United States Patent

[11] 3,561,494

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[21] Appl. No. **710,316**
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[45] Patented **Feb. 9, 1971**

[54] **CASTABLE SILICATE COMPOSITIONS, CASTING METHODS AND ARTICLES PRODUCED THEREBY**
8 Claims, 6 Drawing Figs.

[52] **U.S. Cl.** **138/177,** 138/140, 138/145; 264/66, 106/40
[51] **Int. Cl.** **F16l 9/10**
[50] **Field of Search** ..... 264/66 (For purposes of restriction only); 138/177 (For purposes of restriction only); 106/40 (For purposes of restriction only); 138/140, 141, 143, 145, 177, 149 (Cursory); 106/(Perlite digest)

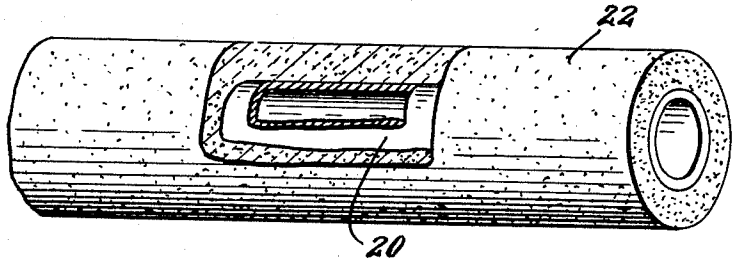
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Attorney—Mattern, Ware and Davis

ABSTRACT: Castable compositions including soluble or colloidal silicates as binding agent. The composition is cast as an aqueous slurry in a mold coated with a reagent for precipitating the silicate, to prevent penetration of silicates into the mold surface. A lightweight, expandable, refractory tube having excellent resistance to thermal shock is produced.



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Fig. 1

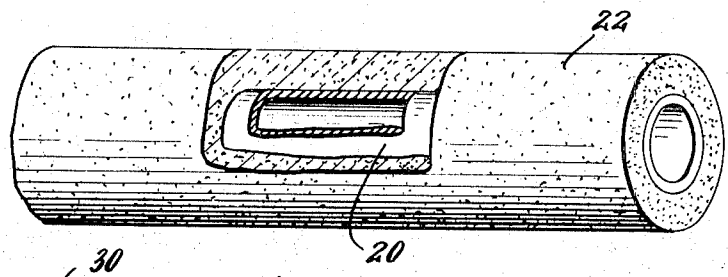


Fig. 2

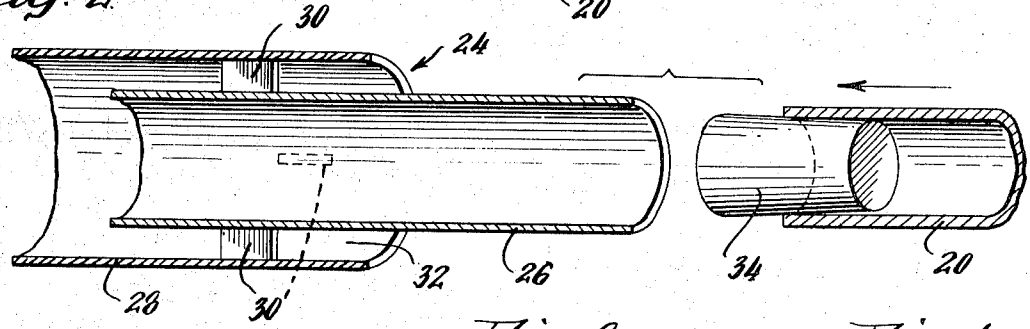


Fig. 3

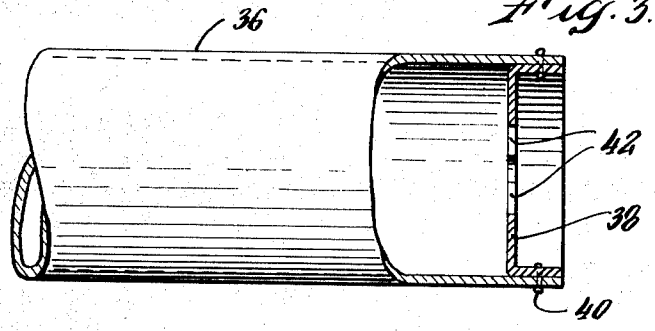


Fig. 4

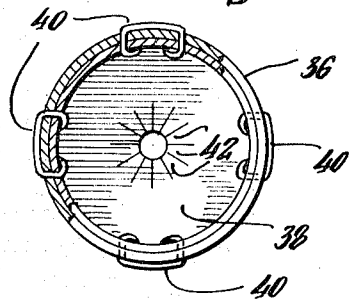


Fig. 5

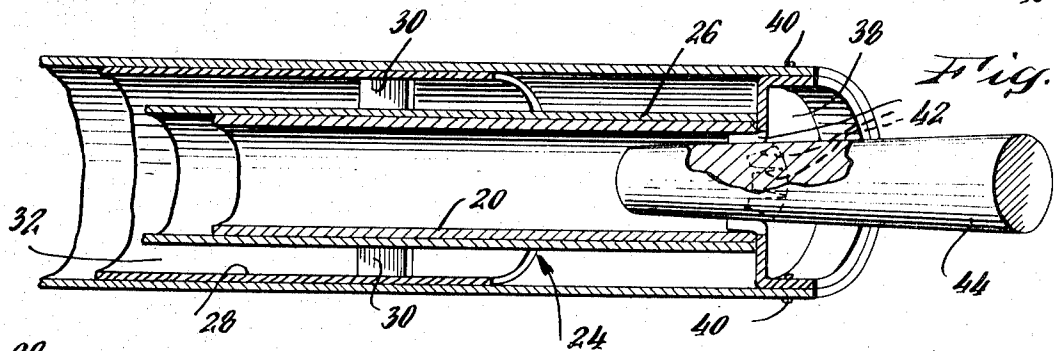
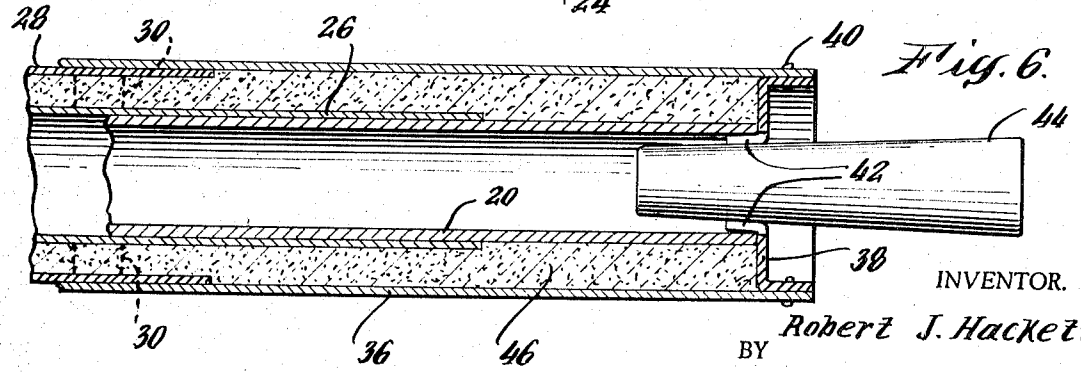


Fig. 6



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CASTABLE SILICATE COMPOSITIONS, CASTING METHODS AND ARTICLES PRODUCED THEREBY

The present invention relates to castable silicate compositions and methods. As a particular aspect of the invention, a refractory, expendable, lightweight tube is produced.

Refractory tubes are used for a number of purposes, such as for withdrawing molding metal for analysis, for determining temperatures of molten substances, for injecting gases into molten metals, etc. Since such tubes are normally used only once or a few times before being discarded, they must be inexpensive. Particularly, in applications where the tube will be plunged into molten metals, it must withstand great thermal shock.

Known prior art tubes for these applications include a steel tube covered with layers of paper. The paper, although destroyed in use, protects the steel tube for a limited period of time. Another known prior art construction has the steel tube coated with asbestos fibers admixed with fibers such as cotton. Each of these known prior tubes are somewhat hazardous to use, and have a service life of only a few seconds.

According to one major aspect of the present invention, the steel tube is protected by a foamed ceramic composition including refractory materials bonded together with silicate. The resulting tube withstands high temperatures much better than known prior art tubes, and has a greater service life under severe conditions. Other major aspects of the invention include particular refractory compositions, methods of formulating these refractory compositions and methods of casing silicate-containing compositions generally.

Accordingly, a primary object of the invention is to provide methods of casing silicate-containing compositions.

A further object is to provide such methods which are particularly suited for use with porous molds which are to be separated from the cast article.

A further primary object is to provide inexpensive refractory castable compositions.

A further object is to provide compositions of the above character which can be formed to produce lightweight, insulating, refractory ceramic structures.

A further primary object of the invention is to provide a metal tube coated with compositions of the above character.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation of one or more said steps with respect to each of the others, the compositions possessing the characteristics, properties, and the relation of constituents which will be exemplified in the compositions hereinafter described, and the articles which possess the relation of elements, all as exemplified in the detailed disclosure hereinafter set forth, and the scope of the invention will be indicated in the claims.

For a more complete understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connecting with the accompanying drawing, in which:

FIG. **1** is a perspective view, partly broken away, of a ceramic coated metal tube produced according to one aspect of the invention;

FIG. **2** is an action view, partly in section, showing the metal tube being assembled into a nozzle for applying the castable compositions to the exterior of the tube;

FIG. **3** is a side elevation view, partly broken away of a paper mold;

FIG. **4** is an end view of the mold shown in FIG. **3**;

FIG. **5** is a sectional view of the assembled tube and mold on the nozzle, just prior to injection of the castable composition; and

FIG. **6** is an action view similar to FIG. **5**, showing an intermediate stage in the injection of the composition into the space bounded by the tube and mold.

THE CASTING OPERATION

The composition and process according to the invention are disclosed in the context of producing the tube illustrated in FIG. **1**, which includes tube **20** surrounded by a cylindrical ceramic casting **22** bonded to tube **20**. As will be disclosed, casting **22** is refractory, lightweight and inexpensive. FIGS. **2**—**6** illustrate suitable apparatus for producing the FIG. **1** product.

Referring to FIG. **2**, nozzle **24** includes inner and outer coaxial cylindrical walls **26** and **28** spaced apart by ribs **30** to define an annular passage **32**. A plug **34** is inserted in the left end of the tube **20**, which is then telescopically inserted into cylinder **26** until the right end of tube **20** is flush with the right end of cylinder **26** (FIG. **5**). The dimensions of cylinder **26** are selected for easy sliding reception of tube **20**. Since in this application it is intended that casting **22** adhere to tube **20**, the surface of tube **20** is preferably etched or otherwise thoroughly cleaned prior to insertion in cylinder **26**.

As illustrated in FIG. **3**, mold **35** includes cylinder **36**, formed for example of kraft paper, and a cup-shaped mold end piece or cap **38** secured as by staples **40** at the right end of cylinder **36**. The central bottom portion of cap **38** is slit to provide tabs **42** extending radially inward from a distance approximately equal to the radius of tube **20**. The interior surface of cylinder **36** and the cap **38** are coated with a release coat of a character to be described. The dimensions of cylinder **28** are selected so that coated cylinder **36** can telescope thereon, as shown in FIG. **5**. When the mold **35** has been installed on cylinder **28**, tapered pin **44** is inserted through the center of cap **38**. This wedges tabs **42** into contact with the inner surface of tube **20** and seals mold **35** to tube **20**. Mold **35** and tube **20** thus define an annular volume for receiving the castable composition in the form of slurry **46** which is injected through passage **32** by conventional pumping means (not shown).

Tube **20** and mold **35** are pushed to the right as a unit as their enclosed annular volume is filled by slurry **46**. When the enclosed volume is filled with slurry **46** and tube **20** and mold **35** are removed from nozzle **24**, the left or open end is preferably closed with a further release-coated cap **38** and tapered pin **44**, so that both ends are identical and tube **20** is centered within cylinder **36**. For this purpose, cylinder **36** is preferably slightly longer than tube **20**, to accommodate end caps **38**. The slurry should substantially completely fill the mold when both end caps **38** are installed. After this slurry **46** in the resulting intermediate product has been cured or set, pins **44** and mold **35** are removed, to produce the final product shown in FIG. **1**.

THE SLURRY COMPOSITION

The preferred specific composition for refractory casing **22** is as follows:

Ingredient:	Weight percent
Mullite	40–60
Aqueous silicate, solids	8–20
Perlite	0–10
Clay	0–10
Total water	20–30
Surface active agent	<1

The mullite is an inexpensive refractory substance, and can be replaced by other refractory substances depending upon the desired end use.

The preferred aqueous silicate in the above composition is available from Philadelphia Quartz Company as their product S-35, and contains 6.75 percent by weight Na_2O, 25.3 percent SiO_2 and 67.95 percent water. This results in approximately 440 ounces of "silicate solids" combined with 936 ounces of water. In terms of weight percent of the total slurry composition, the silicate expressed as SiO_2 (348 ounces) constitutes some 10.5 percent of the slurry, or about 14.7 percent of the cured casting.

The perlite is a lightweight refractory extender, and contributes to ease of foaming of the slurry.

The clay in the composition adds to the strength of the casting and reduces the viscosity of the slurry. It is also believed to reduce the size of the foam bubbles.

The free water is added to this particular composition for two reasons. When using the particular aqueous silicate as specified above, the resulting slurry is rather difficult to pump. Addition of this small amount of further water makes the slurry conveniently pumpable. If substantially more water were added, the final casting **22** would tend to crack upon curing. The other purpose of the free water is to facilitate blending the surface active agent into the slurry. The preferred surface active agent is an anionic surfactant commercially available as Santomerse No. 1 from Monsanto Company, and is believed to be essentially dodecyl benzene sulfonate. A number of other surface active agents are commercially available and would be suitable. The principal function of the surface active agent is to stabilize the foam produced when the slurry is stirred so as to entrain air.

Operative ranges for the above ingredients are generally as follows:

Ingredient	Weight, ounces	Weight percent
Mullite	1,600	48.0
Aqueous silicate	1,376	41.3
Perlite	172	5.1
Clay (kaolin)	154	4.6
Free water	34.5	1.0
Surface active agent	0.21	Trace
Totals	3,336.71	100.0

COMPOUNDING THE SLURRY

The several ingredients are preferably combined as follows. The aqueous silicate, clay and mullite are thoroughly mixed with approximately 17 ounces of the free water and then let stand for 2 or 3 days. The perlite is then blended in. The surface active agent is then dissolved in the remainder of the free water (which may be warmed) and added to the mixture. The mixture is then stirred so as to entrain air and produce a foamed slurry stabilized by the surface active agent. Stirring is discontinued when the mixture has expanded to about 110 percent to 115 percent of its original volume. The foamed slurry is then ready for extrusion through nozzle **24**.

It should be understood that the specific aqueous silicate composition indicated above can be replaced by other aqueous silicates containing different amounts of alkaline oxide (either sodium or potassium oxide), and different amounts of total solids in water. In such cases it may be necessary to add differing amounts of free water, or perhaps no free water, or to make other adjustments in the composition. The term aqueous silicate as used in the specification and claims is intended to include silicates present either as colloidal dispersions or in true solution.

The indicated range of foamed expansion is significant in that a less expanded slurry would be difficult to pump while one expanded to a considerably greater degree would tend to crack upon curing. The foamed structure contributes to the insulating qualities of the casting, improves its thermal shock resistance and makes it lightweight and less expensive.

SETTING THE SLURRY

The slurry **46** in the intermediate product is preferably cured by drying between 180° and 210° F. for a period of time depending on the radial thickness of the slurry, and then gradually raising the temperature to about 400°—500° F., to set the silicate. When the radial thickness of the slurry is substantially 0.22 inch, the following schedule has been found to give excellent results.

Temperature, °F.	Time
180—210	5—6½hours
212—225	15 minutes
300	15 minutes
400	30 minutes
450	10 minutes
470	10 minutes
500	5 minutes

Of these heating periods, the first is considered to be highly desirable with the above formulation, and the second heating period is also of considerable importance. If the temperature is too low during the first period, the foamed slurry tends to collapse and settle while if the temperature is too high, the ceramic tends to blister and crack. The ceramic **22** cured in accordance with the above schedule can be plunged directly into molten steel without cracking.

Assuming that all the water is removed during the curing, the casting using the above specific slurry composition will have the following approximate empirical composition:

Ingredient	Weight Percent
mullite	67.5
SiO_2	14.7
Na2O	4.2
perlite	7.1
clay	6.5
TOTAL	100.0

SEPARATION OF CASTING FROM MOLD

According to another major aspect of the invention, means are provided for preventing an aqueous silicate from sticking to a surface, such as to mold **35**, particularly when the mold is porous. It has been discovered that such sticking can be prevented by coating the surface with a setting agent, which is defined as a substance which chemically reacts quickly with aqueous silicate to form an insoluble material. The insoluble material is believed to form a film or layer which prevents penetration of the unreacted aqueous silicate to the surface being protected. The insoluble material can be, for example, polysilicic acid (formed when the setting agent is more acidic than silicic acid, e.g., sulfuric or acetic acid), or insoluble silicate salts (formed when the setting agent donates cations forming insoluble silicate salts, e.g., copper, zinc or calcium silicate). Selection of a particular setting agent for a given application is within the scope of one skilled in the art.

The presently preferred setting agent is calcium stearate, which is commercially available in the form of a wettable powder. When using this wettable calcium stearate powder as the setting agent for coating the interior surfaces of mold **35**, it is preferably sprayed as an aqueous slurry and dried so as to leave a film approximately 0.015 to 0.030 inch thick on the interior mold surfaces. A considerably thicker coating might prevent proper escape of water vapor through the mold walls during the curing of the slurry, while considerably thinner coatings would not provide an effective barrier.

The calcium stearate apparently reacts substantially instantaneously with the aqueous silicate to form a layer of insoluble calcium silicate. This in turn prevents penetration of the aqueous silicate to the mold, so that the mold can be readily stripped from casting **22**.

It should be understood that the use of a setting agent to prevent adhesion of silicate-containing compositions to surfaces (such as molds) is not restricted to production of the article shown in FIG. **1** or to the specific compositions herein disclosed, but is of general application.

From the above disclosure and the accompanying drawing it may be seen that there is provided a method using setting agents for casting silicate-containing compositions, which method is particularly useful when the mold is to be separated from the cast article. The setting agents may be applied to the mold surface as thin coatings, permitting ready release of the mold. The preferred castable compositions disclosed herein are well suited for exposure to extremely high temperatures, and are inexpensive. When foamed as above disclosed, the

resulting castings are lightweight and provide substantial insulating properties. The disclosed metal tube coated with foamed refractory ceramic is rugged and inexpensive, and can withstand sudden immersion into molten steel.

While the objects of the invention are efficiently achieved by the preferred forms of the invention described in the foregoing specification, the invention also includes changes and variations falling within and between the definitions of the following claims.

I claim:

1. An article of manufacture, comprising:

A. a metal tube; and

B. a foamed ceramic body surrounding and bonded to said tube, said ceramic body essentially comprising:

1. 40—67.5 percent mullite;
2. 5—15 percent SiO_2;
3. 3—5 percent Na_2O;
4. 0—10 percent perlite; and
5. 0—10 percent clay;

said ceramic body having an outer peripheral layer comprising a blend of said ceramic body and an insoluble silicate salt, said insoluble silicate salt resulting from the reaction of calcium stearate and the aqueous silicate of said body to form a substantially nonporous insoluble layer.

2. An article of manufacture as defined in claim 1, wherein said nonporous, insoluble layer comprises polysilicic acid.

3. An article of manufacture as defined in claim 1, wherein said nonporous, insoluble layer comprises a copper salt.

4. An article of manufacture as defined in claim 3, wherein said silicate salt comprises calcium silicate.

5. An article of manufacture as defined in sinc 1, wherein said nonporous, insoluble layer comprises a zinc salt.

6. The article defined in claim 1, wherein said ceramic body is cellular in structure.

7. The article defined in claim 6, wherein said ceramic body contains about 10 to 15 percent entrained gas, by volume.

8. An article of manufacture, comprising:

A. a metal tube; and

B. a foamed ceramic body surrounding and bonded to said tube, said ceramic body consisting essentially of about:

1. 67.5 percent mullite;
2. 14.7 percent SiO_2;
3. 4.2 percent Na_2O;
4. 7.1 percent perlite; and
5. 6.5 percent clay;

said ceramic body having an outer peripheral layer comprising a blend of said ceramic body and an insoluble silicate salt, said insoluble silicate salt resulting from the reaction of calcium stearate and the aqueous silicate of said body to form a substantially nonporous insoluble layer.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,561,494 Dated February 9, 1971

Inventor(s) Robert J. Hackett

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 31, "casing" should read -- casting --

Line 34, "casing" should read -- casting --

Column 2, line 54, "casing" should read -- casting --

Columns 2 and 3, the Tables are reversed

Column 3, line 76, which is illegible, should read

-- 400 30 minutes --

Column 4, line 76, which is illegible, should read

-- and are inexpensive. When formed as above disclosed, the --

Claim 5, line 1, "sinc" should read -- claim --

Signed and sealed this 7th day of September 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Pa