July 27, 1943. H. M. SCHLEICHER ET AL 2,325,553

REFRACTORY AND METHOD OF PRODUCING THE SAME

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Fig. 1.

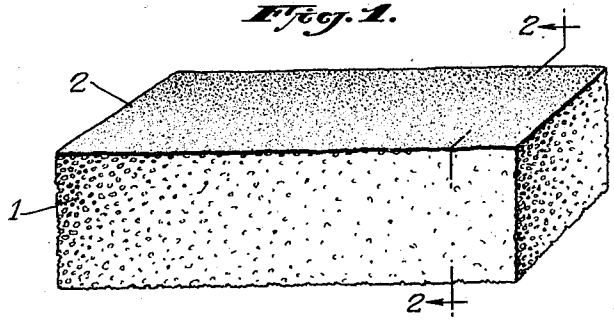



Fig. 2.

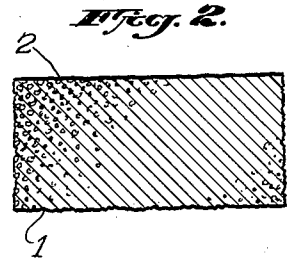



Fig. 3.

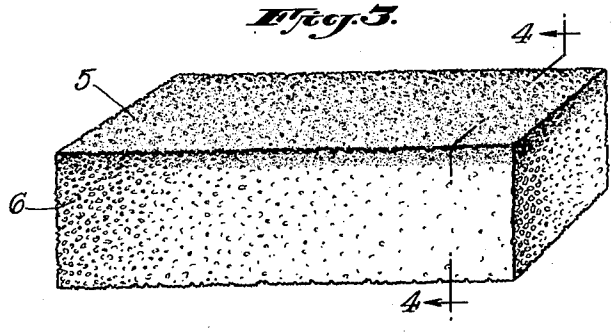



Fig. 4.

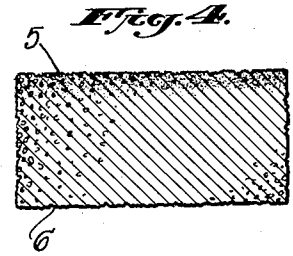



Fig. 5.

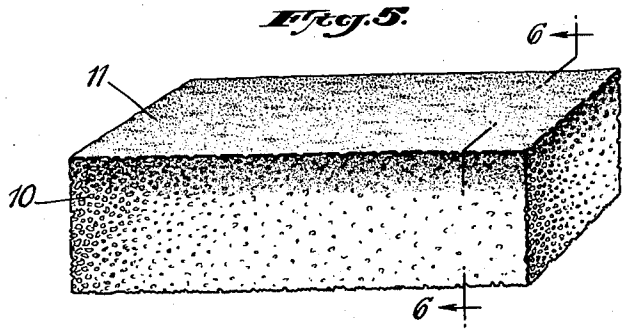



Fig. 6.

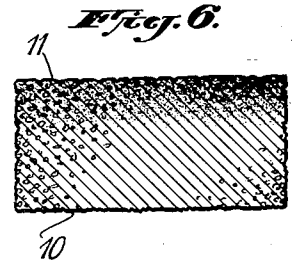



Fig. 7.

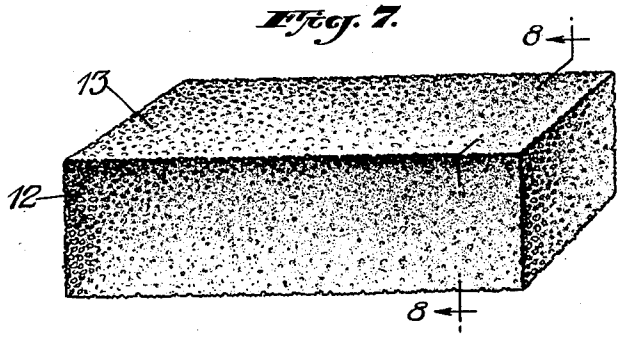
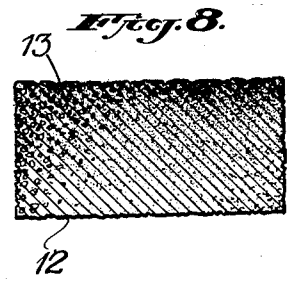



Fig. 8.

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REFRACTORY AND METHOD OF PRODUCING THE SAME

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Fig. 9. Fig. 10. Fig. 11. Fig. 12.

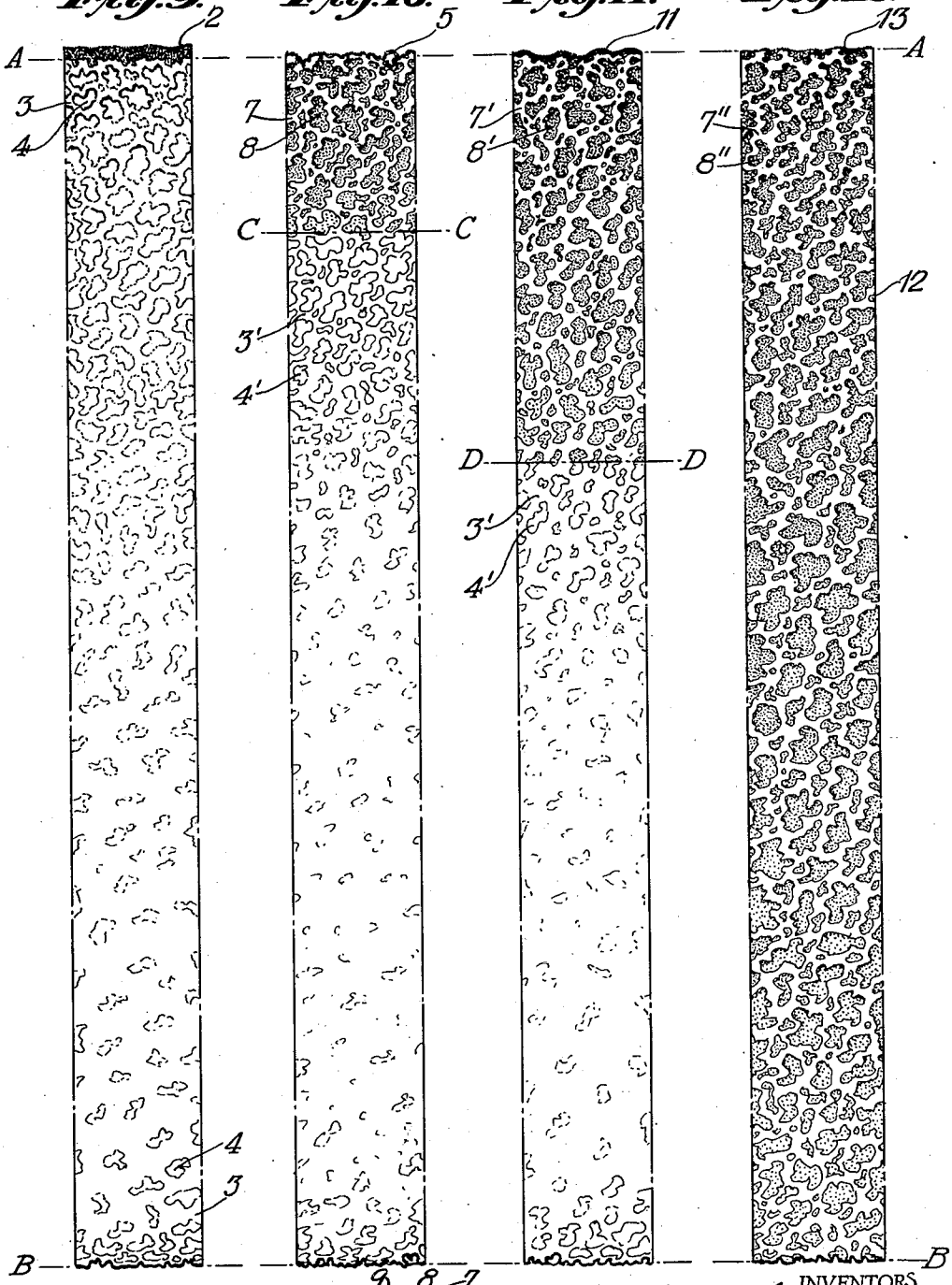
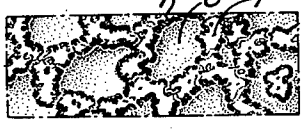



Fig. 13.

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Patented July 27, 1943 2,325,553

# UNITED STATES PATENT OFFICE

2,325,553

## REFRACTORY AND METHOD OF PRODUCING THE SAME

Henry M. Schleicher, Elizabeth, and William E. Iverson, Woodbridge, N. J., assignors, of one-half to Scovill Manufacturing Company, Waterbury, Conn., a corporation of Connecticut, and one-half to United States Metal Refining Company, Carteret, N. J., a corporation of New Jersey

Application April 14, 1941, Serial No. 388,438

16 Claims. (Cl. 117—54)

This invention relates to refractories and method of producing the same. More particularly the invention relates to ceramic bodies (such as porous insulating bricks or the like) having a highly resistant refractory portion or zone and to the method of producing the same. The invention has proven to be particularly useful in providing a porous insulating brick or the like ceramic body with an application of bonded zircon or the like refractory integral therewith.

It is well known that in structures subjected to high temperatures, such for example as furnaces, furnace flues, ovens, kilns, retort settings, hearths, crucibles, etc., a heat insulating structure is desirable to reduce heat losses, and due to the relative weakness of such insulating or body structures it has been necessary to provide a protective interior lining or layer of greater resistance to deterioration brought about by heat, abrasion, strain and the action of gases or other chemical compounds to which they are exposed in use. For example, it is customary to use an inner layer of highly refractory material and an outer layer of insulating brick or the like material, and it has been proposed to use a composite brick made of two parts, one a backing of insulating material (such as diatomaceous earth brick) and the other an interior lining of highly refractory material (such as carborundum, zircon or zircon and zirconia refractory) and in the case of the zirconium refractories these being in the form of blocks cemented on the insulating backing by a suitable bonding material. These and other expedients are practised but often involve the use of more material than desirable. Furthermore insulating bricks are rated according to the temperature they can withstand and those of higher insulating power have the lower temperature rating. By producing a zone of higher temperature resisting qualities at and within the exposed surface of the better insulating bricks they can be used at higher temperatures, thus enlarging the scope of their use, and in addition in many cases the use of a layer of more resistant bricks in front of the insulating bricks is thus rendered unnecessary.

According to this invention we have devised an entirely satisfactory product providing an insulating body, or a body of relatively low cost, having a highly refractory face or zone of desired thickness, and the method of producing the same. The word refractory as herein used is intended in its broader sense as meaning a substance resistant to heat, abrasion, strain and the action of gases or other chemical compounds to which it is intended to be exposed in use.

We have discovered that an ordinary porous insulating brick or the like body may be provided with a refractory portion or zone comprising a substance of substantially different relative coefficient of expansion, and according to our invention it is possible to economically and readily produce refractory faced porous insulating brick or the like ceramics. For example, we have discovered that an ordinary porous insulating brick of relatively low cost or the like body having a porous surface zone, may be so treated with a refractory substance as to provide a highly refractory zone in said brick or the like body and also to materially strengthen said body, by the use of a small amount of relatively more costly refractory material.

Due to its superior refractory properties, its whiteness, and ease of application in accordance with this invention, zircon is a very suitable material to be used to produce a reflective surface in the manner to be described. We believe the use of such a reflective surface is highly desirable where "Globars" are used as the heating medium. However, it is to be understood that reflectiveness is only one of the results achieved by the invention according to which the other properties of refractories hereinabove mentioned may be provided wherein the reflectiveness may be minor or practically negligible.

The invention also lends itself to the treatment of the interior cellular structure of a porous brick or the like body; whereby interior cells of such body may be lined with a bonded zirconium refractory. Thus it is possible according to our invention to provide a cellular structure of bonded zirconium substance possessing substantial insulating properties and relatively great strength.

An object of this invention is to provide a method of producing a highly refractory surface zone in a less refractory porous ceramic body, and the resulting product.

Another object is to provide an insulating porous brick or the like body having a surface zone penetrated with a highly refractory material secured to said body so as to present a face resistant to relatively high temperatures, abrasion, strain and other disintegrating actions, and the process of producing the same.

Another object of the invention is to provide a relatively soft porous ceramic body with a substantially hard surface zone highly resistant to abrasion and heat, and a method of producing the same.

Another object is to provide a relatively strong zircon refractory cellular structure possessing substantial insulating properties, and of a method of producing the same.

The invention consists in the novel features, arrangement and construction provided by way of example in the products hereinafter described and in the methods hereinafter described for producing said products, as illustrating representative preferred forms of the invention, and the invention will be more particularly pointed out in the appended claims.

Further objects, features and advantages of the invention will more fully appear from the following description taken in conjunction with the accompanying drawings, in which—

Figs. 1, 3, 5 and 7 are perspective views of bricks (all except Figs. 1 and 2 showing bricks produced in accordance with the invention illustrative of various embodiments of the invention) showing the comparative surface and interior conditions of said bricks;

Figs. 2, 4, 6 and 8 are cross-sectional views respectively of the articles illustrated in Figs. 1, 3, 5 and 7;

Figs. 9, 10, 11 and 12 are partly diagrammatic enlarged vertical sectional views respectively of said bricks, further illustrating the relative structural characteristics of the said bricks, and

Fig. 13 is a partly diagrammatic, greatly enlarged, segmental view showing the interior cellular arrangement of the refractory material in Figs. 3–8 and 10–12, both inclusive.

We have discovered that an ordinary porous brick or like substances may be impregnated with a bonded zirconium refractory, by first subjecting the brick to a treatment of phosphoric acid, and then applying a mixture of a zirconium compound (such as zircon) and phosphoric acid of a paint-like consistency to the surface to be treated, and causing a surface zone of the brick to be permeated thereby, and then heating the body thus treated to the desired temperature to effect the bonding of said zircon particles. Substantial depths of the treated zone may be affected, even to the entire thickness of certain commercial bricks. Similarly, a surface composed of bricks or pieces of bricks may be so treated. It will be understood that the body to be treated must be of a porous or absorptive nature and must possess interstices such as provided by a cellular structure or a like arrangement providing spaces within the body through which the zircon mix may pass. Thus it will be understood that other porous bodies which are provided with a cellular or like structure (providing interconnected interstices) and which bodies maintain such body characteristics to a sufficient degree under bonding temperature to permit the zircon mix to become bonded, may likewise be treated in accordance with this invention. If the size of the interstices or channels in the body are such that the particles of the refractory "paint" cannot be made to penetrate sufficiently, the zone cannot be produced; hence the degree of penetration for a given treatment is dependent upon the interstices within the body as well as the absorptive properties of the body material. From this it will be understood that the present invention is not directed primarily to a relatively thick layer disposed entirely on the exterior face of a body and attached thereto; but is primarily directed to an impregnation of said body wherein the impregnating material may also be disposed on the outer face of the body in varying degrees, but preferably limited to a relatively thin external coating. In fact one of the salient features of the invention is that the external coating may be kept at a minimum; and this is considered beneficial in view of the difference in the coefficient of expansion between the refractory substances and the body, and likewise for the sake of economy in view of the relatively great cost of the refractory material. For many commercial uses the depth of impregnation of the zircon below the body surface may be from 1/64" to 1/4".

The depth of penetration, the coating of the surface and the hardness and strength of the conditioned surface are all a function of the acid-water ratio in both the preconditioning liquid and the mixes subsequently applied. If the zircon paint be applied for example to a dry brick, a superficial crust is formed which is readily perforated. If the brick be preconditioned with water intermediate results are obtained; whereas if the brick be preconditioned with phosphoric acid in concentrated form there results a facing of maximum hardness and strength, whether the zircon is all within the interstices of the brick or partly as a coating on the outside. The preconditioning of the brick is essential and in the preferred embodiment of the invention should be done with phosphoric acid in concentrated condition (such as 85% orthophosphoric acid); the acid being applied only to the surface of the brick to be treated and, of course, the brick being penetrated thereby to the desired depth. The greater the acid-water ratio of both the preconditioning liquid and the mix the deeper is the zone and the stronger and harder the surface of the treated article, but correspondingly less is the amount of zircon remaining at the outer surface. For example, with a brick which has been preconditioned with concentrated acid, the depth of the zone may be further controlled by the ratio of acid to water in the zircon mixes. Even in shallow zones, such as would result from using a zircon mix having a low acid content, the treated portion would be strong and hard. Thus a mix with acid predominating is preferably used to obtain the depth of zone desired. In this case the surface texture of the brick is not obscured. If, in addition, a smooth white surface is wanted, then a mix with the predominance of water is finally applied. For purposes of illustration, and so that comparison may be made between the various examples to be given, cellular clay porous insulator bricks commercially available will be the bodies used in the following examples. In the case of facing porous insulator bricks, the amount of concentrated acid used for preconditioning may be of the order of from 7 to 13 ounces per square foot of surface—depending upon the depth of penetration desired. This preconditioning of the brick has a two-fold purpose. First, it fills the pores of the material of which the brick is composed, thus preventing the absorption of phosphoric acid from the refractory mix of paint-like consistency and therefore prevents the lessening of the bonding effect of the phosphoric acid constituent of the mix (which is a very important feature) and it also supplies to the mix additional available phosphoric acid to enhance the bonding of the zircon; and secondly, by sealing the pores of the material constituent of the body with the relatively high viscosity acid the absorbing action is greatly diminished, or prevented entirely, and the applied mix retains its consistency which enables it to

flow down the channels or interconnected cellular spaces or interstices to a greater extent than would be possible if the zircon mix were thickened, due to absorption therefrom of its liquid constituent, with the resultant clogging of the channels or interstices. For example, if water alone were used, as the pre-treating fluid, an action corresponding to that of slip-casting ensues when the mix is applied, and channels adjacent to the surface are quickly filled with compacted zircon.

Accordingly in the preferred form of the invention 85% orthophosphoric acid is applied to the face of the brick to be treated in sufficient quantity to cause a penetration to the depth desired.

With respect to the character of the mixes: A suitable formula for a moderate depth of treatment zone would be as follows:

| | Parts by weight |
|---|---|
| Milled zircon | 53 |
| Orthophosphoric acid (U. S. syrupy, 85%) | 29.5 |
| Water | 17.5 |

This mix will have a density of about 2.16. Our tests show that for such mixes in which acid predominates (hereinafter termed "acid mix") no digestion and no aluminum hydroxide are required.

For mixes in which water predominates (hereinafter termed "water mix") the following formula is suitable:

| | Parts by weight |
|---|---|
| Milled zircon | 100 |
| Orthophosphoric acid (U. S. syrupy, 85%) | 8 to 13 |

To the foregoing is added 40 parts by weight of water and the resultant mix is digested at 180 to 200° F. until it becomes a thick paste; water is thereafter added to produce a density of about 2.0. Instead of digestion by the application of heat, the mixture may be aged for a day or two at room temperature and then brought to a density of about 2.0 by the addition of water.

The acid mix alone may be applied to the pretreated surface or may be first applied and then followed by an application of the water mix. For example, the acid mix is applied to the brick at the surface to produce a zone of depth desired (usually ⅛ to ¼" depth for a facing zone for usual purposes). This may be produced by two applications of about 1 lb. each of said acid mix per square foot of surface for a depth of zone of about ¼". This results in a weight, after firing, of about 1 lb. 3 ozs. per square foot of surface. The applications follow each other in a few minutes without intermediate drying. The brick thus treated is dried at 180–200° F., baked at 300–600° F. and finally fired at 2300° F. or higher. The resulting product will have a rough surface in which the relatively thin film of zircon refractory of the body material will follow more or less the original general surface contour of the brick.

If a smoother and more reflective surface is desired, the above procedure will be modified as follows. After the two applications of the acid mix and before applying heat, a water mix is used over the acid mix, without prior drying to such extent as is necessary to provide the degree of smoothness of the surface desired. For a thin coating, on a zone previously formed with the acid mix, one application of the water mix may suffice. After the bricks have thus been treated, they are dried, baked and fired as above indicated.

As a further modification, two applications of the water mix may be applied directly to a preconditioned surface and the bricks are then dried, baked and fired as above; producing a surface coating on the bricks with some zone underneath or penetrating into the body of the brick to a limited extent only.

Instead of using milled zircon entirely in the above formulae grained zircon may be included as a part of the zircon constituent of the mix, but such grained zircon will block the penetration and the resulting treated zone will not be as strong as in the case where milled zircon alone is used.

We have not yet accurately determined the optimum thickness of zone or depth of penetration for particular purposes; but we have found that for bricks of the above type where a surface zone only is desired a penetration averaging about ¼" in depth is sufficient for most purposes. In such cases where a penetration appreciably greater than ¼" is desired, the acid-to-water ratio in the above "acid mix" is increased, even to the exclusion of water. By "penetration" is meant the depth to which the zircon has passed into the body interstices. As above explained, the zircon does not necessarily, or usually fill all the larger channels (even closely adjacent to the surface, except when a smooth surface is desired) but covers the brick substance in the zone of treatment. We consider it desirable not to fill the spaces in the treated zone completely because of the great differential in thermoexpansivities of zircon and brick substance. Additionally the insulating properties are greater if spaces are maintained in the treated zone.

The following range of proportions of the ingredients of the mix are at present believed to be the practical limits for most purposes, but are not intended to represent the actual possible maximum and minimum limits for obtaining useful results:

| | Per cent by weight |
|---|---|
| Zircon | 55–63 |
| 85% orthophosphoric acid | 35.5–7 |
| Water | 9.5–30 |

In order to enable those skilled in the art to obtain the full benefits of the invention, we have selected from a large number of tests four separate specimens of bricks to show the effect of variation in treatment; and the method of pretreatment, the mix formula and application of mix for the respective specimens will be set forth following in conjunction with a brief description of the typical representative specimen selected.

*Example I*

This example is for purposes of comparison only and does not embody the teachings of this invention. It is intended to show the character of product resulting from merely applying a zircon-phosphoric acid mix without pretreatment of the brick.

Figs. 1, 2 and 9 illustrate a brick body 1 of the type previously described provided with a surface facing 2 of zircon refractory applied to the brick in the form of a mixture and without any preconditioning of the brick and wherein water predominated in the zircon mix; the mix being produced in accordance with the following formula:

| | | |
|---|---|---|
| Milled zircon | grams | 227 |
| Aluminum hydroxide | do | 5 |
| 85% orthophosphoric acid | ccs | 15 |
| Water | ccs | 100 |

This formula provides an acid constituent amounting to approximately 6.5% of the total dry constituents. The mix was not digested by heating or aging. The acid-to-water ratio, on a weight basis, was approximately 1 to 4, and two applications of the mixture were applied to the brick; the brick then being dried, baked and fired, as heretofore described. Referring to the drawings, it will be noted that the surface coating 2 while relatively smooth, yet follows somewhat the original contour of the brick (Fig. 9) and has no penetration into the body of the brick, whose upper body surface is designated in general by the line A—A (common to Figs. 9–12 inclusive) and whose lower body surface is designated by the line B—B (also common to Figs. 9–12 inclusive). Fig. 9 represents a sectional view through the depth of the brick about seven times the actual size of the brick; while Figs. 1 and 2 are approximately two-thirds actual size. Referring more particularly to Fig. 9, it will be seen that the body material 3 and the interstices or cellular spaces 4 have been unaffected below the surface plane A—A of the brick.

It will thus be seen that the bonded zircon external coating 2 thus provided, while extremely hard furnishes little strength to the brick as a whole, the coating 2 may be easily perforated and the resulting breaking of the coating 2 will cause the body 1 to become fractured. While the coating 2 provides an excellent refractory surface of high reflectiveness yet the brittle external coating of dense zircon body is only superficial and is subject to easy fracture and spalling.

*Example II*

Figures 3, 4 and 10 illustrate the product resulting from the following treatment in accordance with this invention and serves to clearly illustrate the salient feature of pre-treatment. The surface of the brick is preconditioned with 85% orthophosphoric acid and a mixture made according to the following formula applied:

| | | |
|---|---|---|
| Milled zircon | grams | 227 |
| 85% orthophosphoric acid | ccs | 15 |
| Water | ccs | 100 |

The acid constituent in the said mix amounts to approximately 6.5% of the total dry constituents. The above mixture was digested, and water added to make a density of about 2.07; the acid-to-water ratio, on a weight basis, being 1 to 4.25; and two applications of the above mixture were applied to the preconditioned brick surface, and the brick then dried, baked and fired as above described. Accordingly it will be seen at the outset that the relative acid content of the dry constituent of the mix, the acid-to-water ratio and the density of the mix are substantially the same, and the number of applications the same, as in Example I. The controlling difference between the examples being the pre-treatment in this example as compared with the absence of pre-treatment in Example I. It will be seen following that this difference is critical.

Referring to Figs. 3, 4 and 10 of the drawings, it will be seen that the surface texture 5 is considerably rougher than that of Fig. 1 and that the zircon has penetrated to an appreciable extent into the body 6 (Fig. 10) extending down to the level designated by the lines C—C; also that the external coating above the upper surface A—A is only of film-like thickness. Such penetration is due to the acid treatment which, for the reasons previously described, blocks the absorptive properties of the body material 7 thereby causing the zircon of paint-like consistency to flow from the surface down through the interstices thus coating the interior of the cellular spaces designated 8 in Fig. 10. In order to more clearly illustrate the body structure of the treated portion, we have illustrated in Fig. 13 a more enlarged section showing the interconnection between the cells 8 thus providing channels through which the zircon mix flows. In Fig. 13 the body material is represented by the lighter areas such as 7 and the cellular spaces by the darker areas such as 8 and the bonded zircon coating by the darkest outlines designated 9. From this it will be seen clearly that in the penetrated zone well within the body of the brick the cellular spaces or interstices are not filled with the zircon but are provided with an interior cellular coating. Therefore it is possible in accordance with our invention to produce a cellular zircon bonded structure, in the instant embodiment this zircon film or cellular coating being superimposed on the cellular body structure of the puffed clay to thereby produce a greatly increased strength of the body structure within the treated zone as well as providing the other characteristics of the refractory. The normal untreated body structure of the brick below the plane C—C and the normal cellular spaces of the untreated body of the brick are designated respectively 3' and 4'.

*Example III*

Figs. 5, 6 and 11 illustrate a brick of the above type which has been treated in accordance with this invention, the body being designated as 10 (Figs. 5 and 6) and the surface as 11. In this example the brick is likewise preconditioned by an application of undiluted acid (85% orthophosphoric acid) and the mix has the following formula:

| | | |
|---|---|---|
| Milled zircon | grams | 227 |
| Aluminum hydroxide | do | 5 |
| 85% orthophosphoric acid | ccs | 30 |
| Water | ccs | 100 |

In this formula the acid constituent amounts to approximately 13% of the total dry constituents. The mixture is first digested and water is thereafter added to make a density of about 1.86; the acid-to-water ratio on a weight basis being about 1–3. A plurality of applications of the mix, such for example as three applications, are applied in the manner previously described and the brick is then dried, baked and fired as above described.

Referring to the drawings, it will be seen that the penetration thus effected is appreciably deeper than that of the previous examples and the surface 11 has a texture whose smoothness is intermediate that of the bricks illustrated in Figs. 1 and 3. According to Fig. 11, it will be seen that the relative depth of penetration is indicated by the lines D—D; the body structure in the treated zone being designated 7' and the coated cells being designated 8'—it being understood that the treated zone structure is comparable to that illustrated in Fig. 13. The surface 11 follows the original contour of the brick surface to a greater extent than is the case in Fig. 9 and to a lesser extent than is the case in Fig. 10, the film of the zircon refractory on the exterior of the treated face being somewhat greater than that shown in Fig. 10 and much thinner than the external coating shown in Fig. 9.

*Example IV*

Figs. 7, 8 and 12 illustrate a brick of the character above described in which the body 12 has been substantially entirely impregnated, in accordance with this invention, and therefore the zircon refractory is disposed throughout the cellular structure of the entire body. It will be noted that in this example the surface 13 follows very closely the original surface texture of the brick before treatment. In this example the brick was preconditioned as before with 85% orthophosphoric acid, except that a greater amount of acid has been utilized in a quantity sufficient to pierce through the depth of the brick. The same formula was utilized for the mix as that utilized in Example III, except that after digestion of the mix no water was added, but instead acid was added to produce a density of about 2.4; the acid-to-water ratio on a weight basis being about 3–1. A greater number of applications of the mix were applied than in the previous example, such for example six applications. The brick thus treated was dried, baked and fired as above described. By referring to Fig. 12 it will be seen that the penetration extends throughout the depth of the brick from the lines A—A to the lines B—B. The body material of the brick is designated as 7'' and the coated cellular spaces as 8''; it being noted that the degree of coating of the cells, i. e. the density of application of the zircon coating within the interstices is greatest adjacent the top of the brick to which the mixture was applied and decreases toward the bottom of the brick; being diagrammatically indicated by the heavier shading of the spaces 8' at the top and the relatively lighter shading of the spaces downwardly, the deposition of the coating in the body structure being also in accordance with Fig. 13.

Although aluminum hydroxide is shown in the above formulae of Examples III and IV, we have found that this ingredient is not necessary and may be omitted from the formulae if desired. This ingredient was actually used in Examples III and IV but in the previously given general formulae it was not used.

With water predominating in the mix, absorptive action of acid preconditioned bricks is restored—perhaps to the degree to which the acid in the pores of the material itself becomes diluted, and therefore the deposition of the zircon mix becomes more superficial. With little water in the mix, and with heavy acid pre-treatment, only slight dilution ensues and penetration may go to the extent as in Example IV. From our experience in connection with such penetration, it appears that with the procedure followed in Example IV the mix could be applied to one face until it would merely seep out on the lower surface of the brick. Accordingly, if the effective blocking of the "channels" is desired a greater water content must be present in the mix than remains after digestion.

When a mix is digested it loses water by evaporation, but the amount of acid remains practically constant. Therefore, if water only is to be added to a digested mix, it makes no difference how much water has been evaporated so long as the density of the digested mix is greater than that desired. However, when acid is to predominate, and the mix is to have a certain density and ratio of acid to water, then the quantity of water remaining in the digested mix is critical. Of course, a density of 2.4 can be gotten over a wide range of ratios of acid to water. For example:

227 grams zircon, no water, 153 cc. acid
227 grams zircon, 40 cc. water, 71 cc. acid
227 grams zircon, 76 cc. water, no acid

It is our present belief that a satisfactory procedure would be to digest at 175–200° F. until the mix weighs 83% of the original weight. It will then contain about 40% of the water added before digesting and can be diluted for any desired density with water, or if it be desired to produce a condition in a porous brick like that produced in Example IV, acid is added in volume equivalent to 58% of the volume of water originally added to the mix.

It will be noted that the brick produced in accordance with Example IV still retains a cellular body structure of the same general order as that of the original untreated brick, and therefore possesses a relatively high insulating value. This brick also provides an extremely hard strong body structure differing radically in strength, hardness and refractoriness from the untreated cellular clay structure. The same is true to a lesser extent of depth in Examples II and III. We have determined by tests that this is due to the zircon content distributed throughout the cellular structure. For example, the same untreated brick when treated with an equivalent amount of 85% orthophosphoric acid only; and heated, baked and fired, as above described, produces an article which is not appreciably harder or stronger or more refractory in other respects than the untreated brick.

Having thus described our invention with particularity with reference to certain presently preferred forms of the products and method of producing the same, and having referred to some of the possible modifications of the invention, it will be obvious to those skilled in the art after understanding the invention, that other changes and modifications may be made therein without departing from the scope of the invention, and it is our intention to cover in the appended claims such changes as come within the scope of the invention.

What we claim is:

1. A ceramic body having a surface zone comprising relatively weak porous material and relatively hard bonded zirconium material, said relatively weak material being disposed in a body structure providing interstices dispersed therethrough and said relatively hard material being disposed in said interstices, whereby said body structure is substantially strengthened and said surface zone is materially hardened.

2. As an article of manufacture, a ceramic body having a porous surface zone provided with interstices extending from the outer face thereof into said porous surface zone, and a thin penetrating coating having portions extending into said interstices for a predetermined depth interiorly of said surface zone and being secured to said surface zone of said body thereby, said body portion material being of substantially greater heat-insulating character than said penetrating coating material and said penetrating coating comprising a bonded zirconium refractory providing a substantial reinforcement for said body portion.

3. As an article of manufacture, a ceramic body having a porous surface zone provided with interstices extending from the outer face thereof into said porous surface zone, and a thin penetrating coating having portions extending into

said interstices for a predetermined depth interiorly of said surface zone and being secured to said surface zone of said body thereby, said penetrating coating comprising a bonded zircon refractory resulting from a mixture having the following approximate formula by weight, 55—63% milled zircon, 35.5—7% orthophosphoric acid (U. S. syrupy 85%), 9.5—30% water, digested to a paint-like consistency.

4. As an article of manufacture, a ceramic body having a porous surface zone provided with interstices extending from the outer face thereof into said porous surface zone, and a thin penetrating coating whose outer surface follows the surface contour of said body into and out of certain of said interstices and whose inner surface has corresponding portions extending into said interstices for a predetermined depth interiorly of said surface zone and being secured to said surface zone of said body, said penetrating coating comprising a bonded zircon refractory, said body material being of substantially greater heat-insulating character than said penetrating coating material and said penetrating coating providing a substantial reinforcement for said body portion.

5. As an article of manufacture, a brick having a puffed clay body providing a cellular structure with interstices extending outwardly through a face of said body, a bonded zirconium material within said interstices and dispersed through said cellular structure in a surface zone extending an appreciable depth inwardly of said clay body from said face thereof, whereby said puffed clay body is provided with an integral reinforced surface zone highly resistant to abrasion and heat.

6. As an article of manufacture, a porous brick comprising a porous substance capable of withstanding a temperature of the order of 2300° F. without substantial body deformation and whose body is provided with channels extending from a face inwardly of said body and a thin coating of bonded zircon particles secured to said porous body face and extending into said channels in anchored relationship with said porous substance below the surface of said porous body whereby said brick is provided with a penetrating zircon refractory facing.

7. As an article of manufacture, a porous brick comprising a porous substance and whose body is provided with channels extending from a face inwardly of said body and a thin coating of a zircon refractory comprising zircon bonded with phosphoric acid and anchored to said face and to said body within said channels to a depth of from 1/64–1/4 inch from said porous body face, whereby said brick is provided with a penetrating zircon refractory zone.

8. As an article of manufacture, a ceramic body having a porous surface zone provided with interstices extending from the outer face thereof into said porous surface, said surface zone having disposed in the interstices thereof from the outer surface for a predetermined depth inwardly a bonded zircon refractory, the major depth of said zircon refractory being disposed within the said porous surface zone.

9. As an article of manufacture, a ceramic body having a porous surface zone provided with interstices extending from the outer face thereof into said porous surface, said surface zone having disposed in the interstices thereof from the outer surface for a predetermined depth inwardly a bonded zircon refractory, the disposition of said zircon in said interstices being insufficient to fill said interstices, the major depth of said zircon refractory being disposed within the said porous surface zone.

10. Method of reinforcing a porous insulating ceramic body with a zirconium compound refractory comprising applying phosphoric acid to a surface of said body to be faced, applying to the said surface so as to penetrate said body to a predetermined depth a mixture comprising zirconium, phosphoric acid and water so constituted and prepared as to have a paint-like consistency, then drying, baking, and firing said body portion so treated to a temperature of the order of 2300° F.

11. Method of providing a zircon refractory penetrating coating in a porous insulating ceramic body which comprises applying phosphoric acid to a surface of said body to be faced, applying to the said surface so as to penetrate said body to a desired depth and providing a thin film on the outside of said body with a mixture comprising by weight 55—63% zircon, 35.5—7% orthophosphoric acid (U. S. syrupy 85%) and 9.5—30% water so prepared as to have a paint-like consistency, then drying, baking, and firing said body portion so treated to a temperature of the order of 2300° F.

12. Method of securing a bonded zircon refractory to a porous insulating ceramic body having interstices which comprises the following steps, preparing a zircon refractory mixture of paint-like consistency comprising zircon particles of a fineness permitting passage into said interstices, phosphoric acid as a bonding agent and water, wetting the surface of said body with phosphoric acid, applying a thin coating of said mixture over a surface of said body so that said mixture passes into the interstices adjacent said surface of said body, drying and baking the zone of said body thus treated and the mixture applied thereto and firing the same at a relatively high temperature.

13. Method of bonding a zircon refractory to a porous insulating ceramic body having interstices which comprises the following steps, preparing a digested zircon refractory mixture of paint-like consistency comprising 55—63% by weight zircon particles of a fineness permitting passage into said interstices 35.5—7% by weight orthophosphoric acid (U. S. syrupy 85%) as a bonding agent and water, wetting the surface of said body with orthophosphoric acid (U. S. syrupy 85%), applying a thin coating of said mixture over a surface of said body so that said mixture passes into the interstices adjacent said surface of said body, drying at approximately 180°–200° F. and baking at approximately 300°–600° F. the zone of said body thus treated and the mixture applied thereto and firing the same at a temperature of at least about 2300° F.

14. Method of providing a zirconium compound refractory penetration into a puffed clay brick which comprises applying orthophosphoric acid (U. S. syrupy 85%) to a surface of said brick to be treated, introducing into said surface interstices a mixture comprising a zirconium compound, phosphoric acid as a bonding agent and water, said mixture being so constituted and prepared as to have a paint-like consistency, then drying, baking and firing said brick.

15. Method of producing a refractory insulating body which comprises the following steps, preparing a zircon refractory mixture of paint-like consistency comprising zircon particles of a fineness permitting passage into said interstices, phosphoric acid as a bonding agent and water,

applying relatively concentrated phosphoric acid to a body of absorptive material having interconnected interstices therein until said body material has been impregnated to the depth of zircon penetration desired, applying said zircon mixture to a surface of said body to thereby cause the same to pass into said body interstices until said mixture has penetrated to the desired depth, drying and baking said body thus treated and firing at a relatively high temperature.

16. As an article of manufacture, a refractory body comprising cellular spaces surrounded by bonded zircon walls and having intervening substantially softer porous material over which said walls are disposed.

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