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FOUNDRY COMPOSITION WITH CROSS-LINKED POLYESTER BINDER

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Fig. 1.

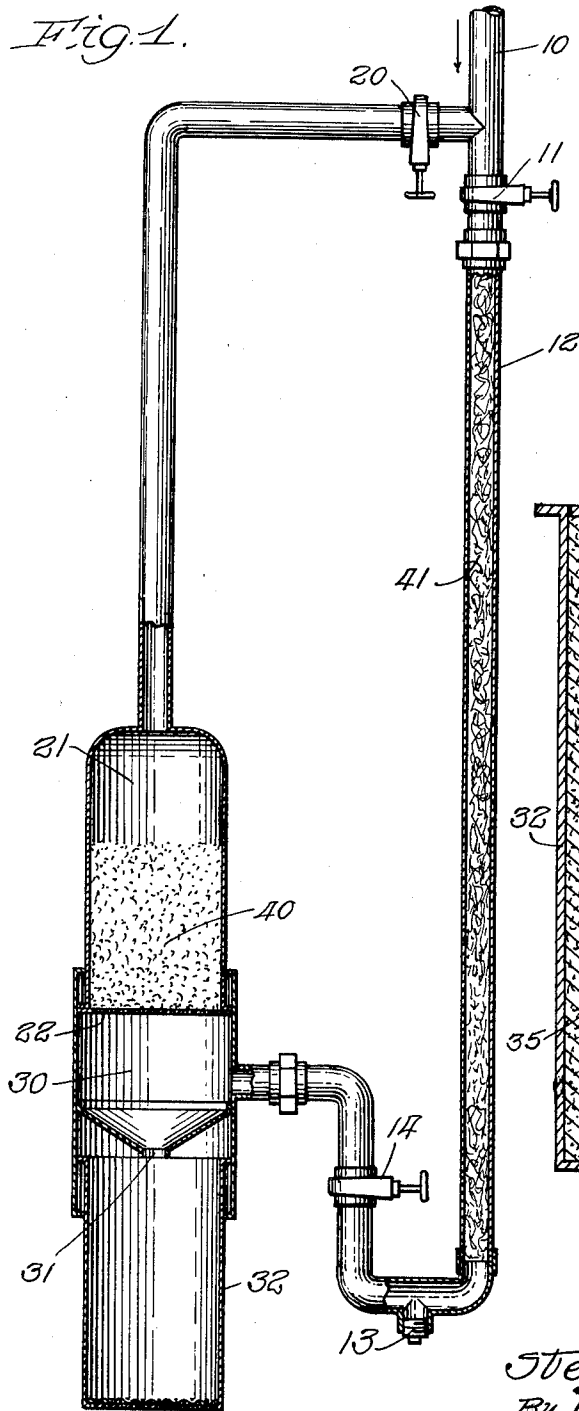
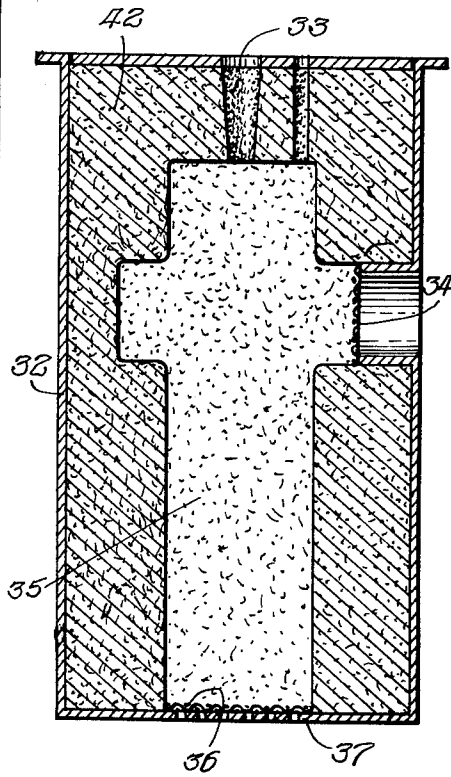


Fig. 2.



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FOUNDRY COMPOSITION WITH CROSS-LINKED POLYESTER BINDER

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This application is a continuation-in-part of my co-pending application Serial No. 636,434, filed January 25, 1957, now abandoned.

This invention relates to compositions, methods, and apparatus for the production of foundry cores.

In casting metal objects having a cavity, a foundry core may be positioned in the mold, which core, during the pouring of molten metal into the mold, occupies and thus forms the final cavity.

Foundry cores may be conventionally produced by mixing refractory core such as core sand mixtures and molding sand with a binder such as drying oils, as exemplified by linseed oil, or thermosetting resins such as urea-formaldehyde, phenol-formaldehyde and melamine-formaldehyde. The refractory-binder mix may then be shaped into the desired form and heated or baked at elevated temperatures which may reach as high as 250° to 600° F. in order to dry the oil or cure the resin, thus enabling the refractory material to be bound together by the binder into a rigid structure which will not collapse in the mold before the molten metal "freezes" or "sets." If desired, cereals such as dextrin and starch mixed with water may be added to the refractory material and conventional binders in order to enable the shaped core to develop green strength so that it maintains its shape and does not crumble prior to the application of heat in the baking step.

The application of heat to induce or facilitate the drying or curing of the binder and hardening of the mix requires the use of costly and space-consuming equipment such as ovens.

The use of a particular binder with foundry refractory material to make foundry cores is a highly specific use which requires that the resulting core have particular characteristics which are not generally associated with refractory-binder or filler-binder mixes used in other arts. For example, the ideal foundry core mix (i.e., refractory material plus binder) should (1) remain plastic sufficiently long to permit shaping of the core, (2) develop green strength within a reasonable period of time, preferably at room temperature, so that the shaped core will maintain its shape prior to and during baking, (3) reach high tensile strength values, (4) permit molten metal to be poured against the hardened core (e.g., baked cores) without undergoing distortion or excessive gassing, (5) enable the hardened core to be permeable so as to permit gases to be evolved therefrom during the casting operation, and (6) enable the hardened core to readily collapse after the molten metal has "set." These are stringent requirements.

My invention contemplates the use of compositions, methods, and apparatus which do not necessitate the application or utilization of heat in order to produce a core which develops, in a comparatively short period of time, sufficient tensile strength and scratch hardness values so as to enable the core to maintain its shape when molten metal is poured against it and collapse after the metal freezes or sets. The core will undergo continuous curing up to the time these values are reached and will rapidly develop green strength during this curing cycle; however, green strength is only an intermediate, transitory condition developed during the curing cycle.

My invention includes the production of foundry cores (e.g., without necessitating the application of heat) by bonding particulate refractory foundry core material with a binder system to form a curable mix. The curable binder system comprises (a) a resin mix having therein an ethylenically unsaturated polyester formed from the reaction of an unsaturated alpha-beta ethylenically unsaturated polycarboxylic acid with a polyhydric alcohol, and a monomeric ethylenically unsaturated polymerizable cross-linking agent, (b) a per-oxidizing polymerization catalyst such as an acyl peroxide or hydroperoxide, (c) a polymerization accelerator in the form of a metallic drier or organic salt when the peroxide catalyst is not an acyl peroxide such as benzoyl or lauroyl peroxide, and (d) an amine polymerization promoter that is free of nitro or nitroso groups. When an amine polymerization promoter is used in the vapor phase, it should be the last of said members of said binder system that is added to the curable mix.

The curable mix produced will develop tensile strength values up to 150-200 p.s.i., and above, as determined by an H. W. Dietert sand strength machine. In addition, the curable mix will develop hardness values up to 80-90, and above, as determined by an H. W. Dietert dry hardness tester No. 673. Cured cores may be immediately used in casting both high and low temperature molten metal such as molten iron, steel, aluminum, brass, magnesium, and the like.

The ethylenically unsaturated polyester resin is the polymerized reaction product of at least one polyhydric alcohol and at least one unsaturated polycarboxylic acid or anhydride thereof. The reaction product may be formed by heating alpha-beta ethylenically unsaturated dicarboxylic acids such as maleic, fumaric, and their anhydrides with a polyhydric alcohol or a glycol such as ethylene glycol, diethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, and 1,3 butylene glycol. Unsaturated tricarboxylic acid or anhydride, such as trimellitic anhydride, may also be used. It is essential that some of the polycarboxylic acid component of the polyester resin contain an unsaturated ethylenic linkage.

The relatively volatile, ethylenically unsaturated compound has the group $\text{CH}_2=\text{C}<$ and serves to render the unsaturated polyester resin less viscous and to cross-link said resin during curing so as to produce a cross-linked or 3-dimensional resin which is thermosetting in character. Cross-linking agents such as exemplified by styrene, vinyl toluene, vinyl acetate, and diallyl esters (e.g., diallyl phthalate) may be used.

The peroxide, peroxidic or per-oxidizing polymerization catalysts should be soluble in the aforesaid polymerizable mixture and must be capable of inducing polymerization of said mixture in the presence of refractory material at temperatures below about 125° C. or, preferably, between 20-40° C. Peroxides or organo-peroxidizing agents such as acyl peroxide and hydroperoxide have been found to be particularly effective. For example, good results are obtained with diacyl peroxides such as benzoyl or lauroyl peroxides and hydroperoxides such as methyl ethyl ketone peroxide, cumene hydroperoxide, and t-butyl hydroperoxide.

Metallic driers or organic salts having active metal therein may be used as the polymerization accelerator. The accelerator is used jointly with the hydroperoxide catalyst, but is not needed when acyl peroxides such as benzoyl and lauroyl peroxides are used. The accelerators are salts of organic acids such as naphthenic acid. They include manganese and, preferably, cobalt (e.g., cobalt naphthenate or octoate). For example, a 50% solution of cobalt naphthenate (containing 6% cobalt) in naphtha may be used.

The amine polymerization promoter must be free of nitro or nitroso groups and have a boiling point sufficiently low so as to volatilize without undergoing decomposition in the presence of the refractory material and other members of the polymerizable mixture at temperatures below about 125° C. or, preferably, between 20–40° C. The promoters of the present invention markedly accelerate or promote the polymerization of the polymerizable mixture at temperatures up to 250° C. in the presence of refractory material. Particularly good results are obtained with N,N-dialkyl aryl tertiary monoamines such as dimethylaniline, diethylaniline, N,N-dimethyl-p-toluidine and N,N-dimethyl-o-toluidine.

If desired, hydroquinone and p-tertiary butyl catechol may be incorporated into the polymerizable mixture as inhibitors and stabilizers. For example, hydroquinone may be present with the polyhydric alcohol and unsaturated dicarboxylic acid or anhydride thereof during the formation of the unsaturated polyester resin, and the p-tertiary butyl catechol inhibitor may be added to the unsaturated polyester resin along with the ethylenically unsaturated cross-linking compound. Care should be exercised so as to avoid the use of excessively high levels of inhibitors and stabilizers in order to obviate an excessive reduction in the polymerization activity of the polymerizable mixture.

The terms "refractory material" or "refractory foundry material" are intended to refer to unused and/or reclaimed, non-deleterious refractory material which may be admixed with members of the polymerizable mixture so as to produce a curable mix which may be shaped and hardened sufficiently, so as to produce a core having a desirable tensile strength value, without necessitating the application of heat. Thus, these phrases are intended to include conventional washed refractory 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 cores. The refractory material should be free of any deleterious materials which tend to interfere with the effective curing of the polymerizable mixture. The most effective results are obtained with dry refractory material.

A core which is suitable for casting metals may be formed, for example, by a method comprising: mulling refractory foundry core material with a polymerizable accelerator in the form of a metallic drier or organic salt, thereby coating the refractory material; adding to the coated refractory material a pre-mix comprising a resin mix having therein an ethylenically unsaturated polyester and cross-linking agent, and a soluble per-oxidizing polymerization catalyst such as a hydroperoxide; mulling the resulting mix to form the first mulled mix; passing the first mulled mix through an amine mixing zone so as to uniformly admix the first mulled mix with an amine promoter (i.e., in the vapor phase) and/or a second mulled mix comprising an admixture of a relatively small amount of refractory material and amine polymerization promoter, to form a curable mix; packing the curable mix into a core box so as to form a shaped curable mix that will rapidly develop green strength (e.g., without necessitating the application of heat); and permitting the shaped core to develop sufficient tensile strength and scratch hardness values as to enable the core to maintain its shape when molten metal is poured against it and collapse after the metal freezes or sets. If one uses an acyl peroxide such as benzoyl peroxide or lauroyl peroxide, said polymerizable accelerator should be omitted.

Other procedures, of course, may be used. For example, the first mulled mix may be packed or blown into the core box, and the amine polymerization promoter, in the vapor phase, may be blown into the first mulled mix in the core box by means of air so as to promptly initiate or cause the shaped curable mix to harden.

If desired, a portion of the accelerator may be incorporated into the pre-mix and added therewith to the mixture of refractory material and remaining portion of accelera-

tor. The peroxidic catalyst may be directly admixed with the refractory material and accelerator; however, extreme care should be exercised so that the peroxidic catalyst is not directly admixed with the accelerator.

The rapid development of said green strength is a transitory, intermediate condition which occurs during curing, but prior to the development of scratch hardness and tensile strength values that permit molten metal to be poured against the core.

The amine polymerization promoter should not be stored in the presence of the peroxidic catalyst or polymerizable mixture of the unsaturated polyester resin and cross-linking agent because a reduction in the rate of curing of the curable mix results. The promoter should be, preferably, the last ingredient added to the curable mixture.

The internal confines of the core box may be coated with a parting-agent, such as starch or a lubricating oil, for facilitating removal of a shaped core from the core box.

The curable mixes of some of the following examples were prepared for test purposes only and were not prepared in complete conformance with the above-described procedure. When the following examples state that the curable mix "hardened" or is "hard," the mix has developed a tensile strength value that is sufficiently high to permit molten metal to be immediately poured against it.

EXAMPLE I

The polymerizable mixture of unsaturated polyester resin and ethylenically unsaturated monomer may be prepared as follows:

A mixture of 15.10 parts by weight phthalic anhydride, 10 parts by weight maleic anhydride, 18.54 parts by weight propylene glycol, and 0.004 part by weight of hydroquinone may be heated to 200° F. in a closed vessel under carbon dioxide gas or other inert atmosphere. The application of heat should be discontinued and the reaction permitted to exotherm to 300–320° F. The reaction mixture may then be heated slowly to 400° F. and the evolution of the water of esterification effected. After the reaction mixture attains an acid value of 33–35, the application of heat should be discontinued and the reaction mixture permitted to cool to 220° F. The resulting product is an unsaturated polyester resin.

20 parts by weight of vinyl toluene solvent and 0.004 part by weight of p-tertiary butyl catechol may be added to the polyester resin while the resin is being agitated at about 220° F. The resulting polymerizable mixture should be cooled to at least 130° F. for storage.

This polymerizable mixture of unsaturated polyester resin-ethylenically unsaturated cross-linking monomer may be stored for at least six months at 70° F.

EXAMPLE II

The same procedure and ingredients set forth in Example I may be used, with the exception that styrene monomer may be substituted for the vinyl toluene monomer.

EXAMPLE III

A curable mix of refractory material and polymerizable mixture was prepared for test purposes in accordance with the following procedure, although said procedure does not conform with my preferred methods of preparing curable mixes and cores set forth, supra:

4000 gm. of dry Ottawa sand (A.F.S.—47) were placed in a mixer. Mixing of the refractory material was effected while 3.3 gm. of 50% dimethyl aniline promoter in varnish maker's and painter's naphtha, hereinafter referred to as "naphtha," was added in a thin stream to the sand. 8.3 gm. of 50% solution of 6% cobalt naphthenate in naphtha (i.e., cobalt naphthenate containing 6% cobalt is admixed with naphtha to form a 50% solution) was added to and mixed with the sand and promoter.

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The polymerizable mixture was prepared by (a) adding 2.1 ml. of 50% methyl ethyl ketone peroxide in dimethyl phthalate to 165 gm. of the polymerizable mixture of Example II, (b) thoroughly mixing this admixture, (c) adding 5 drops of a solution of cobalt naphthenate in naphtha, and (d) mixing the resulting product.

This polymerizable mixture was added in a steady stream to the promoter-sand mix and the resulting curable mix was stirred thoroughly for 4-5 minutes, packed into a mold, and tamped. The mass hardened in 5 to 10 minutes.

EXAMPLE IV

The effect of various levels of p-tertiary butyl catechol on the rate of curing of the curable mix is shown in Table II, *infra*.

Polymerizable Mixture A was prepared by admixing: 40 gm. of the polymerizable mixture of Example II, *supra*, 0.0125%, based on the weight of the styrene monomer, of p-tertiary butyl catechol inhibitor, 0.4 gm. of benzoyl peroxide, and 0.3 ml. of 10% dimethyl aniline in acetone. Polymerizable Mixture B and Polymerizable Mixture C were prepared with the same proportion of ingredients as Polymerizable Mixture A, with the exception that 0.025% and 0.05%, respectively, of the inhibitor (based on the styrene monomer) were used. The composition of each of these polymerizable mixtures is shown in Table I, *infra*.

Table II shows the relative curing rates of (a) Polymerizable Mixtures A, B, and C per se and (b) curable mixes containing each of said polymerizable mixtures, sand, dimethyl aniline promoter and cobalt-accelerator. The rate of curing was found to be directly proportional to the level of inhibitor contained in the polymerizable mixture (i.e., curing rates (expressed in time) of the polymerizable mixtures and curable mixes increased when increased levels of inhibitor were used).

Table I

POLYMERIZABLE MIXTURES

	Polymerizable Mixture A	Polymerizable Mixture B	Polymerizable Mixture C
Curable mixture of Example II, 15.1 parts by weight phthalic anhydride, 10 parts by weight maleic anhydride, 18.54 parts by weight propylene glycol, 20 parts by weight styrene monomer, Benzoyl peroxide, 10% dimethyl aniline in acetone	40 gm. (Contains 0.0125% p-tertiary butyl catechol based on styrene.) 0.4 gm. 0.3 ml.	40 gm. (Contains 0.025% p-tertiary butyl catechol based on styrene.) 0.4 gm. 0.3 ml.	40 gm. (Contains 0.05% p-tertiary butyl catechol based on styrene.) 0.4 gm. 0.3 ml.

Table II

EFFECT OF VARIOUS LEVELS OF INHIBITOR ON THE RATE OF CURE OF THE CURABLE MIX

Ingredients	Sample 1	Sample 2	Sample 3
Polymerizable Mixture A	4 gm. (hard in 20 min.)		
Polymerizable Mixture B		4 gm. (hard in 1 hr.)	
Polymerizable Mixture C			4 gm. (hard in 4 hrs.)
10% dimethyl aniline in acetone	0.5 ml.	0.5 ml.	0.5 ml.
10% solution of cobalt naphthenate (6% cobalt) in naphtha	1.5 ml.	1.5 ml.	1.5 ml.
Ottawa Sand (A.F.S.—47)	96 gm.	96 gm.	96 gm.
Curing rate of curable mix	Hard in 10 min. Cured so rapidly that sand was not bound uniformly.	Hard in 15 min.	Hard in 4 hrs.

EXAMPLE V

0.15 ml. of cobalt naphthenate (containing 6% cobalt) in naphtha was admixed with 97 gm. of Ottawa sand (A.F.S.—47). 0.2 ml. of 50% dimethyl aniline in naphtha and 3 gm. of a mixture of 40 parts by weight of the polymerizable mixture of Example I and 0.5 part by weight of 60% methyl ethyl ketone peroxide in dimethyl phthalate

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were then added to and mulled with the drier-sand mix for 3 minutes; the resulting curable mix was then packed into three paper drinking cups so as to form three core samples.

After two samples were cured for 2 and 5 minutes, respectively, they were removed from their respective cups. The core that cured for 2 minutes was capable of supporting a 1-pound weight without slumping; and when an 8-pound weight was placed on top of the core that was cured for 5 minutes, the core slumped slightly. The third sample was removed from its cup after being cured overnight; this core was uniformly very hard.

EXAMPLE VI

0.3 ml. of 50% cobalt naphthenate (containing 6% cobalt) in naphtha is admixed with 97 gm. of Ottawa sand (A.F.S.—47). 0.1 ml. of N,N dimethyl-p-toluidine and 3 gm. of a mixture of 80 parts by weight of the polymerizable mixture of Example I, 1 part by weight of 60% methyl ethyl ketone peroxide in dimethyl phthalate, and 1.6 parts by weight of 50% benzoyl peroxide in an inert solvent (e.g., dimethyl phthalate) are then added to and mulled with the drier-sand mix for a few minutes. The resulting curable mix may then be packed into a paper cup.

The curable mix will be hard in about 2 minutes and uniformly very hard in 30 minutes.

EXAMPLE VII

When 0.1 ml. of N,N dimethyl-o-toluidine is substituted for N,N dimethyl-p-toluidine in Example VI, a curable mix is formed that cures at the same rate as the curable mix of Example VI.

EXAMPLE VIII

Polymerizable Mixtures E, F, G, and H were prepared by admixing the solvent-free, unsaturated polyester resin

(100% total solids) of Example I with a combination of reactive solvents composed of vinyl toluene and increasing levels of divinyl benzene in the amounts shown in Table III, *infra*.

These polymerizable mixtures were then admixed with the ingredients set forth in Table IV, *infra*, in the amounts therein shown so as to form curable mixes which were

rapidly shaped into cores. Table III and Table IV show that as the percentage of divinyl benzene in the total amount of reactive thinner is increased, the tendency of the cured or hardened core to soften upon the application of heat thereto decreases.

Table III
POLYMERIZABLE MIXTURES

	Polym- erizable Mixture E	Polym- erizable Mixture F	Polym- erizable Mixture G	Polym- erizable Mixture H
Unsaturated polyester resin of Example I (100% total solids), gm.....	66.6	66.6	66.6	66.6
Thinner:				
Vinyl toluene, gm.....	30.0	26.7	20.0	6.7
50-60% divinyl benzene (commercial grade),* gm.....	3.3	6.6	13.32	26.6

*Commercial grade divinyl benzene contains 50-60% divinyl benzene diluted with ethyl vinyl benzene and about 10% of inert solvent such as ethyl benzene and the like.

Table IV

EFFECT OF DIVINYLBENZENE ON REDUCTION OF HEAT SOFTENING

Ingredients	Sample 1	Sample 2	Sample 3	Sample 4
Polymerizable Mixture A.....	9 gm.....	9 gm.....	9 gm.....	9 gm.....
Polymerizable Mixture B.....	9 gm.....	9 gm.....	9 gm.....	9 gm.....
Polymerizable Mixture C.....	9 gm.....	9 gm.....	9 gm.....	9 gm.....
Polymerizable Mixture D.....	9 gm.....	9 gm.....	9 gm.....	9 gm.....
Ottawa sand (A.F.S.—47).....	291 gm.....	291 gm.....	291 gm.....	291 gm.....
Cobalt naphthenate (contains 6% cobalt).....	0.45 ml.....	0.45 ml.....	0.45 ml.....	0.45 ml.....
Dimethyl aniline.....	0.3 ml.....	0.3 ml.....	0.3 ml.....	0.3 ml.....
60% methyl ethyl ketone peroxide in dimethyl phthalate.....	0.15 ml.....	0.15 ml.....	0.15 ml.....	0.15 ml.....
Time required for curable mix to become hard.....	5 minutes.....	5 minutes.....	5 minutes.....	5 minutes.....
Heat distortion (on hot plate) 2 hrs. after formation of curable mix.....	-----	Less thermoplastic than Sample 1.	More rapid reset than Sample 2.	Less thermoplastic than Sample 2.
Heat distortion (on hot plate) 24 hrs. after formation of curable mix.....	-----	Less thermoplastic than Sample 1.	More rapid reset than Sample 2.	Less thermoplastic than Sample 2.

EXAMPLE IX

The following procedure may be used to show the effect of various levels of dimethyl aniline promoter (based on a polymerizable mixture of an unsaturated polyester resin plus cross-linking agent) on the curing characteristics of the curable mixes:

A polymerizable mixture is prepared by admixing (a) 1 part by weight of 50% methyl ethyl ketone peroxide in dimethyl phthalate and 1.6 parts by weight of 50% benzoyl peroxide in an inert solvent (e.g., dimethyl phthalate) with (b) 80 parts by weight of the polymerizable mixture of Example I.

97 gm. of Ottawa sand (A.F.S.—47) are placed in a mixer. The mixer is started, and the desired level of dimethyl aniline is added to the sand. 0.3%, based on the weight of the polymerizable mixture of the polyester resin and cross-linking monomer of Example I, cobalt in the form of cobalt naphthenate is added to the mixer and mullied with the sand and promoter.

Said polymerizable mixture is then added in a steady stream to the contents of the mixer and the resulting curable mix is rapidly, but thoroughly, mixed. The core is then formed.

Curable core mixes produced in this manner will have the following curing characteristics:

The most rapid effective cures (at room temperature) occur with cores containing about 1 to about 5% dimethyl aniline (based on the polymerizable mixture of Example I). When about 1% down to about 0.33% of dimethyl aniline (based on the polymerizable mixture of Example I) is used, a hard core is obtained only after

curing the mix overnight. Cores containing about 6-7% dimethyl aniline (based on the polymerizable mixture of Example I) cure so rapidly that it is difficult to get a uniform curable mix before a portion of the mix cures in the form of lumps. Cores containing more than about 15% dimethyl aniline (based on the polymerizable mixture of Example I) do not cure into hard cores; this indicates that excess promoter may actually retard curing.

Thus, the rate at which a hard core is formed with dimethyl aniline promoter (based on the unsaturated polyester resin plus cross-linking agent) is directly proportional to the level of promoter used when the mix contains about 0.33% to about 6% promoter; when more than about 7% promoter is used, the curing rate is inversely proportional to the level of promoter in the mix.

EXAMPLE X

The following procedure may be used to show the effect of various levels of cobalt (based on the polymerizable mixture of unsaturated polyester resin plus cross-linking agent of Example I), in the form of cobalt

naphthenate, on the curing characteristics of the curable mixes:

A polymerizable mixture containing methyl ethyl ketone peroxide, benzoyl peroxide and the polymerizable mixture of Example I is prepared in accordance with the procedure set forth in Example IX.

97 gm. of Ottawa sand (A.F.S.—47) are placed in a mixer. The mixer is started and 3.3% dimethyl aniline (based on the polymerizable mixture of Example I) is added to the sand. Various percentage levels of cobalt (based on the weight of the polymerizable mixture of Example I) in the form of cobalt naphthenate are added to the mixer and mullied with the sand and promoter.

Said polymerizable mixture is then added in a steady stream to the contents of the mixer and the resulting curable mix is rapidly, but thoroughly, mixed.

Curable core mixes produced in the manner referred to in Example X will have the following curing characteristics:

The most rapid cures (at room temperature) occur with cores containing about 1% cobalt (based on the polymerizable mixture of Example I) which has been added as cobalt naphthenate. Curable mixes containing at least about 0.025-0.03% cobalt (based on the polymerizable mixture of Example I) produce cores that are fairly hard after an extended number of hours. When about 0.07%, 0.1%, and 1% cobalt (based on the polymerizable mixture of Example I) are used, hard cores are produced in about 5 minutes, 2 minutes, and instantaneously, respectively. When about 2% cobalt (based on

the polymerizable mixture of Example I) is used, the core hardens in about 2 minutes.

The rate at which a hard core is formed with cobalt (based on the polymerizable mixture of Example I), in the form of cobalt naphthenate, is directly proportional with the level of cobalt used when the mix contains about 0.025% to about 1% cobalt; when more than about 1% cobalt is used, the curing rate is inversely proportional to the level of cobalt in the mix. Excessive levels of cobalt may, thus, actually retard curing. Effective results may be obtained with about 0.025% to 3% cobalt (added as a drier), based on the unsaturated polyester resin plus cross-linking agent; however, the use of about 0.5% to 1% cobalt (added as a drier), based on the unsaturated polyester resin plus cross-linking agent, is preferred.

Today, foundry cores are being produced by machines which blow the refractory material and binder into the core mold with a blast of air. The binder serves to lend green strength to the core so that it may be removed from the mold after it has been shaped. The core may then be baked so that it develops sufficient tensile strength so as to enable the core to maintain its shape when molten metal is poured against it; the core should collapse after the metal freezes or sets.

FIGURE 1 is a diagrammatic drawing of apparatus which may be used to produce curable mixes, with the above-described components, which rapidly develop green strength and sufficient tensile and scratch hardness values without necessitating the application of heat.

FIGURE 2 is an enlarged diagrammatic view of the core box shown in FIGURE 1.

Refractory material may be suitably milled with a polymerizable mixture containing an unsaturated polyester resin, ethylenically unsaturated cross-linking monomer, peroxidic polymerization catalyst and drier-accelerator to form a mix 40 which may be placed in the reservoir 21.

Column 12 should be packed with a suitable absorbent 41, such as steel wool, which has been soaked with the amine promoter.

Valves 11, 14, and 20 should be opened and compressed air (at 90 p.s.i.) introduced into the system through air pipe 10. The air pressure will force the mix 40 through openings 22 in reservoir 21 into mixing zone 30 and through a stream of promoter vapor which has been forced by the compressed air from column 12 into the mixing zone 30. The curable mix (i.e., refractory material and polymerizable mixture of unsaturated polyester resin, cross-linking agent, peroxidic catalyst, promoter, and drier-accelerator) will be forced through the opening 31 in mixing zone 30 into the core box 32.

The curable mix will enter the core box 32 through blow hole 33 and will be packed into the core cavity 35 of the mold 42 onto a screen 36 which is positioned above the opening 37 at the bottom of the core box. Air may escape from the core box through the screen 36 as well as through the screened vent 34.

The curable mix will harden in about one minute so it will have sufficient green strength to stand without collapsing. After about 1-2 minutes or more at room temperature, the mix will uniformly and thoroughly harden to develop sufficient tensile strength so as to enable molten metal to be poured against it; in the event that low levels of amine polymerization promoter are used, the time required for the mix to harden will be increased. Mild heat will accelerate the development of this tensile strength.

If desired, valves 11 and 14 may be closed and valve 20 left open so that compressed air (90 p.s.i.) entering the system through pipe 10 will force the mix 40 into the cavity 35 of the core box 32. Valve 20 should then be closed and valves 11 and 14 opened so as to enable the promoter to be forced into the core box through blow hole 33 and through the mix 40.

The mix 40 shown in FIGURE 1 may be prepared by (a) mulling 970 gm. of Ottawa sand (A.F.S.—47) with 3.0 ml. of 50% solution of cobalt naphthenate (containing 6% cobalt) in naphtha, (b) adding a polymerizable mixture containing 30 gm. of the polymerizable mixture of Example II, 0.37 gm. of 50% methyl ethyl ketone peroxide in dimethyl phthalate, and 0.60 gm. of 50% benzoyl peroxide in dimethyl phthalate to the accelerator-sand mix, and (c) mulling the resulting mix 40. When the mix 40 is combined with 1-3 gm. of dimethyl aniline vapor, a curable mix is formed that will develop sufficient tensile strength values on about 1-2 minutes so as to permit molten metal to be poured against it.

As pointed out above, care should be exercised in selecting the level of promoter and drier-accelerator because excessive levels of these components, like insufficient levels, may serve to extend the time required for the core to reach tensile strength values which permit molten metal to be poured against it, or entirely inhibit the development of such values.

Effective curing of the curable mix may be obtained when the polymerizable mixture of unsaturated polyester resin plus cross-linking agent contains about 67% polyester resin and about 33% monomeric cross-linking agent. (The proportions referred to, infra, are based upon polymerizable mixtures containing approximately this proportion, or equivalent proportions, of polyester resin plus cross-linking agent.)

Suitable curable mixes for core use which rapidly develop tensile strength and hardness values sufficient for casting purposes may be prepared with about 0.5% to 6% by weight of a polymerizable mixture of unsaturated polyester resin plus cross-linking monomer and about 99.5%-94% by weight refractory material. However, I prefer to use curable mixes having about 2-4% by weight polymerizable mixture of unsaturated polyester resin plus cross-linking monomer and 98-96% by weight refractory material. When more than about 6% polymerizable mixture of unsaturated polyester resin plus cross-linking monomer is used with about 94% refractory material, dense, hard cores will be produced which do not possess sufficient gas permeability properties. These percentages are based on the weight of the unsaturated polyester resin, cross-linking agent, plus refractory material.

The relative proportion of peroxidic catalyst used in my curable mix is not particularly critical. For example, about 0.3-4%, or higher, catalyst (based on the unsaturated polyester resin plus cross-linking agent) may be used; however, curable mixes containing about 1.0-2.0% catalyst (based on the unsaturated polyester resin plus cross-linking agent) are particularly effective. Excessively high levels of peroxidic catalyst tend to produce brittle cores which possess poor tensile strength values.

Metal-containing accelerators, such as cobalt driers, may be present in the curable mix in the range of about 0.025-3% metal (added as a drier) based on the unsaturated polyester resin plus cross-linking agent; however, curable mixes containing a cobalt drier as an accelerator should, preferably, contain about 0.5-1.0% cobalt (added as a drier) based on the unsaturated polyester resin plus cross-linking agent. As indicated in Example X, excessively high levels of cobalt drier-accelerator may serve to retard curing of the curable mix, or prevent curing of the mix.

Promoters, such as dimethyl aniline, may be present in the curable mix in the range of about 0.18-6%, preferably about 1-5%, based on the unsaturated polyester resin plus cross-linking agent. As indicated in Example IX, excessively high levels of dimethyl aniline may serve to retard curing of the curable mix, or prevent curing of the mix.

For example, the following formulations exemplify suitable curable mixes (the term "part" and "parts" refer to part or parts by weight):

- 99.5-94 parts refractory material.
 0.5-6 parts polymerizable mixture of the type illustrated in Examples I and II.
 0.0025 or more part peroxidic catalyst.
 0.00165-0.36 part amine promoter such as dimethyl aniline.
 0.00015-0.18 part metal accelerator such as cobalt in the form of cobalt naphthenate.

The percentage values expressed in the claims are intended to be on a weight basis. The term "up to" in the claims excludes zero. The term "resin mix" in the claims includes the polyester resin and cross-linking agent.

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.

I claim:

1. The method of producing foundry structures which comprises: forming a foundry core mix with a mixture of about 99.5-94% of refractory foundry material and up to about 6% of polymerizable resin mix containing ethylenically unsaturated polyester resin formed from the reaction of an unsaturated polycarboxylic acid and polyhydric alcohol and monomeric, ethylenically unsaturated, polymerizable cross-linking agent, at least about 0.8% of peroxide polymerization catalyst that is soluble in said resin mix, a polymerization accelerator when said catalyst does not include acyl peroxide, said accelerator being in the form of a soluble organic salt which provides at least about 0.025% metal in an active state that induces acceleration of the polymerization of said resin mix, and at least about 0.18% of vapor phase N,N-dialkyl tertiary monoamine polymerization promoter free of nitro and nitroso groups, said promoter being introduced in the vapor phase to form a hardenable foundry core mix that hardens into a hard, self-supporting, porous foundry core against which molten metal may be poured and shaped before said core undergoes distortion or collapses, said percentages of refractory material and resin mix being based on said refractory material plus said polymerizable resin mix, the percentages of said catalyst, metal and promoter being based on said resin mix.

2. The method of producing foundry cores as defined in claim 1 wherein said catalyst is selected from the group consisting of benzoyl peroxide, lauroyl peroxide, methyl ethyl ketone peroxide, cumene hydroperoxide and t-butyl hydroperoxide, said accelerator is selected from the group consisting of cobalt naphthenate, cobalt octoate, manganese naphthenate and manganese octoate, and said promoter is selected from the group consisting of dimethylaniline, diethylaniline, N,N-dimethyl-p-toluidine and N,N-dimethyl-o-toluidine.

3. The method of producing foundry structures which comprises: forming a foundry mix with a mixture of about 99.5-94% of refractory foundry material and up to about 6% of polymerizable resin mix containing ethylenically unsaturated polyester resin formed from the reaction of an unsaturated polycarboxylic acid and polyhydric alcohol and monomeric, ethylenically unsaturated, polymerizable cross-linking agent, at least about 0.3% of a hydroperoxide polymerization catalyst that is soluble in said resin mix, a polymerization accelerator in the form of a soluble organic salt which provides at least about 0.025% metal in an active state that induces acceleration of the polymerization of said resin mix, and at least about 0.18% of vapor phase N,N-dialkyl tertiary monoamine polymerization promoter free of nitro and nitroso groups, said promoter being introduced in the vapor phase, to form a hardenable foundry core mix that hardens into a hard, self-supporting, porous foundry core against which

molten metal may be poured and shaped before said core undergoes distortion or collapses, said percentages of refractory material and resin mix being based on said refractory material plus said polymerizable resin mix, the percentages of said catalyst, metal and promoter being based on said resin mix.

4. The method of producing foundry structures which comprises: forming a foundry mix with a mixture of about 99.5-94% of refractory foundry material and up to about 6% of polymerizable resin mix containing ethylenically unsaturated polyester resin formed from the reaction of an unsaturated polycarboxylic acid and polyhydric alcohol and monomeric, ethylenically unsaturated, polymerizable cross-linking agent, at least about 0.3% of an acyl peroxide polymerization catalyst that is soluble in said resin mix, and at least about 0.18% of vapor phase N,N-dialkyl tertiary monoamine polymerization promoter free of nitro and nitroso groups, said promoter being introduced in the vapor phase, to form a hardenable foundry core mix that hardens into a hard, self-supporting, porous foundry core against which molten metal may be poured and shaped before said core undergoes distortion or collapses, said percentages of refractory material and resin mix being based on said refractory material plus said polymerizable resin mix, the percentages of said catalyst and promoter being based on said resin mix.

5. The method of producing foundry cores which comprises: forming a hardenable foundry core mix with a mixture of about 99.5-94 parts by weight of refractory foundry core material, about 0.5-6 parts by weight of polymerizable resin mix containing ethylenically unsaturated polyester resin formed from the reaction of an unsaturated polycarboxylic acid and polyhydric alcohol and monomeric, ethylenically unsaturated, polymerizable cross-linking agent, and, based on the weight of said polymerizable resin mix, at least about 0.3% of a hydroperoxide polymerization catalyst that is soluble in said resin mix, a polymerization accelerator in the form of a soluble organic salt which provides about 0.025-3% metal in an active state that induces acceleration of polymerization of said resin mix, and about 0.18-6% of vapor phase N,N-dialkyl tertiary monoamine polymerization promoter free of nitro and nitroso groups, said promoter being introduced in the vapor phase, to form a hardenable foundry core mix that hardens into a hard, self-supporting, porous foundry core against which molten metal may be poured and shaped before said core undergoes distortion or collapses.

6. The method of producing foundry cores which comprises: forming a hardenable foundry core mix with a mixture of about 99.5-94 parts by weight of refractory foundry core material, about 0.5-6 parts by weight of polymerizable resin mix containing ethylenically unsaturated polyester resin formed from the reaction of an unsaturated polycarboxylic acid and polyhydric alcohol and monomeric, ethylenically unsaturated, polymerizable cross-linking agent, and, based on the weight of said polymerizable resin mix, at least about 0.3% of an acyl peroxide polymerization catalyst that is soluble in said resin mix, and about 0.18-6% of vapor phase N,N-dialkyl tertiary monoamine polymerization promoter free of nitro and nitroso groups, said promoter being introduced in the vapor phase, to form a hardenable foundry core mix that hardens into a hard, self-supporting, porous foundry core against which molten metal may be poured and shaped before said core undergoes distortion or collapses.

7. The method of producing foundry cores which does not necessitate the use of heat comprising: admixing up to about 6% of polymerizable resin mix containing ethylenically unsaturated polyester resin formed from the reaction of unsaturated polycarboxylic acid and polyhydric alcohol and monomeric, ethylenically unsaturated, polymerizable cross-linking agent, and at least about 0.3% of hydroperoxide catalyst with an admixture of refractory foundry core material and polymerization accelerator in

the form of a soluble organic salt that provides at least about 0.025% metal in an active state that serves as a polymerization accelerator; and adding to and admixing with the resulting admixture at least about 0.18% of a vapor phase N,N-dialkyl tertiary monoamine polymerization promoter free of nitro and nitroso groups to form, without necessitating the use of heat, a hardenable foundry core mix having about 99.5-94% of refractory material and that hardens into a hard, self-supporting, porous foundry core against which molten metal may be poured and shaped before said core undergoes distortion and collapses; said percentages of said resin mix and said refractory material being based on the total weight of those materials and the remaining percentages being based on said resin mix.

8. The method of producing foundry cores which does not necessitate the use of heat comprising: admixing up to about 6% of polymerizable resin mix containing ethylenically unsaturated polyester resin formed from the reaction of an unsaturated polycarboxylic acid and polyhydric alcohol and monomeric, ethylenically unsaturated, polymerizable cross-linking agent, and at least about 0.3% of acyl peroxide catalyst with refractory foundry core material; and adding to and admixing with the resulting admixture at least about 0.18% of a vapor phase N,N-dialkyl tertiary monoamine polymerization promoter free of nitro and nitroso groups to form, without necessitating the use of heat, a hardenable foundry core mix having about 99.5-94% of refractory foundry material and that hardens into a hard, self-supporting, porous foundry core against which molten metal may be poured and shaped before said core undergoes distortion and collapses; said percentages of said resin mix and said refractory material being based on the total weight of those materials and the remaining percentages being based on said resin mix.

9. The method of producing foundry cores which does not necessitate the use of heat comprising: admixing up to about 6% of polymerizable resin mix containing ethylenically unsaturated polyester resin formed from the reaction of an unsaturated polycarboxylic acid and polyhydric alcohol and monomeric, ethylenically unsaturated, polymerizable cross-linking agent, and at least about 0.3% of hydroperoxide catalyst with an admixture of about 99.5-94% of refractory foundry core material and polymerization accelerator in the form of a soluble organic salt that provides at least about 0.025% metal in an active state that serves as a polymerization accelerator; packing the resulting admixture into a core box; and propelling at least about 0.18% of a vapor phase N,N-dialkyl tertiary monoamine polymerization promoter free of nitro and nitroso groups into said resulting admixture to form a hardenable foundry core mix that hardens at room temperature into a hard, self-supporting, porous foundry core against which molten metal may be poured and shaped before said core undergoes distortion and collapses; said

percentages of said resin mix and said refractory material being based on the total weight of those materials and the remaining percentages being based on said resin mix.

10. The method of producing foundry cores as defined in claim 9 wherein said catalyst is selected from the group consisting of benzoyl peroxide, lauroyl peroxide, methyl ethyl ketone peroxide, cumene hydroperoxide and t-butyl hydroperoxide, said accelerator is selected from the group consisting of cobalt naphthenate, cobalt octoate, manganese naphthenate and manganese octoate, and said promoter is selected from the group consisting of dimethylaniline, diethylaniline, N,N-dimethyl-p-toluidine and N,N-dimethyl-o-toluidine.

11. The method of producing foundry cores which does not necessitate the use of heat comprising: admixing up to about 6% of polymerizable resin mix containing ethylenically unsaturated polyester resin formed from the reaction of an unsaturated polycarboxylic acid and polyhydric alcohol and monomeric, ethylenically unsaturated, polymerizable cross-linking agent, and at least about 0.3% of acyl peroxide catalyst with about 99.5-94% of refractory foundry core material; packing the resulting admixture into a core box; and propelling at least about 0.18% of a vapor phase N,N-dialkyl tertiary monoamine polymerization promoter free of nitro and nitroso groups into said resulting admixture to form a hardenable foundry core mix that hardens at room temperature into a hard, self-supporting, porous foundry core against which molten metal may be poured and shaped before said core undergoes distortion or collapses; said percentages of said resin mix and said refractory material being based on the total weight of those materials and the remaining percentages being based on said resin mix.

12. The method of producing foundry cores as defined in claim 11 wherein said catalyst is selected from the group consisting of benzoyl peroxide, lauroyl peroxide, methyl ethyl ketone peroxide, cumene hydroperoxide and t-butyl hydroperoxide, and said promoter is selected from the group consisting of dimethylaniline, diethylaniline, N,N-dimethyl-p-toluidine and N,N-dimethyl-o-toluidine.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,179,990

April 27, 1965

Stephen E. Freeman

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's 5 and 6, Table II, first column, line 6 thereof, for "cabalt" read -- cobalt --; columns 7 and 8, Table IV, first column, lines 1 to 4 thereof, for "A", "B", "C", and "D", respectively, read -- E --, -- F --, -- G --, and -- H --, respectively; column 7, lines 71 and 72, for "dimethly" read -- dimethyl --; column 9, line 68, for "values" read -- valves --; column 10, line 14, for "on" read -- in --; line 32, for "develope" read -- develop --; column 11, line 30, for "0.8%" read -- 0.3% --; column 14, line 53, for "10/16" read -- 10/56 --.

Signed and sealed this 30th day of November 1965.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents