with a sufficient amount of water to form a sprayable mixture;  
and

spraying the mixture onto an inner surface of a molten metal holding vessel to form a disposable lining therein.

20. A refractory composition according to Claim 1 substantially as hereinbefore described in any of the examples.

**Dated 11 June, 1996**  
**Minteq International Inc.**

**Patent Attorneys for the Applicant/Nominated Person**  
**SPRUSON & FERGUSON**



# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/ISA 43/01862

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>4</sup>				
According to International Patent Classification (IPC) or to both National Classification and IPC				
IPC <sup>5</sup> : C 04 B 35/68, C 04 B 35/66, F 27 D 1/16, B 22 D 41/02				
<b>II. FIELDS SEARCHED</b>				
Minimum Documentation Searched <sup>7</sup>				
Classification System <sup>1</sup>	Classification Symbols			
IPC <sup>5</sup>	C 04 B, F 27 D, B 22 D, C 21 B, C 21 C			
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>4</sup>				
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>6</sup></b>				
Category <sup>8</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>		
X	EP, A1, 0 425 139 (QUIGLEY COMPANY INC.) 02 May 1991 (02.05.91), the whole document. --	1-19		
X	EP, A1, 0 123 755 (AIKOH CO. LTD.) 07 November 1984 (07.11.84), the whole document. --	1, 2, 3, 18, 19		
X	EP, A2, 0 178 154 (THE DOW CHEMICAL COMPANY) 16 April 1986 (16.04.86), the whole document. --	1, 18, 19		
X	EP, A2, 0 213 900 (FOSECO INTERNATIONAL LIMITED) 11 March 1987 (11.03.87), the whole document. --	1, 18, 19		
X	EP, A1, 0 065 034	1, 18,		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> <sup>*</sup> Special categories of cited documents: <sup>14</sup>                      "A" document defining the general state of the art which is not considered to be of particular relevance                      "E" earlier document but published on or after the international filing date                      "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)                      "O" document referring to an oral disclosure, use, exhibition or other means                      "P" document published prior to the international filing date but later than the priority date claimed                 </td> <td style="width: 50%; border: none; vertical-align: top;">                     "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention                      "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step                      "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art                      "Z" document member of the same patent family                 </td> </tr> </table>			<sup>*</sup> Special categories of cited documents: <sup>14</sup> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family
<sup>*</sup> Special categories of cited documents: <sup>14</sup> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family			
<b>IV. CERTIFICATION</b>				
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report			
09 June 1993	0 2. 07. 93			
International Searching Authority	Signature of Authorized Officer			
EUROPEAN PATENT OFFICE	BECK			

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
	(CHAMOTTE- UND TONWERK KURT HAGENBURGER) 24 November 1982 (24.11.82), the whole document. --	19
P.A	WO, A1, 92/04 293 (SHUBOW) 19 March 1992 (19.03.92), claims. ----	1-19

ANHANG

ANNEX

ANNEXE

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

to the International Search Report to the International Patent Application No.

au rapport de recherche international relatif à la demande de brevet international n°

PCT/US 93/01862 SAE 71019

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visé ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A1 425139	02-05-91	AU A1 64893/90 AU B2 635078 BR A 9005349 CA AA 2028026 JP A2 3205376 KR B1 9302669 US A 5073525 ZA A 9008420 ZA A 9008429	16-05-91 11-05-92 17-09-91 24-04-91 06-09-91 07-04-92 17-12-91 24-06-92 26-08-92
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