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2,220,411
Refractory and Method of Making Same
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No Drawing. Application February 17, 1939, Serial No. 236,928
10 Claims.

This application is a continuation in part of our copending applications Serial No. 189,808, filed February 10, 1938 and Serial No. 246,156, filed December 16, 1938.

5 Our invention relates to bonded refractories and especially to new methods of bonding refractories, and new refractory compositions.

The special refractories field is characterized not only by a group of special and usually expensive materials, but also by the mode of fabrication and manufacture indigenous to the particular refractory, none of which are normally applicable to the manufacture of other refractories. This special refractories field has developed because of certain unusual demands on refractories not satisfactorily fulfilled by refractories already in existence.

For example, some applications demand extremely high softening points; others, extreme resistance to thermal shock and to spalling; others, a minimal dimensional change through a wide range of temperatures; others, the possibility of direct fabrication to accurate and controlled sizes; others, certain special electrical properties; others, high heat conductivity; others, low heat conductivity; others, low specific gravity; others, high hot strength; others, high hot strength and low cold strength or vice versa, etc. plus any combination of the above properties besides a large number of special properties too numerous to mention.

One industry, which demands suitable refractories particularized to probably a greater extent than in any other, is the dental industry where the fabrication of investment for the casting of inlays and bridge work has become specialized to a very high degree. For example, an ideal refractory for the dental industry should have properties somewhat as follows: It should be able to be cast from slip form of sufficient fluidity completely to fill all recesses and interstices of the mold, no matter how minute, without the formation of bubbles. It should remain in fluid form after mixing for at least 5 to 10 minutes without segregation or separation of the constituents. After remaining for from 5 to 10 minutes in fluid form, it should be capable of setting in the next 5 to 10 minutes to a hard, tough, strong piece with a controlled porosity factor as well as preferably undergoing setting expansion of approximately one half to one per cent. It should then be capable of being dried and fired with extreme rapidity. It should also be capable of completely controllable thermal expansion properties, either temporary or permanent and above the size of the original mold in the temperature range from 1200° to 3000° F. or higher if necessary, so as to compensate for the usual shrinkage on the cooling of cast alloys. It should not give off much gas at 1200° to 3000° F. and it should have sufficient porosity to absorb any gases emitted by the casting metal. It should be strong when cast and weak when cold after use to permit easy removal of the cast. It should not react in any way chemically with the casting alloy. It should not dust. It should be a super-refractory. These properties are the major requirements of a refractory for dental use. There are several other characteristics, but they are of minor importance.

Another use of refractories is for heavy duty at high temperatures. For this purpose zircon alone has the disadvantage that it is from 20% to 50% heavier than other refractories used in the high temperature field. Furthermore, the very low thermal conductivity of zircon is comparable to the best of thermal solid insulators. For many applications, strong tough refractory ware of good thermal conductivity is a desired condition. Such applications are for refractory walls behind boiler tubes, such as used on ships where weight-saving and good thermal conductivity are required, for kiln furniture and kiln car bate, etc. A known refractory for this purpose consists of a mixture of zircon and silicon carbide. Silicon carbide has a heat conductivity approximately from 10 to 15 times that of zircon, and a specific gravity of 3.1 as against 4.6 for zircon. Hitherto the bonding agent employed in such refractories has been phosphoric acid. However, in the manufacture of pieces of refractory ware in which the length and breadth are very large in proportion to its thickness, the green strength during drying and preliminary firing is so low that handling pieces of any size is very difficult. Secondly, the finished fired strength is seldom greater than a modulus of rupture of 600-900 pounds per square inch. Thirdly, on firing above approximately 2800° F. the phosphate bond tends to be dissipated so that the ware becomes weak and crumbly, thereby permanently losing its strength characteristics.

Another application of special refractories, as described and claimed in our copending application Serial No. 204,392, filed April 26, 1938, is in the high temperature insulation field. In this field, the insulating qualities of zircon or other insulating refractory are greatly increased by rendering the materials porous. This may be accomplished by incorporating in such refrac-
tories a pore-forming material such as coke, and then burning out the pore-forming material.

Still another application of special refractories is for slip casting or mold casting, or in methods of plastic mixes, or in dipping, spraying or brushing, so that very thin refractory coats may be prepared when desired. Zircon refractories hereinafter developed have been suitable only for ramming in damp, non-plastic forms in such shapes where ramming procedures are applicable.

Their green strength is poor; no increase in strength is obtainable on long standing at room temperatures, and their plasticity is low. For these reasons, such zircon mixtures are not suitable for slip casting or mold casting, or in methods of plastic mixes; hence the manufacture of intricate shapes, not amenable to ramming, cannot be made. Although the addition of organic bonds may be used to develop satisfactory green strength; these additions are, notwithstanding, of no avail when the mix is fluid enough to cast or pour.

We have discovered novel and improved methods, compositions, and bonding agents, which more or less completely fulfill the exacting demands for refractories, particularly in the dental industry. Furthermore by the use of these novel bonding agents and methods, we have found it possible adequately to bond practically any super-refractory materials which can be obtained in suitable grain sizes, or any desired combination of these refractory materials, with the exception of the highly basic magnesite or fused magnesia bodies.

Not only are these improved methods applicable to super-refractory materials, but also to normal refractories, with the exception of magnesite and dolomite, that are capable of being obtained in suitable grain sizes, and to combinations of these normal refractories with each other, or with the super-refractories. By the use of these novel bonding agents and methods, we have found it possible economically to prepare in a strong form the highly porous light-weight type of refractory known as insulating firebrick.

These novel bonding agents comprise the following double silicate with the oxide of the named element; or by thermally reacting a pore-forming material such as coke, and then burning out the pore-forming material.

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These novel bonding agents comprise the following double silicate with the oxide or carbonate of the named element; or by thermally reacting zirconium oxide and silicic acid with the oxide or carbonate of the named element; or by thermally reacting zirconium oxide with the silicate of the named element. A suitable setting agent involving alumina is an aqueous mixture of clay and zirconium oxide, mixed molar ratio, milled after firing at 2100° F. for 3 hours, in which form it is suitable for use. The zirconates may be prepared by thermal decomposition of one or more of the following acids: phosphoric, nitric, or hydrochloric.

Of these acids we prefer to use HPO₄ because of the reactivity of its thermal products, its ease in use, and also its relatively low corrosive activity in comparison with the other acids. A HPO₄ content up to 10% may be used, but we prefer to use between 3% and 7%, since the lower the satisfactory HPO₄ content, the less is the danger of disintegration at high temperatures.

Of the double silicates, calcium zirconium silicate is the most refractory and may be used up to a content of 5% to 7% without serious decrease in refactoriness. The quantity of the other double silicates, particularly those of the first group, should not exceed 3% if high refactoriness is desired. Combinations of calcium zirconium silicate and the other silicates provide the refactoriness of the calcium compound plus the greater reactivity of the more alkaline materials.

While up to 7% Ca₂Zr₂SiO₇ may be used to advantage, we prefer to use 4% or less when used alone, and 3% or less when used in combination with HPO₄. When Ca₂Zr₂SiO₇ is used in combination with the other double silicates, a satisfactory refractory can be used at combinations of zirconium and calcium in parts of the other silicates (parts by weight). While up to 5% of such combinations may be used either with or without HPO₄, we prefer to use 3% or less when used alone, and 2% or less when used with HPO₄.

We also have found that percentages higher than 5% of Zn₂Zr₂SiO₉ and above 10% Na₂Zr₂SiO₇ when used with zircon refractories, cause cracking on setting. Since these materials present desirable properties from the standpoint of high green strength, it is desirable to use them. We also have found that mixtures of these two double silicates with calcium zirconium silicate produce to a large extent the high green strengths attainable with the use of the former, and without the cracking sometimes encountered.

In combination with HPO₄ no more than 1% to 3% of the above named oxides of the fourth group need be used, although up to 20% ZrO₂ or TiO₂ of zircon be used to advantage, 3% or less of ZrO₂ or TiO₂ causes undesired swelling.

Any of the standard organic binders may be used to produce green strength; however, we have found that a 5% gelatine solution is the best for general usage, particularly for zircon ware.

Refractory materials which can be bonded by means of the bonding agents of the present invention comprise a wide variety of materials. Amongst the most important of these is zircon. Others comprise silicon carbide, refractory aluminum oxide, mullite, sillimanite, chromite, olivine, forsterite, quartz or other forms of refractory silica, refractory clays, electrically fused zirconia, talc, feldspar, beryl, rutile, kaolin, spinel, kyanite, thorium oxide, thorite, ceria, antipathite, nutite, porcellain, quartz. These materials may be used in the form of sand, crushed granule, or as calcined quartzs.

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which has been previously and suitably heated above 1470° C. so as to form cristobalite. The refractory clays include the various types of non-plastic fireclays, the flint clays, the kaolins, etc.

These refractory materials may be used alone, or in combination with described bonding agents, a casting refractory for practically every known application may be advantageously made, with controlled working and setting times and also with practically any desired set of properties.

For example we have obtained for the dental industry, by continually varying a suitable mixture of zircon and quartz sands from pure zircon to pure quartz, permanent changes in dimensions varying all the way from 6.5% shrinkage to 3.5% expansion with any desired thermal expansion in the range of 25° to 33° C. normally required in dental refractories.

We have also found that the refractory combinations may be still further modified for special applications and for special properties by the addition of materials not properly considered refractory.

For example, the addition of a small amount of fluor spar produces high setting expansion and also contributes to a low temperature vitreous bond. Sodium-silico-fluoride promotes high setting shrinkage and also contributes to low temperature vitreous bond. Lead compounds produce very low temperature vitreous bonds and produce bodies having valuable electric insulating properties.

Barium compounds add valuable electrical resistivity and insulating properties. Various colored oxides may be added to produce desired body colors. Boron and magnesium compounds also contribute to the maintenance of high temperature electrical resistivity.

The use of silicon carbide as a base enables us to produce an extremely highly refractory body with a high heat and electrical conductivity and a good resistance to thermal shock. It can be used in reducing atmospheres. Combinations of silicon carbide and zircon in cement form are also suitable as refractory cast for electrical heating elements. Refractory ware comprising a mixture of zircon and silicon carbide containing the bonding agents of the present invention develops very high green and preliminary fire strength, and shows moduli of rupture between 1500 and 3000 pounds per square inch in the finished fired piece. Such ware also permits firing at much higher temperatures than 2800° F. without dissipation of strength characteristics of the bond. Finally, by use of these bonding agents in conjunction with HgPO₄, ware of Sic plus zircon of the most compressive, sprayed, or extruded, or dipped with the advantageous green strength developed at temperatures between 30° and 50° C.

Still further to decrease the weight of this high conductivity zircon-silicon carbide ware, we may replace part of the refractory grain mix with coke, which, on firing, burns out so as to produce light weight finished ware. Reductions in weight of over 50% may be obtained and still result in worthwhile ware.

To reduce weight, it is advisable to add not more than 20% by weight of coke.

Fused alumina base bodies produce steady and even thermal expansion from room temperature to 1500° C. totaling 1.2 per cent. Spinel, sillimanite, or kyanite bodies bonded by our improved methods have excellent electrical resistance at high temperatures. High kyanite additions produce rapid volume increases above 1100° C. Andalusite increases in volume in volts above 1200° C. Natural baddeleyite shows rapid expansion at 2900° F. Forsterite, sillimanite, and mullite produce high temperature bodies with extreme resistance to spalling as well as high hot load strengths, etc.

The possible combinations of desirable properties which can be obtained with our bonding agents and procedures may be expanded to cover practically every refractory application known in the casting field.

A description of the manner in which we practice our invention is as follows: The refractory grains suitable for the desired purpose are first prepared in a physical state so that the aggregate is amenable to good casting procedure. For example, a mixture of equal parts by weight of minus 35 mesh grain size and minus 300 mesh grain size normally will afford a smoothly flowing mix when incorporated in water. A refractory aggregate consisting entirely of minus 200 mesh material also produces good working properties resulting in a still finer grained product. Aggregates consisting wholly or in part of more than 35 mesh coarseness usually cause a granular mixture which interferes with good application.

To the properly sized refractory aggregate or mixture of various refractory aggregates is added about 6% by weight of phosphoric acid of specific gravity 1.71; while 6% is satisfactory for most purposes, the phosphoric acid may be reduced as low as 2% or increased as high as 9% for particular applications. The acid and refractory grains are completely mixed, and then passed through a 10 to 20 mesh screen to insure complete distribution of the acid throughout the refractory.

To 100 parts by weight of this damp mixture is added between 3 and 10 parts by weight of the bonding agent or proper mixtures of these bonding agents. While normally not more than 3 parts of the bonding agent used does produce proper casting cold strength, more than 10 parts may be used if necessary or desired for particular applications. The bonding agent is thoroughly mixed with the acid-refractory aggregate. To this mixture is then added sufficient water to produce an easily workable mixture. For a high density material consisting of zircon, the amount of water necessary will vary between 8 and 12 cc. per 100 grams of the mix. For a relatively low density material, such as quartz, clay, silicon carbide, etc., the amount of water necessary will vary between 10 and 15 cc. per 100 grams of the mix. Tap water may usually be used directly as the water addition. However, we have found that time of set is normal when water has a high pH of 7.5-8.5, due to dissolved lime compounds, and that the time of set is appreciably increased when the tap water is neutral or on the acid side. The pH of neutral or acid waters may be suitably built up by proper treatment with lime.

The refractory-acid aggregate, bonding agent and water are thoroughly mixed until a smooth free-flowing slip is obtained and the fluid is then cast into place. The casting is allowed to stand quietly until sufficiently hard for easy handling.
the mold demounted, and the piece dried and fired.

The speed and extent of the drying and firing operations depend on the size of the piece, the strength of the bond, the chemical and physical nature of the base refractory, and to some extent the final application of the piece. For example, a refractory clay should be dried and fired slowly due to the shrinkage on drying and also changes in crystal modification on the increase in temperature. A zircon casting may be dried and fired with extreme rapidity because it does not suffer from such defects. A mullite body is normally fired to 2400° to 2600° F. If its final application is high temperature service, a zircon body need be fired only to 1800° F, where its final application is resistance to low temperature fused phosphate corrosion, etc. To secure satisfactory hardness and strength in zircon ware containing H$_3$PO$_4$, it should be fired to 1800°-1800° F, where such ware which does not contain H$_3$PO$_4$ should be fired to at least 2400° F, to reach a satisfactory strength. The great advantage in the H$_3$PO$_4$ addition is that low temperature bonding is commercially inexpensive.

As to the amount and type of mixture of these bonding agents, several examples will clarify what is meant. For example, the thermal reaction product of zirconia, silicas, and limes will produce a set in about 1 hour and the casting can be handled in 1 to 2 hours more. An excellent high temperature bond results. The speed of setting may be increased by adding a small amount of the corresponding compound of soda, potash, or lime to the lime compound. These compounds also increase the strength of vitreous bond. Use of the zinc, barium, magnesium compounds produces the set in 30 minutes to an hour, and the casting can be handled in 1 1/2 hours. Here also, speed of setting may be further increased by the addition of the alkali products to any of these last three compounds. Normally about one part of alkali zirconium silicate may be added for every 2 to 3 parts of other corresponding compounds to produce the satisfactory set additions.

In general the thermal reaction products of zirconia and the oxides mentioned in respect to the bonding agents (forming zirconates) will produce a faster and harder set than an equal amount of the corresponding zirconia, silicas, and the oxide compound. For example, castings using magnesium zirconate can be made to set with extreme rapidity; an interval of 2 or 3 minutes need elapse after casting before the casting is quite hard, so that the piece can be removed from mold and easily handled in approximately 10 minutes after casting. Here again mixtures of zirconates and the double silicates as bonding agents show definite advantages. For example, magnesium zirconate alone remains relatively non-vitreous even on firing to quite high temperatures.

This property is a decided advantage in dental refractory applications for the refractory should be relatively weak even after exposure to high temperatures. Development of the vitreous bond at high temperatures enhances the strength and utility of the body for high temperature service which is accomplished by adding to magnesium zirconate small quantities of alkali or alkaline earth compounds of zirconia and silica. A vitreous bond is thereby developed at high temperatures which produces a strong tough hard body of excellent utility for high temperature application. For example, a practically heat shockproof body of zircon is made by bonding with a mixture of 2 parts by weight magnesium zirconate and 1 part by weight of sodium zirconium silicate or calcium zirconium silicate.

To form the light-weight, porous insulating refractories, the casting cement is prepared just as we have heretofore described except that just before casting, a definite volume of granular organic material, such as corn cob, coke, or wood, is added and well mixed in. The mixture is then cast, dried and fired; on firing the organic materials burn out leaving voids so as to produce a cellular refractory body of excellent utility for thermal and sound insulation and also of very low specific gravity.

In the foregoing description relative to the properties required in the dental industry, a working time of several minutes was found to be necessary. We have found magnesium zirconate in combination with H$_3$PO$_4$, to be a very satisfactory bonding agent in every respect, except one, for use in making dental refractories of practical utility. The chief drawback when used as we have described is the extremely rapid setting which does not allow time for sufficient workability.

We have found that this working time may be varied at will in a practical range simply by varying the ratio of the weight of magnesium zirconate to the weight of acid used. For example, 100 parts of a base refractory of zircon containing 5 parts by weight of phosphoric acid will set in 1 to 3 minutes after complete mixture when 10 parts of magnesium zirconate are used. Increasing the acid concentration to 15 parts by weight without varying the other constituents will increase the time of set by several hours. We have found that smaller quantities of other added acids are more efficient in this regard.

Such acids include the solid organic acids such as oxalic, tartaric, citric, etc., and the inorganic and organic strongly acid salts. Such inorganic and organic acid salts are sodium or potassium acid sulphate, sodium or potassium acid phosphates, ammonium acid sulphate, the acid fluorides of sodium, potassium or ammonia. The organic acid salts are the acid salts of sodium, potassium or ammonium with oxalic, tartaric, citric acids, etc., for example, sodium acid oxalate, etc. To a lesser extent, boric acid may be used.

From an industrial handling point of view, these acids may also be considered more efficacious than heavy concentrations of liquid phosphoric acid, due to the difficulties involved in handling sludges highly concentrated in a liquid corrosive acid. Furthermore, the organic acids are eliminated easily in the firing cycle, and can not complicate the possible utility of the finished body since no fixed residue remains. In the dental field, for example, a body containing 100 parts of zircon, 8 parts of H$_3$PO$_4$, 10 parts of magnesium zirconate, and 1 part of oxalic acid (all parts by weight) may be worked in fluid form for 5 to 7 minutes after mixing, and will then set hard in 15 to 20 minutes after mixing, thereby eliminating the main disadvantage of 70 magnesium zirconate for use in dental refractories. Magnesium zirconate also produces a setting expansion of 1/2% of 1%, which is a desirable quality in dental refractories.

While we have heretofore dealt chiefly with 75
casting procedures, we do not limit ourselves to this type of application alone. Simply by reducing the amount of added water the cements may be applied by ramming or pressing.

To illustrate more in detail the methods of practicing our invention we will set forth several examples.

**Example 1**

The charge is made up of the following ingredients, parts by weight:

- 35 mesh granular zircon: 50
- 200 mesh milled zircon: 44
- $\text{H}_3\text{PO}_4$ specific gravity 1.71: 6
- Oxalic acid: 1
- Magnesium zirconate: 10
- Water: 10

We mix the first four items thoroughly and then add the magnesium zirconate, mix, add water, mix and cast. A super-refractory is then formed for dental work of low expansion when fired to 2200°F. and permanent shrinkage when above 2500°F.

**Example 1—A**

The charge is made up of the following ingredients, parts by weight:

- 35 mesh granular zircon: 50
- 200 mesh milled zircon: 22
- $\text{H}_3\text{PO}_4$ specific gravity 1.71: 6
- Oxalic acid: 1
- Magnesium zirconate: 10.5
- Water: 11

We then mix as in Example 1 and cast. Omission of the oxalic acid produces a much more rapid set. A super-refractory is then formed for dental and other work of high thermal expansion when fired to 2800°F. and showing approximately 3.5% permanent expansion on firing to 2800°F.

**Example 1—B**

The charge is made up of the following ingredients, parts by weight:

- 35 mesh zircon sand: 50
- 200 mesh milled quartz: 44
- $\text{H}_3\text{PO}_4$ specific gravity 1.71: 6
- Oxalic acid: 1
- Magnesium zirconate: 10
- Water: 11

We mix same and cast as in Example 1 to produce a super-refractory for dental and other work. Omission of the oxalic acid greatly speeds the set. This refractory shows high expansion up to at least 2800°F., undergoing a permanent expansion of 3.5% on short firing to 2800°F.

**Example 1—C**

The charge is made up of the following ingredients, parts by weight:

- 35 mesh quartz sand: 50
- 200 mesh milled quartz: 44
- $\text{H}_3\text{PO}_4$ of specific gravity 1.71: 6
- Oxalic acid: 1
- Magnesium zirconate: 10
- Water: 12

We mix same and cast as in Example 1 to produce a super-refractory for dental and other work. Omission of the oxalic acid greatly speeds the set. This refractory shows very high expansion from 400°F. to at least 2800°F., undergoing a permanent expansion of 3.5% on short firing to 2800°F.

**Example 2**

The charge is made up of the following ingredients, parts by weight:

- 35 mesh granular quartz: 50
- 200 mesh milled quartz: 44
- $\text{H}_3\text{PO}_4$ specific gravity 1.71: 6
- Bonding agent (*): 10
- Water: 12

We mix and handle as in Example 1. The bonding agents (*) consist of (a) the thermal reaction products of zirconia, silica, and any oxide of the group CaO, MgO, BaO, SrO, ZnO, Al₂O₃; (b) a 2:1 mixture of any of (a) with the thermal reaction product of zirconia and silica with $\text{Li}_2\text{O}$, $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$; (c) the hydrates of titanias, zirconias, thorias or tin. We dry and fire on schedule to 1800°F. where a porous non-vitreous body is desired, as in the dental casting industry. A tighter, more vitreous body with better high temperature properties is obtained by schedule firing to 2400°F.

**Example 2—A**

The charge is made up of the following ingredients, parts by weight:

- 35 mesh granular quartz: 50
- 200 mesh milled quartz: 44
- $\text{H}_3\text{PO}_4$ specific gravity 1.71: 6
- Bonding agent (*): 5
- Water: 12

(*) Bonding agent consists of the thermal reaction product of zirconia, silica, and any oxide of $\text{Li}_2\text{O}$, $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$. We mix and handle as in Example 2 and then dry and fire as stated in Example 2.

**Example 2—B**

The charge is made up of the following ingredients, parts by weight:

- 35 mesh granular quartz: 50
- 200 mesh milled quartz: 44
- $\text{H}_3\text{PO}_4$ specific gravity 1.71: 6
- Bonding agent (*): 10
- Water: 12

(*) Bonding agent consists of (a) the thermal reaction product of zirconia and any oxide of the group $\text{Li}_2\text{O}$, $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$, $\text{CaO}$, $\text{MgO}$, $\text{BaO}$, $\text{SrO}$, $\text{ZnO}$, $\text{Al}_2\text{O}_3$; or (b) a 2:1 mixture of any of the above zirconates including magnesium zirconate with any of the thermal reaction products of silica, silica, and any oxide of the group $\text{Li}_2\text{O}$, $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$, $\text{MgO}$, $\text{CaO}$, $\text{BaO}$, $\text{SrO}$, $\text{ZnO}$, $\text{Al}_2\text{O}_3$. We mix and handle as in Example 2 and then dry and fire as stated in Example 2.

**Example 3**

The charge is made up of the following ingredients, parts by weight:

- Refractory aggregate (**): 35 mesh size: 50
- Milled refractory material (**): 200 mesh: 44
- $\text{H}_3\text{PO}_4$: 6
- Magnesium zirconate: 1
- Oxalic acid: 1
- Water: 8 to 15

(**) Includes either aluminum oxide, silicon carbide, rutile, fused silicon dioxide, mullite, sillimanite, quartz, olivine, forsterite, chrome, refractory clay, kaolin, bauxite, spinel, zircon, thorium oxide, thortveit, ceria, falerner, cordulite, talc, baddiepyrit, porcelain, coated or uncoated, aluminum mixed with each other or with silic. (***) A complete list is given in (*).

We mix as in Example 1 and then cast, dry, and fire to 1800°F. or to higher temperature predicated by the use. Where the body does not have to withstand temperatures above 2400°F., %
the firing is carried out by schedule firing to 1800°F. A tighter and more vitreous body with better high temperature properties is obtained by firing to at least 2400°F. Where the body contains more than 50% tacle, feldspar or porcelain, the upper firing limit need not exceed 2200°F. In general, where high temperature service or tight non-porous bodies are desired, the upper limit of firing temperatures is used. Otherwise the lower limit is used.

**Example 3—A**

The charge is made up of the following ingredients, parts by weight:

<table>
<thead>
<tr>
<th>Parts</th>
<th>Refractory aggregate —35 mesh (same as (*) in Example 3)</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Refractory milled —200 mesh (same as (**) in Example 3)</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>H₃PO₄</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Bonding agent (see list in Example 2)</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>8  to 15</td>
</tr>
</tbody>
</table>

We mix and handle as in Example 1 and dry and fire as in Example 3.

**Example 3—B**

The charge is made up of the following ingredients, parts by weight:

<table>
<thead>
<tr>
<th>Parts</th>
<th>Refractory aggregate —35 mesh (same as (*) in Example 3)</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Refractory milled —200 mesh (same as (**) in Example 3)</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>H₃PO₄ specific gravity 1.71</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Bonding agent (see * Example 2—A)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>8  to 12</td>
</tr>
</tbody>
</table>

We mix and handle as in Example 1 and dry and fire as in Example 3.

**Example 3—C**

The charge is made up of the following ingredients, parts by weight:

<table>
<thead>
<tr>
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<th>Refractory aggregate —35 mesh (same as (*) in Example 3)</th>
<th>50</th>
</tr>
</thead>
<tbody>
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<td>44</td>
</tr>
<tr>
<td></td>
<td>H₃PO₄ specific gravity 1.71</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Bonding agent (see *) Example 2—B</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>8  to 12</td>
</tr>
</tbody>
</table>

We mix and handle as in Example 1 and dry and fire as in Example 3.

**Example 3—D**

The charge is made up of the following ingredients, parts by weight:

<table>
<thead>
<tr>
<th>Parts</th>
<th>Refractory aggregate —200 mesh (see Examples 1, 1—A, 1—B, 1—C and 3)</th>
<th>94</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₃PO₄ specific gravity 1.71</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Bonding agent (see Examples 1, 2, 2—A, 2—B)</td>
<td>5  to 10</td>
</tr>
<tr>
<td></td>
<td>Oxalic acid (may omit if desired)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>12  to 20</td>
</tr>
</tbody>
</table>

We mix and cast in all these Examples 3 as in Example 1 and then dry and fire as in Example 3. Much finer grained castings will result than in the previous examples.

**Example 4**

The charge is made up of the following ingredients, parts by weight:

<table>
<thead>
<tr>
<th>Parts</th>
<th>Refractory aggregate —35 mesh (see Example 1, 1—A, 1—B, 1—C and 3)</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Refractory milled —200 mesh (see Example 1, 1—A, 1—B, 1—C and 3)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>H₃PO₄ specific gravity 1.71</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Bonding agent (see Example 1, 2, 2—A, 2—B)</td>
<td>5  to 10</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>15  to 20</td>
</tr>
<tr>
<td></td>
<td>Oxalic acid (may omit if desired)</td>
<td>100</td>
</tr>
</tbody>
</table>

We mix all the ingredients except the cork as before, and then add cork and cast. We then dry and fire as in Example 3.

**Example 4—A**

The charge is made up of the following ingredients, parts by weight:

<table>
<thead>
<tr>
<th>Parts</th>
<th>Refractory milled —200 mesh (see Example 1, 1—A, 1—B, 1—C, 3)</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phosphoric acid specific gravity 1.71</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Bonding agent (see Examples 1, 2, 2—A, 2—B)</td>
<td>5  to 10</td>
</tr>
<tr>
<td></td>
<td>Oxalic acid (may omit if desired)</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>1</td>
</tr>
</tbody>
</table>

We mix all the ingredients except the cork as before, and then add cork and cast. We then dry and fire as in Example 3.

**Example 5**

The following charge is made by intimate mixing, parts by weight:

<table>
<thead>
<tr>
<th>Parts</th>
<th>60 mesh zircon sand</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200 mesh milled zircon</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Milled calcium zircon silicate (or BaZr₂SiO₇, Mg₂Zr₂SiO₇, SrZr₂SiO₇, ZnZr₂SiO₇, or mixtures of these)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Phosphoric acid</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>5</td>
</tr>
</tbody>
</table>

The thick slurry is then poured into suitable molds and entrapped air is removed by unusual vibratory methods. At room temperatures, the final set is obtained in about one hour, and the mold may then be stripped. The shape is then dried and fired to about 1000°C in accordance with approved refractory procedures. The final ware does not soften at 3000°F.

The above mix is made suitable for dipping, brushing or spraying by the addition of 2 or more parts of water.

Although this example specifies 5 parts of milled setting agents, up to 20 parts of setting agent may be used in every case, except when ZnZr₂SiO₇ is used. Any increase of the amount of setting agent increases the green strength after the set, decreases time of set and hardness of finished ware. As low as 2 parts of the setting agent can be used where prolonged time of set, relatively low green strength, etc., are desired. Smaller amounts of setting agent, are not important for the finished article. In the case of ZnZr₂SiO₇, no more than 5 parts should be used, since larger quantities cause splitting of thick sections on setting.
Example 5—A

The mix comprises the following:

| Parts | 60 mesh zircon sand | 50 | 200 mesh milled zircon | 47 | Sodium zirconium silicate (or lithium zirconium silicate or potassium zirconium silicate or mixtures of these) | 3 | Phosphoric acid | 4 | Water | 7 |

The mix is treated in the same manner as in Example 5.

The addition of two or more parts of water makes the mix amenable to spraying, dipping, or brushing. Set is obtained in about one hour. The finished refractory does not soften at 2800°F.

Although this Example 5—A specifies 3 parts of milled setting agent, up to 10 parts can be used, resulting in a pronounced decrease in time of set and decrease in refractory properties. The use of more than 5 parts of the setting agent causes the piece to split on setting, particularly in thick sections.

Example 5—B

The mix comprises the following:

| Parts | 60 mesh zircon sand | 50 | 200 mesh milled zircon | 45 | Fired equi-molecular mixture of clay and zirconium dioxide (or parts zirconium spinel) | 5 | Phosphoric acid | 5 | Water | 6 |

This mix is treated in the same manner as in Example 5; the time of set is 1 hour, and the finished article is stable at 3000°F. The addition of 2 or more parts water makes the mix amenable to dipping, spraying, or brushing.

Although 5 parts of setting agent are specified, up to 20 parts can be used. Any increase in the amount of the setting agent decreases the time of set with no marked decrease in refractory properties.

Example 5—C

The mix comprises the following:

| Parts | 60 mesh zircon sand | 50 | 200 mesh milled zircon | 45 | Powdered zirconium dioxide (or TiO₂, SnO₂, or ThO₂ or mixtures) | 5 | Phosphoric acid | 5 | Water | 6 |

This mix is treated in the same manner as in Example 5; the time of set is 1½ hours, and the finished article is stable at 3000°F. The addition of 2 parts of water makes the mix amenable to dipping, spraying, or brushing.

Any increase in the amount of the setting agent decreases the time of set with no marked decrease in refractory qualities. Any increase of ZrO₂ and ThO₂ increases the refractoriness of the ware.

Example 5—D

The mix comprises the following:

| Parts | 60 mesh zircon | 70 | 200 mesh milled zircon | 45 | Calcium zirconium silicate | 8 | Sodium zirconium silicate | 2 | Phosphoric acid | 5 | Water | 7 |

The mix is treated in the same manner as in Example 5; the time of set is 30 minutes, and the finished article is stable at 3000°F. The addition of 2 or more parts of water makes the mix amenable to dipping, spraying, or brushing.

Example 5—E

The mix comprises the following:

| Parts | 60 mesh zircon | 50 | 200 mesh milled zircon | 45 | Calcium zirconium silicate | 7 | Zinc zirconium silicate | 3 | Phosphoric acid | 5 | Water | 7 |

The mix is treated in the same manner as in Example 5; the time of set is 30 minutes, and the finished article is stable at 3000°F. The addition of 2 or more parts of water makes the mix amenable to dipping, spraying, or brushing.

In Examples 5, 5—A, 5—B, 5—C, 5—D and 5—E, the mix may be used as a ramming mixture by adding about 40% of the water specified for a casting mix so as to form a mealy, partially dry mixture. The zirconium silicate as well as the double zirconium silicates referred to in these examples are definitely based on pure zirconium silicate of the following composition:

<table>
<thead>
<tr>
<th>Percent</th>
<th>Zirconium silicate (ZrSiO₄)</th>
<th>97</th>
<th>to 100</th>
<th>50</th>
<th>TiO₂</th>
<th>0</th>
<th>to 0.20</th>
<th>20</th>
<th>Fe₂O₃</th>
<th>0</th>
<th>to 0.05</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na₂O</td>
<td>0</td>
<td>to 0.04</td>
<td>20</td>
<td>Rare earths, Ce, La, etc</td>
<td>0</td>
<td>to 0.20</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Free quartz</td>
<td>0.10</td>
<td>to 2.00</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The zircon composition which we prefer to use in this process and for use in making the double silicates specified herein has approximately the following composition:

<table>
<thead>
<tr>
<th>Percent</th>
<th>ZrSiO₄</th>
<th>59.70</th>
<th>60</th>
<th>TiO₂</th>
<th>0.30</th>
<th>60</th>
<th>Fe₂O₃</th>
<th>0.010</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na₂O</td>
<td>0.03</td>
<td>60</td>
<td>Al₂O₃</td>
<td>0.20</td>
<td>60</td>
<td>CeO₂</td>
<td>0.030</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>ZrO₂</td>
<td>0.005</td>
<td>60</td>
<td>PbO</td>
<td>0.005</td>
<td>60</td>
<td>CaO</td>
<td>0.002</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>MgO</td>
<td>0.001</td>
<td>60</td>
<td>CuO</td>
<td>0.001</td>
<td>60</td>
<td>SnO₂</td>
<td>0.002</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Re₂O₃</td>
<td>0.001</td>
<td>60</td>
<td>with practically no trace of free quartz</td>
<td>60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Example 6

The following charge is made by intimately mixing the following ingredients:

<table>
<thead>
<tr>
<th>grams</th>
<th>1333.3</th>
<th>60</th>
<th>666.7</th>
<th>50.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 mesh pure zircon sand</td>
<td>200 mesh pure zircon sand</td>
<td>35 mesh silicon carbide</td>
<td>Phosphoric acid of specific gravity 1.71</td>
<td></td>
</tr>
<tr>
<td>cc</td>
<td>73.0</td>
<td>50.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Either sodium zirconium silicate powder, or potassium zirconium silicate powder, or lithium zirconium silicate powder, or barium zirconium silicate powder, or magnesium zirconium silicate powder, or zircsil powder, or strontium zirconium silicate powder</td>
<td>70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>grams</td>
<td>100</td>
<td>78</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Or 8 parts of calcium zirconium silicate powder plus 2 parts of sodium zirconium silicate powder; or 2 parts of potassium zirconium silicate powder; or 2 parts of lithium zirconium silicate powder; or 2 parts of barium zirconium silicate powder; or 2 parts of potassium barium zirconium silicate powder; or 2 parts of potassium zirconium silicate powder; or 2 parts of sodium zirconium silicate powder; or 2 parts of strontium zirconium silicate powder.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Grams</th>
<th>cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mesh zircon</td>
<td>835</td>
<td></td>
</tr>
<tr>
<td>200 mesh zircon</td>
<td>415</td>
<td></td>
</tr>
<tr>
<td>35 mesh silicon carbide</td>
<td>1250</td>
<td></td>
</tr>
</tbody>
</table>

The gelatine solution in this latter case is increased to 150 cc.

Where a close-grained, tight, low porosity body is desired, the mix is fabricated entirely of -200 mesh zircon and -200 mesh silicon carbide. For such a mix patterned after Example 6, we increase the amount of phosphoric acid to 125 cc and the amount of gelatine solution to 160 cc. When equal weight mixtures of zircon and silicon carbide are used in the -200 mesh state, we increase the amount of phosphoric acid to 125 cc and the amount of gelatine solution to 190 cc.

The above ingredients are completely mixed, screened, pressed into the proper shape, which is then dried and fired in accordance with standard refractory procedures to 1300°F. Example 6—A

For casting, dipping or spraying, the mix comprises:

- 35 mesh pure zircon sand—grams—1333.3
- 200 mesh pure zircon sand—grams—666.7
- 35 mesh silicon carbide—grams—500.0

Phosphoric acid of specific gravity 1.71—cc—73.0

5% gelatine solution plus—do—125.0

Either sodium zirconium silicate powder; or potassium zirconium silicate powder; or lithium zirconium silicate powder; or magnesium zirconium silicate powder; or barium zirconium silicate powder; or strontium zirconium silicate powder; or calcium zirconium silicate powder.

Or calcium zirconium silicate powder—grams—200

Or 8 parts of calcium zirconium silicate powder plus 2 parts of sodium zirconium silicate powder; or 2 parts of potassium zirconium silicate powder; or 2 parts of lithium zirconium silicate powder; or 2 parts of magnesium zirconium silicate powder; or 2 parts of potassium barium zirconium silicate powder; or 2 parts of strontium zirconium silicate powder; or 2 parts of zircon zirconium silicate powder—grams—200

Or TiO₂ or SnO₂—grams—100

Or ZrO₂ or ThO₂—grams—125

Where a close-grained, tight, low porosity body is desired, the mix is fabricated entirely of -200 mesh zircon and -200 mesh silicon carbide. For such a mix patterned after Example 6—A, we increase the amount of gelatine solution to 200 cc, of phosphoric acid to 125 cc.

The above ingredients are completely mixed into a thick slurry, cast or sprayed into place, allowed to set at room temperature and are then dried and fired to 1800°F. In accordance with standard refractory procedures.

Example 6—B

The mix comprises the following ingredients:

- 35 mesh zircon sand—grams—1066.6
- 200 mesh zircon sand—grams—533.4
- 35 mesh silicon carbide—grams—400.0
- 10 20 mesh petroleum coke—grams—500.0
- Phosphoric acid of 1.71 sp. gr.—cc—85.0

5% gelatine solution—cc—140.0

Plus

Either sodium zirconium silicate powder; or potassium zirconium silicate powder; or lithium zirconium silicate powder; or magnesium zirconium silicate powder; or strontium zirconium silicate powder; or barium zirconium silicate powder; or zircon zirconium silicate powder—grams—50

Or calcium zirconium silicate powder—grams—100

Or 8 parts of calcium zirconium silicate plus either, 2 parts of sodium zirconium silicate; or 2 parts of potassium zirconium silicate; 2 parts of lithium zirconium silicate; 2 parts of magnesium zirconium silicate; 2 parts of strontium zirconium silicate; 2 parts of barium zirconium silicate; 2 parts of zircon zirconium silicate—grams—125

Or TiO₂ or SnO₂—grams—100

Or ZrO₂ or ThO₂—grams—100

Up to 400 grams of ZrO₂ or ThO₂ may be used to advantage by adding 5 cc. of gelatine solution for each 200 gram addition above 100 grams.

All the above ingredients, except the coke, are intimately mixed, and the coke is folded in last. The ware is pressed, dried and fired in accordance with usual refractory procedures up to 1800°F. It produces a body weighing 50% less per unit volume than that derived in Example 6.

Example 6—C

The mix comprises the following ingredients:

- 35 mesh zircon sand—grams—1333.3
- 200 mesh zircon milled—grams—666.7
- 35 mesh silicon carbide—grams—500.0

5% gelatine solution—cc—125.0

Plus

Either sodium zirconium silicate powder; or potassium zirconium silicate powder; or lithium zirconium silicate powder; or magnesium zirconium silicate powder; or zircon zirconium silicate powder; or strontium zirconium silicate powder; or barium zirconium silicate powder—grams—75.0

Or calcium zirconium silicate powder—grams—125.0

Or a mixture of 8 parts of calcium zirconium silicate powder plus 2 parts of sodium zirconium silicate powder; or potassium zirconium silicate powder; or lithium zirconium silicate powder; or magnesium zirconium silicate powder; or zircon zirconium silicate powder; or strontium zirconium silicate powder; or barium zirconium silicate powder—grams—100.0

Or TiO₂ or SnO₂—grams—50

Or ZrO₂ or ThO₂—grams—125.0

Or ZrO₂ or ThO₂—grams—125
Where a close-grained, tight, low porosity body is desired, the mix is fabricated entirely of —200 mesh zircon and —200 mesh silicon carbide. For a mix with a mix patterned after Example 6—C, we increase the amount of gelatine used to 280 cc.

When the whole charge is mixed we press same into shape, dry, and fire according to standard refractory procedures up to 2400°F.

From the standpoint of utility and in further explanation of the above examples we present the following advantages: Ionic alone as added to other bodies adds a good measure of refractoriness, increases resistance to acid fluxes, adds hot strength at high temperatures, and enables a choice of any expansion value practically desired in the dental range particularly.

Zircon alone or added to other bodies produces super-refractoriness, increases resistance to acid fluxes, produces very dense bodies of high thermal shock resistance. It affords very low thermal expansion and low heat conductivity. Zircon refractories are also highly useful in applications involving pronounced resistance to corrosion by alkali phosphate fused bathes. The corrosive nature of this type of fusion is such as to rapidly disintegrate the usual refractory bricks, such as fireclay, mullite, fused quartz, fused alumina, silicon carbide, magnesite, chromite, etc. Our zircon refractories have been found to withstand the action of such melts for 100 times better than any other commercially known refractory of this type.

Of the other refractories, silicon carbide increases thermal resistance in reducing atmospheres, adds heat and electrical conductivity, reduces density, is super-refractory and shows excellent high temperature properties. Aluminum oxides afford steady and definite thermal expansions through a wide range of temperatures, adds poor thermal shock characteristics, adds resistance to basic fluxes and is super-refractory. The mullites, sillimanites, andalusite, kyanite, olivine, forsterite, etc. are super-refractories with excellent high temperature properties. Eutectics, show excellent resistance to glasses and glassy slags. Chromite is super-refractory, neutral to slags, has poor thermal shock resistance. Beryl, talc, spinel, and rutil, certain porcelains have excellent electrical properties. Poor super-refractory qualities with the exception of spinel. The magnesia minerals in general show good temperature characteristics of electrical resistivity. The feldspars, clays, and kaolin are well known with respect to properties and afford cheap sources of refractoriness. Thorite, thoris, and ceria are super-refractories and possess good electrical properties. Zirconium dioxide is a neutral material, with a very high melting point.

By means of the above materials alone or in mixture each develops its particular set of properties to the extent that it is present, and results in a collection of compositions which permits practically every known refractory application. For example, combinations of zircon with rutile or rutile alone, with magnesia containing materials, and bonded by the barium compounds, suitably shaped and fired produce an excellent set of electrical properties. Combinations of zircon and carborundum produce a body which is once heat resistant and heat conducting. In other words each material develops the properties for which it is known when used alone or in combination with others by the use of the bonds we have heretofore described. This statement is true only when the bodies are fired or used considerably below the vitrification or combination point of any particular refractory combination. Above this temperature the refractory is modified by the possible formation of eutectics. For example, mixtures of zircon and aluminum silicates soften and melt rapidly at approximately 3000°F, because of the formation of relatively low melting point eutectics. In the appended claims, the term "finely-divided refractory materials" includes not only the materials of suitable grain size but not more than 25 mesh coarseness but also the finely-divided materials of minus 200 mesh grain size as well as mixtures thereof as set forth in the various examples.

We claim as our invention:

1. A composition suitable for forming refractory masses comprising a major proportion of a refractory material and a minor proportion of a preformed zirconate of a metal taken from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, and strontium

2. A composition suitable for forming refractory masses comprising a major proportion of a refractory material, a minor proportion of a preformed zirconate of a metal taken from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, and strontium, and a minor proportion of an acid taken from the group consisting of HPO₄, HCl, H₂SO₄ and HNO₃.

3. A composition suitable for forming refractory masses comprising a major proportion of a refractory material, a minor proportion of a preformed zirconate of a metal taken from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, and strontium, and a minor proportion of a metal salt of a metal taken from the group consisting of H₂PO₄, HCl, H₂SO₄ and HNO₃.

4. A composition suitable for forming refractory masses comprising a major proportion of a refractory material, a minor proportion of a preformed magnesium zirconate, and a minor proportion of an acid taken from the group consisting of H₂PO₄, HCl, H₂SO₄ and HNO₃.

5. A composition suitable for forming refractory masses comprising a major proportion of a refractory material, an organic acid, a minor proportion of a preformed magnesium zirconate, and a minor proportion of an acid taken from the group consisting of H₂PO₄, HCl, H₂SO₄ and HNO₃.

6. A composition suitable for forming refractory masses comprising a major proportion of a refractory material, an organic acid salt, a minor proportion of a preformed magnesium zirconate, and a minor proportion of an acid taken from the group consisting of H₂PO₄, HCl, H₂SO₄ and HNO₃.

7. A composition suitable for forming refractory masses comprising a major proportion of a refractory material, an inorganic acid, a minor proportion of a preformed magnesium zirconate, and a minor proportion of an acid taken from the group consisting of H₂PO₄, HCl, H₂SO₄ and HNO₃.

8. A method of making refractory materials which comprises mixing a major proportion of a refractory material with a minor proportion of a preformed zirconate of a metal taken from the group consisting of lithium.
dium, potassium, magnesium, calcium, barium, and strontium, drying the mixture, and firing at an elevated temperature.

9. The method of making refractory materials which comprises mixing a major proportion of a refractory material with a minor proportion of a preformed zirconate of a metal taken from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, and strontium, and a minor proportion of an acid taken from the group consisting of H$_3$PO$_4$, HCl, H$_2$SO$_4$, and HNO$_3$, drying the mixture, and firing at an elevated temperature.

10. The method of making refractory materials which comprises mixing a major proportion of a refractory material with a minor proportion of a preformed magnesium zirconate and a minor proportion of phosphoric acid, shaping the mass, drying, and firing at an elevated temperature.

CHARLES J. KINZIE. EUGENE WAINER.
CERTIFICATE OF CORRECTION.

CHARLES J. KINZIE, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 12, for "detrscribed" read --described--; page 6, second column, line 52, for the word "unusual" read --usual--; page 9, second column, line 29, claim 2, for "strontium" read --strontium--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of December, A. D. 1940.

Henry Van Arsdale,
Acting Commissioner of Patents.