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FOUNDRY COMPOSITION CONTAINING FURFURYL ALCOHOL POLYMER, FOUNDRY STRUCTURE THEREOF, AND METHOD OF MAKING SAME

Stephen E. Freeman, Thiensville, Wis., and John Steiner, Chicago, Ill., assignors to Freeman Chemical Corporation, Port Washington, Wis., a corporation of Delaware

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This invention relates to essentially solid, shapeable, hardenable foundry mixes comprising particulate refractory foundry material and a stable, heat curable binder containing a curable furfuryl alcohol polymer component and boron-containing component, hard foundry structures that are produced from said foundry mixes, and methods of producing said hardened foundry structures.

This application is a continuation-in-part of our allowed copending application Serial No. 614,817, filed October 9, 1956.

More specifically, this invention relates to essentially solid, shapeable, hardenable, foundry mixes which comprise about 91–99.5% by weight of refractory foundry material (based on the weight of the entire foundry mix), and about 0.5–6% by weight of a heat curable resinous binder (based on the weight of the entire foundry mix) containing a stable, heat curable binder having about 0.5–4.5% by weight curable furfuryl alcohol polymer component (based on the weight of the entire foundry mix) and at least about 1% by weight boron-containing component (based on the weight of the furfuryl alcohol polymer component). The stable, heat curable binder is stable at temperatures of up to at least about 125° F. Further, this invention relates to foundry structures produced from the hardenable mixes, against which molten metal may be poured without having the structures collapse or become distorted to the "setting" or "freezing" of the metal. Still further, this invention relates to methods of forming said hard foundry structures comprising heating the hardenable foundry mixes to about 180–500° F.

If desired, other resinous binders, such as ureaformaldehyde resins, may be used in conjunction with the stable, heat curable resinous binder of furfuryl alcohol polymer component and boron-containing component. However, the foundry mix must not contain more than a total of about 6% by weight resinous binder based on the total weight of the entire foundry mix.

Our invention contemplates the use of stable, heat curable reaction products that may be used as heat curable binders for particulate refractory foundry material to form foundry structures such as cores. These curable binders contain a curable furfuryl alcohol polymer component and a boron-containing component or reaction modifier. The curable binders are stable at normal storage temperatures, produce foundry cores having sufficient green strength for some foundry purposes, are capable of rapid curing in the presence of refractory foundry material at moderately elevated temperatures, and may be used to produce foundry cores having high tensile strength and scratch hardness values. The cores that are formed with these curable binders possess sufficient porosity to permit the satisfactory escape of gases formed during the casting operation. In addition the binder permits the core structure to collapse after molten metal is poured against it and after the metal has assumed its proper shape.

The moderately elevated curing temperatures of our curable binders shorten the oven curing time or baking cycle when they are substituted for conventional linseed oil binders. These moderately elevated curing temperatures permit shaped mixtures of refractory foundry material and curable binder to be economically heated or cured in dielectric ovens and, in cases of relatively thin cores, in infrared ovens. However, the use of dielectric ovens is generally restricted to cores that contain water or green strength binders such as a mixture of ceral and water. In conventional core binders which contain cereals or silicates, there is a decided loss in tensile strength and scratch hardness when the cured cores are stored in humid atmospheres. However, a baked core containing our cured binder may be stored for comparatively long periods without deterioration.

Still further, when our curable binder is mixed with refractory foundry material and formed into shell molds which are cured at moderately elevated temperatures and used to case high temperature molten metals (e.g., steel), the resulting molds have many advantages over the phenolic resins presently being used. For example, lower levels of our curable binder may be used to satisfactorily bond the refractory foundry material.

Foundry cores may be produced with our curable binder by a method which comprises mixing or mulling particulate refractory foundry material with a binding proportion of a curable binder containing desired proportions of a curable furfuryl alcohol polymer component and a boron-containing component whereby a shapeable foundry mix is produced, forming a shaped core from the mix that may be suitably hardened at moderately elevated temperatures, and curing the curable binder and refractory material at an elevated temperature so as to harden sufficiently the mix and produce a foundry core.

The curable furfuryl alcohol polymer component and boron-containing component may be added separately to the refractory material to form a foundry core mix or they may be premixed and added to the refractory foundry material as a mixture. Therefore, reference herein to the use of the curable binder in combination with the refractory foundry material is intended to infer that components of the curable furfuryl alcohol polymer component and refractory foundry material may be incorporated into the mix (i.e., refractory foundry material, and curable combination of furfuryl alcohol polymer component and boron-containing component) separately or as an admixture. In either case, the curable polymer and refractory components will be present in the foundry core mix as a curable mixture. For purpose of this invention, the relative proportion of curable furfuryl alcohol polymer component to boron-containing component is not influenced by the manner in which they are added to the refractory material.

The phrases "refractory foundry material," "refractory material," "refractory foundry core material" and "refractory foundry sand material" are intended to refer to unused and/or reclaimed, non-deleterious, refractory foundry material that may be mulled with a binding proportion of the curable binder to form a mix that may be shaped after the mulling step and then hardened sufficiently so as to produce a core or foundry structure having satisfactory tensile strength value. Thus, these phrases are intended to include conventional washed refractory foundry materials, such as exemplified by washed crude alumina, silicas, and clays. For example, zircon sands, Ottawa sand, and Mississippi sand from Rockford, Illinois, produce satisfactory foundry cores. In addition, these phrases refer to refractory foundry material that may include other foundry ingredients, such as exemplified by iron oxide and various forms of carbon such as seacoal. The refractory foundry material should be free of deleterious materials which interfere with the curing of the curable mixture of curable binder and refractory foundry material.

The "curable furfuryl alcohol polymer component" is herein intended to refer to partially polymerized furfuryl

alcohol, polymerizable furfuryl alcohol-containing resin complexes or reaction products, or suitable admixtures thereof, which are capable of undergoing polymerization or condensation-type reactions, herein referred to as curing, with the boron-containing component in the presence of refractory material at about 180–500° F., preferably about 200–400° F., so as to effectively and uniformly harden the refractory foundry material into a foundry core or structure having satisfactory tensile strength. This term is not intended to exclude the presence of minor, non-deleterious proportions of furfuryl alcohol monomer and/or reaction product impurities or components in the curable furfuryl alcohol polymer component as a part thereof; a minor proportion of the monomer serves as an extender for the partial polymer and cures at elevated temperatures in the presence of the boron-containing component.

It has been observed that in cases wherein the curable furfuryl alcohol polymer component contains furfuryl alcohol monomer, a portion of the monomer volatilized from the refractory foundry material-curable binder mix during curing at moderately elevated temperatures, as indicated by the odor emitted from the mix; the remaining portion of monomer cured in the presence of or with the boron-containing and refractory foundry material and served as a binder. As the relative proportion of monomer to polymer is increased in the curable furfuryl alcohol polymer component, the resulting increased loss of potential binding properties may be compensated for by increasing the proportion of curable binder (i.e., curable reaction mixture of furfuryl alcohol polymer component and boron-containing component) to refractory foundry material so as to provide an additional amount of partial polymer as well as monomer. The herein described and claimed heat curable binder is intended to relate to admixtures wherein the partial polymer constitutes all or at least a major or predominate portion thereof, and the monomer is present, if at all, in minor proportions (i.e., less than 50% by weight of the curable furfuryl alcohol polymer component) only.

We have observed that as the relative proportion of monomer to partial polymer is increased in the curable furfuryl alcohol polymer component, the curable binder (i.e., curable furfuryl alcohol polymer component plus boron-containing component) should likewise be increased in order to produce cured cores having high tensile strength values. For example, the curable mixture may consist of about 30 parts by weight of boric acid, 52 parts by weight curable furfuryl alcohol partial polymer, and 48 parts by weight furfuryl alcohol monomer in order to produce a cured core having a tensile strength equivalent to that produced by a curable mixture consisting of 10 parts by weight of boric acid and 100 parts by weight of partial polymer.

The following curable furfuryl alcohol polymer components exemplify some of commercial products that may be used in accordance with our invention: furfuryl alcohol-phenolformaldehyde resins such as Durez 14363, distributed by Durez Plastics Division of Hooker Electrochemical Co.; furfuryl alcohol-formaldehyde resins such as Varcum 8250, distributed by Varcum Chemical Corporation, and Quaker Oats Resin 199–153, distributed by Quaker Oats Co.; and a monomer-free furfuryl alcohol polymer such as Quaker Oats Resin 220–73 distributed by Quaker Oats Co.

A suitable curable furfuryl alcohol polymer component may be prepared for use in our curable mix by reacting furfuryl alcohol in the presence of an acid or proton donor, for example, strong acids at low temperatures, or dilute solutions of strong acids, or weak acids at elevated temperatures. This reaction leads to polymerization or condensation identifiable by an increase in molecular weight of the furfuryl alcohol and readily observable by a darkening in color and gradual increase in viscosity.

The exothermic nature of this type of furfuryl alcohol polymerization necessitates careful control of reaction conditions, and the exercise of caution. Where an exotherm raises the temperature too rapidly, undesirable secondary reactions may ensue leading to unwanted products, or the reaction may accelerate beyond the scope of control so as to react violently or to explode, thus rupturing the reaction vessel and filling it with a hard, infusible resinous mass. In the last stages of a runaway polymerization, the temperature may rise hundreds of degrees within moments and, simultaneously, vast quantities of gas may be generated.

The furfuryl alcohol polymer component may be made by a batch process such as set forth in Example 1, infra, or a continuous process such as exemplified by the procedure described in Example 1 of U.S. Patent No. 2,570,027.

The terms "boron-containing component" and "boron-containing reaction modifier" herein refer to boron-containing materials that are free of an interfering moiety, ion, or substance, and when admixed with the furfuryl alcohol polymer component, with or without the presence of refractory foundry material, forms a stable, heat curable foundry binder that when admixed with a major proportion (i.e., at least about 91% by weight based on the entire foundry mix) of refractory foundry material, forms a foundry mix that is benign at room temperature but hardens into a hard, self-supporting foundry structure at temperatures of about 180°–500° F.

The following boron-containing components exemplify some of the materials which may be used in accordance with our invention: boric oxide; boric acids or hydrates of boric oxide; certain boron esters such as ammonium borate, sodium pentaborate, and boron acetate; and boron complexes such as diorthotolyl guanidine salt of dicatechol borate.

However, the presence of alkalies or predominantly alkaline ions in the boron-containing component tend to interfere with our reaction mechanism; thus, decidedly alkaline borates (e.g., sodium meta or tetra borate) may not be used in accordance with our invention unless their alkalinity is reduced by the addition of acidulous material. In cases where the alkali is volatile (e.g., ammonium salts such as ammonium borate), the negation may remain only until the alkali is volatilized. Alkaline borates of intermediate alkalinity (i.e., a pH of about 7–8), have some curing activity but in order to effect relatively rapid curing, acidulous material must be added to the mulled mix; for example, 10 parts by weight of sodium pentaborate and 90 parts by weight of the polymer produced in accordance with Example 1, infra, yielded perceptible improvement in curing rate, although the presence of added acidulous material would induce still more rapid curing.

In addition, when anions or other materials are present in the boron-containing component which materially remove the borate from solution (e.g., by an insolubilizing action), effective amounts of the borate will not be present to undergo effective curing with the furfuryl alcohol polymer component. For example, lead ions tend to form insoluble lead borate—which is not suitable for our purposes.

Furthermore, certain borate esters which consist of a preponderance of non-borate moiety (e.g., trioleyol borate and tricresyl borate) have been found not to be satisfactory because they do not permit the furfuryl alcohol polymer component to undergo effective curing. The non-borate moiety may interfere with effective curing due, possibly, to its plasticizing action on polymers formed during curing, or to steric hindrance.

If decidedly alkaline salts of borates are neutralized, such as would result from the addition of acids, acidulous refactory material, or non-metallic oxides thereto, they may be used in accordance with our invention. On the other hand, the high activity of acidic boron-containing

components may be reduced where alkaline substances such as certain alkaline clays, alkaline metallic oxides, and the like, are present in the refractory foundry material; as the acidity of the boron-containing component and/or refractory foundry material is increased, the resulting increase in the curing rate may require careful control of the reaction mixture.

The boron-containing component enables lower boiling fractions of the curable furfuryl alcohol polymer component to be cured below their respective volatilization points, thus enabling a greater mass of the curable furfuryl alcohol polymer component to be cured and the resulting hardened core or foundry structure to possess higher tensile strength and scratch hardness values. As the relative proportion of boron-containing component to curable furfuryl alcohol polymer component is increased in the heat curable binder, there is a tendency for the cured or hardened core to collapse more readily in the presence of molten metal at a given temperature. Furthermore, the boron-containing component has the outstanding characteristic of being capable of being mixed with the curable furfuryl alcohol polymer component so as to produce a heat curable binder that is stable at conventional storage temperatures and yet curable at moderately elevated temperatures.

When the boron-containing component is highly soluble in the curable furfuryl alcohol polymer component (e.g., boric acid, boric oxide, ammonium borate, or certain borate esters), the reaction mixture or binder ultimately becomes a homogeneous solution when moderately elevated curing temperatures are reached; as a consequence of this solubility, uniform curing and a more homogeneous reaction product results.

We have noted that boron-containing compounds and complexes contemplated by our invention serve to reduce the time required to cure, at about 180–500° F., the curable furfuryl alcohol polymer component in admixture with the refractory foundry material. That is, the time required to cure a given curable furfuryl alcohol polymer component at a selected concentration (i.e., ratio of curable furfuryl alcohol polymer component to refractory foundry material) may be reduced 10% and more (as measured by the development of tensile strength), with our boron-containing component.

The term "stable," when used with respect to the stable, heat curable binder, is herein intended to refer to a heat curable binder or reaction mixture which contains a furfuryl alcohol polymer component and boron-containing component and that is benign at temperatures up to at least about 125° F. and may be admixed with particulate refractory foundry material and then heated at temperatures of about 180–500° F. to form a hard, self-supporting foundry structure. The stable, heat curable binder includes reaction mixtures of furfuryl alcohol polymer component and boron-containing component that may be stored in a sealed container for at least 48 hours at temperatures up to at least about 125° F. without losing their usefulness as an effective foundry binder, although there might be some increase in their viscosity and some small tendency for them to develop gel particles. On the other hand, the stable binder may retain its stability in a sealed container for many months, or even a year or more, at 70° F.

The composition of various suitable furfuryl alcohol polymer components and boron-containing components vary (for example, the furfuryl alcohol polymer component may contain a minor proportion of a furfuryl alcohol monomer and/or impurities or components); therefore, the minimum proportion of boron-containing component that may be effectively used (in the heat curable binder) with the furfuryl alcohol polymer component cannot be stated with exact precision. Generally, curable furfuryl alcohol polymer component-boron-containing component binders containing as low as about 1% by weight of boron-containing component, based on the weight of furfuryl alcohol polymer component, produces a significant improvement in the curing rate of the core.

For example, when boric acid is used, the stable, heat curable binder may contain as low as about 2½% by weight of boric acid with about 97½% by weight of the furfuryl alcohol polymer component (produced by the method set forth in Example 1, infra), and as high as equal parts by weight of boric acid and said polymer. When more than equal proportions of boric acid to furfuryl alcohol polymer component are used, no appreciable advantage is realized in regard to the curing of the binder, although other desired effects which do not effect binding may be obtained. Therefore, the levels of curable binder (i.e., curable furfuryl alcohol component plus boron-containing component) herein specified are intended to infer that additional boron-containing component, but not curable furfuryl alcohol component, may be present in the foundry mix or structure and that this added amount is, however, not essential to the forming of a satisfactory refractory binder and foundry structure. We prefer to use in our curable mixture 10–30% by weight of boric acid and 90–70% by weight of a furfuryl alcohol polymer component such as produced by Example 1, infra. In the event that a proton donor catalyst, such as hypophosphorus acid, is used in conjunction with our curable mixture or binder, comparatively lower proportions of boric acid to furfuryl alcohol polymer component may be used.

When boric oxide is used, the curable binder may contain as low as about 2½% by weight of boric oxide with about 97½% by weight of the polymer produced by the method set forth in Example 1, and, if desired, as much as 15% by weight boric oxide may be used with 85% by weight of said polymer. We prefer to use 6–20% by weight boric oxide with 94–80% by weight of a furfuryl alcohol polymer such as produced by Example 1.

A sufficient amount of curable mixture should be mulled with the refractory foundry material so as to permit the binder to intimately coat the refractory material. For example, mixes containing as low as about 1–3 parts by weight of curable binder for each 100 parts by weight of refractory foundry material have been found to be sufficient for most foundry purposes; thus, a mix containing 1% by weight of a curable binder consisting of boric acid and furfuryl alcohol polymer may be used with 99% by weight of refractory foundry material. The upper limit of the relative proportion of curable binder to refractory foundry material should always be sufficiently low so as to enable the cured core to have sufficient porosity and possess desirable collapse properties.

If desired, cereal (e.g., corn flour) and water may be incorporated into the refractory foundry material heat curable binder mix in order to give the mulled mix green strength properties. These green strength binders may also permit the use of lower proportions of the curable furfuryl alcohol polymer component in the curable mixture of binder and refractory foundry material. For example, one part by weight cereal and 2.5–3 parts by weight water may be added to 100 parts by weight of refractory foundry material, and a desired proportion of boron-containing component and about 0.5 part and above, by weight, of furfuryl alcohol polymer may be added to a mulled mix containing the cereal, water, and refractory foundry material.

When water is present in the mulled core mix, higher proportions of boron-containing component to furfuryl alcohol polymer component as compared to a water-free mix, have been found to be advantageous. As stated above, we prefer to use 10–30% and 6–20% by weight of boric acid and boric oxide, respectively, with the polymer produced in accordance with Example 1; when water is present in the core mix, the upper portion of these ranges are preferred.

In producing foundry cores in accordance with our in-

vention, the curable binder is mulled with refractory foundry material, the resulting mix is shaped, and the shaped mix is heated to about 180–500° F., preferably about 200–400° F., so as to produce a core having the desired properties.

We have found that when the curable binder and refractory foundry material are mulled and then heated below about 180° F., the curing reaction is too slow for conventional foundry purposes. However, at about 200° F., curing of the curable binder and hardening of the core occurs at a satisfactory rate and the hardened or cured core will possess excellent foundry core properties. As temperatures above about 200° F. are used, the curing temperature and curing time should be correlated so as to obtain maximum binding of the refractory foundry material and produce a core having desirable collapsibility and compressibility properties when in contact with the poured molten metal.

Curing conditions (i.e., time and temperature) which produce undercuring, produce soft cores having lower scratch hardness and tensile strength values. On the other hand, curing conditions which produce overcuring, produce cores which have passed their maximum scratch hardness and tensile strength values. In effect, overcuring may be regarded as destroying binding properties at a somewhat lower temperature and rate than is normally effected by contacting the core with molten metal. The destruction of binding properties by heat is referred to as collapse. Thus, the curing temperature and the time allowed for curing should be correlated so as to produce a core having the desired tensile strength. In some cases, it may be desirable to produce cores having less than their maximum potential or obtainable tensile strength for given amounts of furfuryl alcohol polymer component and boron-containing component because of the economies which result from the use of less time and/or lower curing temperatures.

Linseed oil may be incorporated into the core mix as an extender for the curable binder, but when used, the core generally requires the use of a higher curing temperature and/or longer period of curing.

In producing foundry cores in accordance with our invention, the furfuryl alcohol polymer component and boron-containing component may be premixed so as to produce the curable binder. The binder is then mulled with the refractory material until an intimate admixture of these materials is obtained. The mulled mix may then be placed into core boxes with air blowing, or slinging or conventional hand-packing methods. If desired, the filled core box may be jolted or its contents may be rammed so as to assure dense and complete filling of the confines of the core box.

In the event that the refractory foundry material and binder mix is incapable of maintaining its shape without support, hot gas or air may be blown through the mix prior to the removal of the mix from the core box in order to produce sufficient hardening of the core, or, as alternative procedures, the filled core box may be heated in an oven or a hot core box may be used.

If the core possesses sufficient green strength so as to be capable of maintaining its shape without the support of the box, the mix may be removed from the box and hardened in an oven; as an alternative procedure, the core box itself may be heated to effect the final cure of the mix.

After the mix is cured, the hardened core may be used for shaping molten ferrous metals, cuprous metals, zinc, and aluminum. For example, excellent castings are produced by pouring molten iron at about 2900° F. into molds containing our cured cores; the collapse rate of the core and the surface finish of the casting will be of a superior nature. Other metals having relatively low melting temperatures, such as 1200–1500° F., may be poured around the core depending upon the collapse requirement for the core. Where a slowly collapsing core is required for low melting metals, our curable heat binders may possess satisfactory collapse properties when properly controlled proportions of boron-containing component are used.

Our heat curable binders may also be used in so-called "shell mold" processes whenever conditions so permit. A typical phenol-formaldehyde resin commonly used in shell molding permits the formation of a self-sustaining coating at about 350° F. and requires the additional heating of the pattern and adherent coating to about 550° F. in order to effect the ultimate curing of the mix; our curable binder may be cured to bind refractory foundry sand material in a like manner at the same or lower temperatures.

EXAMPLE 1

The following procedure may be used to produce a suitable furfuryl alcohol polymer component: Warm 2,997 lbs. of furfuryl alcohol, while stirring, in a 1,200 gallon gross capacity, stainless steel, heated (about 180° F.), closed reaction kettle equipped with reflux condenser, agitator, jacket for water-cooling, and gas-fired Selas burners automatically set to about 180° F. Add, gradually 169.7 lbs. of a 2% aqueous solution of commercial 85% phosphoric acid in 10 pound increments about 5 minutes apart, adding additional 10 pound increments as any exotherm is dissipated; this operation usually consumes about 1½ hours. Continue stirring and observing the reaction mixture for 10 to 15 minutes in order to be certain that the temperature will drop when heat is removed and that no exotherm will occur; then add a second unit of 84.8 lbs. of 2% phosphoric acid in 10 pound increments, as before, over a period of 45 to 60 minutes, depending on the time required to dissipate the heat. After a second holding period of 10 to 15 minutes and assurance that exothermic heat has subsided, again add, incrementally, another 84.9 lbs. of acid in a period of 45 to 60 minutes.

If at any time an exotherm is observed, maintain the temperature of the contents of the reaction vessel at 180° F. by admitting a sufficient quantity of cold water. If no exotherm occurs after the final addition of the last unit of acid, the temperature of the reaction mixture should be raised slowly to refluxing temperature (i.e., 200–215° F.) and held at gentle reflux until a milky appearance occurs at a viscosity of A to B (Gardner-Holdt scale); controls should be run every 5 minutes until J to L viscosity is reached. Water may be removed by decantation or centrifugation in order to obtain true viscosity values for the furfuryl alcohol component. After a viscosity of about J to L is reached, heat should be removed and the reaction mixture should be neutralized to a pH of 5 by the addition of about 30 lbs. of 10% by weight aqueous sodium hydroxide.

EXAMPLE 2

Curable mixtures of only boric acid (i.e., H_3BO_3) and the furfuryl alcohol polymer component produced in accordance with Example 1 were prepared in the following proportions:

(*a*) 1 part by wt. boric acid
2 parts by wt. furfuryl alcohol polymer component
(*b*) 1 part by wt. boric acid
4 parts by wt. furfuryl alcohol polymer component
(*c*) 1 part by wt. boric acid
9 parts by wt. furfuryl alcohol polymer component
(*d*) 1 part by wt. boric acid
19 parts by wt. furfuryl alcohol polymer component

These curable binders were aged in separate closed containers for fourteen days; no change in their appearance occurred, except for a darkening of their surfaces. Other samples of these curable mixtures which were stored for fifty days showed slight or insignificant loss

of binding properties without observable additional changes in color, except at their surfaces, and viscosity.

EXAMPLE 3

Table I, infra, shows tensile strength data which were obtained by curing separate samples of a mix consisting of refractory core material, furfuryl alcohol polymer component, and boric acid at 200° F. and 300° F. for 1½ hours and 1 hour, respectively. The table also shows that no significant or measurable loss of binding properties was noted after the uncured mulled mixtures were stored in closed containers for 10 days.

The tensile strength data were obtained by preparing standard tensile bars in accordance with standard American Foundry Society methods using Dietert Machines to form, tamp, and break the bars; curing was effected in ovens. The term "parts" is intended to refer to parts by weight.

Table I

Parts refractory material [1]	Parts boric acid (H_3BO_3)	Parts furfuryl alcohol polymer component [2]	Tensile strength (p.s.i.)	
			200° F. cure (for 1½ hrs.)	300° F. cure (for 1 hr.)
100	0.32	2.5	>370	>370
100	0.63	2.5	>300	>370
100	1.25	2.5	>300	>370
CURED, REFRACTORY MATERIAL-BINDER MIX AFTER 10 DAYS				
100	0.32	2.5	>370	>370
100	0.63	2.5	>370	>370
100	1.25	2.5	>370	>370

[1] Ottawa (A.F.S. fineness No. 17) sand.
[2] Component produced in accordance with the method set forth in Example 1.

Refractory foundry material which had been mulled with the proportions of boric acid and furfuryl alcohol polymer set forth in Table I was found to be useful after being stored in closed containers for as much as 6 weeks; the resulting loss of tensile strength was found to be unimportant for most foundry purposes.

EXAMPLE 4

The tensile strength data set forth in Table II, infra, were obtained in the same manner as described in Example 2, supra, with various specified proportions of boric acid and furfuryl alcohol polymer. The term "parts" in Table II refers to parts by weight.

Table II

Parts refractory material [1]	Parts (boric acid) (H_3BO_3)	Parts furfuryl alcohol polymer component [2]	Tensile strength (p.s.i.)	
			200° F. cure (for 1½ hrs.)	300° F. cure (for 1 hr.)
100	0.04	0.5	250	350
100	0.08	0.5	275	350
100	0.19	1.5	>370	-------
100	0.38	1.5	>370	-------
100	0.32	2.5	>370	>370
100	0.63	2.5	>370	>370
100	1.25	2.5	300	>370

[1] Ottawa (A.F.S. No. 17) sand.
[2] Component produced in accordance with the method set forth in Example 1.

Tables III and IV, infra, show tensile strengths which were obtained by incorporating corn flour and water into various refractory mixes. The tensile strength data set forth in these tables were obtained by preparing standard tensile bars in accordance with standard A.F.S. methods using Dietert Machines to form, tamp, and break the bars. Curing was effected in ovens.

EXAMPLE 5

The data in Table III were obtained by testing mixes which contained 100 parts by weight of Ottawa sand, varying parts by weight of boric acid, varying parts by weight of furfuryl alcohol polymer component produced by the method of Example 1, one part by weight of corn flour, and 2.5 parts by weight of water. These data suggests that relatively higher proportions of boric acid may be used in conjunction with the furfuryl alcohol polymer when moisture is present.

Table III

Parts by weight refractory material	Parts by weight of H_3BO_3	Parts by weight furfuryl alcohol ploymer component of Example 1	Parts by weight corn flour	Parts by weight water	Tensile strength (p.s.i.) cores cured at 250° F. for 1 hr.
100 Ottawa sand (A.F.S. No. 17)	0.1	0.5	1	2.5	Low
Do	0.3	0.5	1	2.5	270
Do	0.5	0.5	1	2.5	230
Do	0.25	1.0	1	2.5	160
Do	0.5	1.0	1	2.5	375
Do	1.0	1.0	1	2.5	335
Do	2.0	1.0	1	2.5	185

EXAMPLE 6

The data in Table IV, infra, show that refractory material which contains reclaimed sand or a mixture of unused

Table IV

Parts by weight of lake sand	Parts by weight of reclaimed lake sand	Parts by weight of curable mixture of equal parts by weight of polymer of Example 1 and H_3BO_3	Parts by weight of water	Parts by weight of corn flour	Tensile strength (p.s.i.)			
					Cured at 300° F. after—		Cured at 350°–400° F. after—	
					½ hr.	1½ hrs.	½ hr.	1½ hrs.
50	50	1	2.5	1	100	-------	-------	-------
50	50	1.5	2.5	1	370	370	200	150
50	50	1.5	2.5	1	280	370	200	175
50	50	2.5	2.5	1	370	370	320	325
50	50	2.5	2.5	1	200	370	230	155
100	-------	1.5	2.5	1	155	(370)	-------	-------
-------	100	1.5	2.5	1	180	(370)	-------	-------
50	50	1.5	2.5	1	(200)	(370)	-------	-------

as well as reclaimed refractory foundry material may be used to produce satisfactory foundry cores with our curable mixtures. Three hundred and seventy was the highest reading that could be determined with the tensile-testing machine used in obtaining tensile strength values; the tensile strength values set forth in brackets were obtained by interpolation.

The data in Table IV, supra, show unexpectedly low tensile values for cures at 350°–400° F. In the absence of green strength binders such as water plus cereal, cures within this temperature range produce cores with comparatively higher tensile values which are maintained for comparatively long periods of time.

We have found that an admixture of furfuryl alcohol monomer plus a boron-containing component such as boric acid serves as a parting-agent or lubricant for facilitating removal of a shaped core from the core box. It would appear that the high solubility of the sticky furfuryl alcohol polymer component in the monomer portion of the parting-agent causes a non-stocky, diluted layer to be formed on the walls of the core box. In addition, this admixture does not introduce foreign matter into the core, and, as a result of its use, the cured core may possess additional surface hardness properties. However, when this parting-agent or lubricant is used, the amount of furfuryl alcohol monomer present in the core should never exceed or equal that of the polymer.

The term "consisting essentially of" as used in the claims is intended to exclude the presence of unnamed materials in such amounts as to interfere substantially with the properties and characteristics possessed by the composition set forth but to include the presence of other materials in such amounts as not substantially to affect said properties and characteristics adversely.

The foregoing detailed description has been given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, as modifications will be obvious to those skilled in the art.

We claim:

1. An essentially solid, shapeable, hardenable, porous foundry mix which comprises: about 91–99.5% by weight refractory foundry sand material, based on the weight of the entire foundry mix, and about 0.5–6% by weight, based on the weight of the entire foundry mix, of a heat curable resinous binder containing a stable, heat curable binder having about 0.5–4.5% by weight of curable furfuryl alcohol polymer component, based on the weight of the entire foundry mix, and at least about 1% by weight, based on the weight of the furfuryl alcohol polymer component, of a boron-containing component that provides, with the polymer component, a stable binder at temperatures up to at least about 125° F., said mix suitably hardening at about 180–500° F. into a hard, self-supporting, porous foundry structure against which molten metal may be poured and shaped.

2. The foundry mix of claim 1 wherein said boron-containing component contains a member of the group consisting of boric oxide and hydrates of boric oxide.

3. An essentially solid, hard, porous foundry structure against which molten metal may be poured before said structure undergoes distortion or collapses, which comprises: about 91–99.5% by weight refractory foundry sand material, based on the weight of the entire foundry structure, bonded with about 0.5–6% by weight, based on the weight of the entire foundry structure, of a polymerized reaction product produced by mixing and then heating an admixture of said refractory material and a heat curable resinous binder at about 180–500° F., said heat curable resinous binder containing a stable, heat curable binder having about 0.5–4% by weight of curable furfuryl alcohol polymer component, based on the weight of the entire foundry mix, and at least about 1% by weight, based on the weight of the furfuryl alcohol polymer component, of a boron-containing component that provides, with the polymer component, a binder that is stable at temperatures up to at least about 125° F.

4. The foundry structure of claim 3 wherein said boron-containing component contains a member of the group consisting of boric oxide and hydrates of boric oxide.

5. A method of producing a hardened foundry structure for shaping molten metal comprising: mulling an essentially solid, hardenable foundry mix containing about 91–99.5% by weight refractory foundry sand material, based on the weight of the entire foundry mix, about 0.5–6% by weight, based on the weight of the entire foundry mix, of heat curable resinous binder containing a stable, heat curable binder having about 0.5–4.5% by weight of curable furfuryl alcohol polymer component, based on the weight of the entire foundry structure, and at least about 1% by weight, based on the weight of the furfuryl alcohol polymer component, of a boron-containing component that provides, with the polymer component, a stable binder at temperatures up to at least about 125° F., whereby a shapeable mix is formed, forming a self-supporting, shaped, porous foundry mass which hardens at about 180–500° F., and curing the curable binder in said shaped mass by heating said mass to at least about 180° F. to produce a hard, porous structure against which molten metal may be poured and shaped without undergoing distortion or collapsing.

6. The method of claim 5 wherein said boron-containing component contains a member of the group consisting of boric oxide and hydrates of boric oxide.

7. An essentially solid, shapeable, hardenable porous foundry mix which consists essentially of: a major proportion of refractory foundry sand material and less than about 3.75% by weight, based on the weight of the entire foundry mix, of a stable, heat curable binder containing at least about 0.5% by weight curable furfuryl alcohol polymer component, based on the weight of the entire foundry mix, and at least about 1% by weight, based on the weight of the furfuryl alcohol polymer component, of a boron-containing component that provides a stable binder at temperatures up to at least about 125° F., said mix suitably hardening at about 180–500° F. into a hard, self-supporting, porous foundry structure against which molten metal may be poured and shaped before said hardened structure undergoes distortion or collapses.

8. The foundry mix of claim 7 wherein said boron-containing component contains a member of the group consisting of boric oxide and hydrates of boric oxide.

9. An essentially solid, hard, porous foundry structure against which molten metal may be poured before said structure undergoes distortion or collapses, which consists essentially of: a major proportion of refractory foundry sand material bonded with less than about 3.75% by weight, based on the weight of the entire foundry structure, of a polymerized reaction product produced by mixing and then heating an admixture of said refractory material and a stable, heat curable binder at about 180–500° F., said stable, heat curable binder containing at least about 0.5% by weight curable furfuryl alcohol polymer component, based on the weight of entire foundry structure, and at least about 1% by weight, based on the weight of the furfuryl alcohol polymer component, of a boron-containing component that provides a stable binder at temperatures up to at least about 125° F.

10. The foundry structure of claim 9 wherein said boron-containing component contains a member of the group consisting of boric oxide and hydrates of boric oxide.

11. A method of producing a hardened foundry structure for shaping molten metal comprising: mulling an essentially solid, hardenable foundry mix consisting essentially of a major proportion of refractory foundry sand material with less than about 3.75% by weight, based on the weight of the entire foundry mix, of a stable, heat curable binder containing at least about 0.5% by weight

of curable furfuryl alcohol polymer component, based on the weight of the entire foundry mix, and at least about 1% by weight, based on the weight of the furfuryl alcohol polymer component, of a boron-containing component that provides a stable binder at temperatures up to at least about 125° F., whereby a shapeable mix is formed, forming a self-supporting, shaped, porous foundry mass which hardens at about 180–500° F., and curing the curable binder in said shaped mass by heating said mass to at least about 180° F. to produce a hard, porous structure against which molten metal may be poured and shaped before said structure undergoes distortion or collapses.

12. The method of claim 11 wherein said boron-containing component contains a member of the group consisting of boric oxide and hydrates of boric oxide.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

March 6, 1962

Patent No. 3,024,215

Stephen E. Freeman et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 37, after "distorted" insert -- prior --; column 2, line 6, for "ceral" read -- cereal --; column 10, lines 31 and 32, for "suggests" read -- suggest --.

Signed and sealed this 5th day of November 1963.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWIN L. REYNOLDS

Acting Commissioner of Patents