

Nov. 9, 1965

L. H. BROWN

3,216,075

METHOD FOR MANUFACTURING FOUNDRY CORES AND MOLDS

Filed Feb. 5, 1963

2 Sheets-Sheet 1

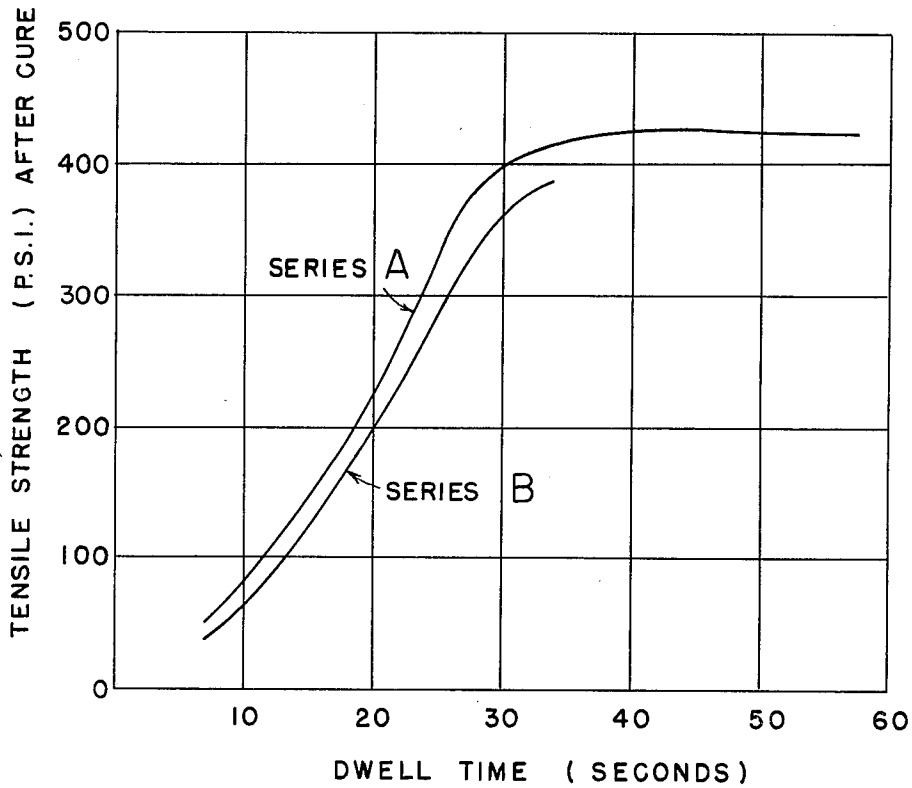


FIGURE 1

INVENTOR :

LLOYD H. BROWN

BY : *Milton C. Hansen*

ATTORNEY

Nov. 9, 1965

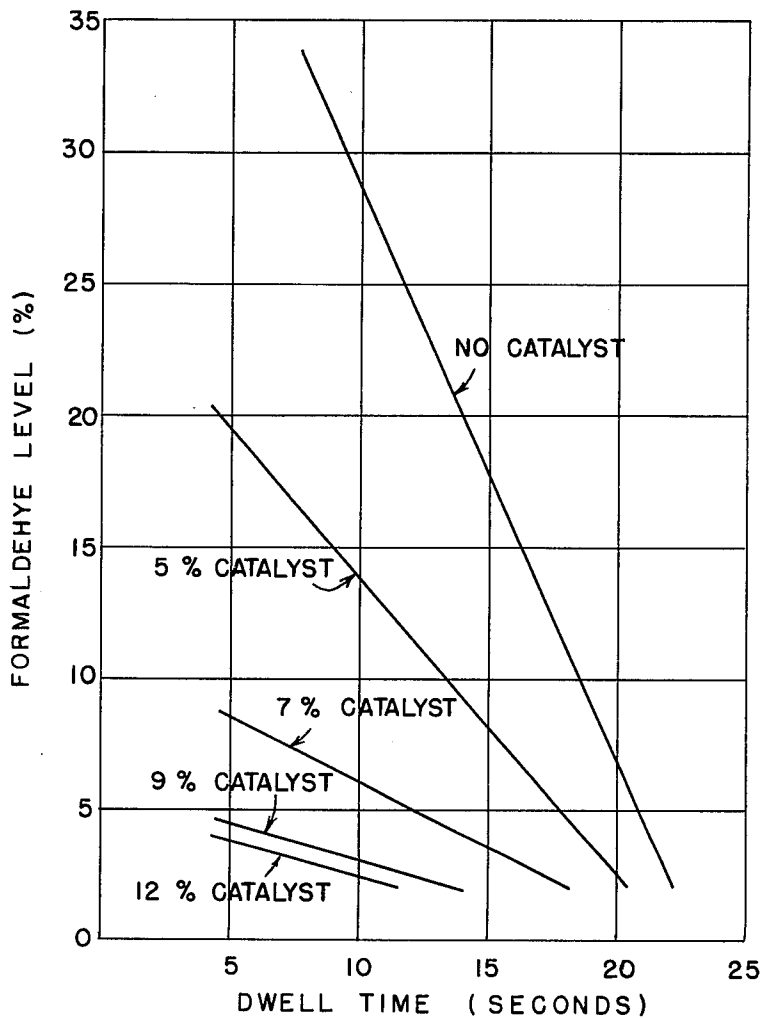
L. H. BROWN

3,216,075

METHOD FOR MANUFACTURING FOUNDRY CORES AND MOLDS

Filed Feb. 5, 1963

2 Sheets-Sheet 2



PROVIDING 200 P.S.I. TENSILE STRENGTH AFTER CURE

FIGURE 2

INVENTOR:

LLOYD H. BROWN

BY: *Milton C. Hansen*

ATTORNEY

1

3,216,075

METHOD FOR MANUFACTURING FOUNDRY CORES AND MOLDS

Lloyd H. Brown, Crystal Lake, Ill., assignor to The Quaker Oats Company, Chicago, Ill., a corporation of New Jersey

Filed Feb. 5, 1963, Ser. No. 256,408

9 Claims. (Cl. 22-194)

This invention relates to a new and useful method for the high-speed manufacture of foundry cores and molds. The method of this invention utilizes a special binder and produces cores and molds having high cold strength, high hot strength, and low gas evolution. This method produces cores and molds which lead to iron and steel castings in which pinholes are virtually absent. A high-speed foundry core and mold making process, particularly one utilizing automatic equipment, is possible only when a complex balance of properties has been achieved in the sand binders. The binders must be stable enough to permit convenient room temperature storage before and after mixing with sand, yet "set" or harden very quickly when applied to a core box or mold. Many binders of the prior art which can be set or hardened quickly are sensitive in regard to over- and under-cure, which can be accompanied by serious diminishing of strength. A process for the high-speed production of cores and molds demands a binder which is not particularly subject to under- or over-cure.

In automatic high-speed hot core and hot pattern operations it is desirable that a minimum period of time be required for the shapable sand mix to become sufficiently self supporting to be removed from the hot core box or pattern and be otherwise handled and manipulated by automatic machinery. In the method of this invention, self-supporting handleable foundry shapes are generally released after dwelling for between about five seconds and 45 seconds in contact with the core box or pattern. Short dwell times (as hereinafter defined) are desirable in order to obtain maximum production of units per hot core box or pattern. Many binders of the prior art require relatively careful treatment in curing ovens in order to obtain final strength after the foundry sand structure has become self supporting. In the high-speed automatic core and mold making processes, it would be desirable to eliminate all oven curing operations, if this could be accomplished without sacrificing core or mold strengths.

While the binder employed in a particular process must impart sufficient strength to the sand core or mold to enable it to withstand the destructive forces resulting from the density and motion of the metal being poured, that very binder must also allow the sand core or mold to disintegrate and "shake out" readily, once the metal has solidified. In this regard metals requiring relatively high pour temperatures, e.g., nodular iron and steel, are particularly demanding on the binders. The ureaformaldehyde-furfuryl alcohol mixtures are, generally speaking, excellent binders in regard to many of the above property balances. However, the nodular iron and steel castings produced from cores and molds utilizing these or many other resins are found to contain large numbers of tiny voids at or near the surface of the casting. These voids are commonly referred to as "pinholes."

An object of the present invention is to provide a comparatively inexpensive method for the high-speed production of foundry cores and molds which are suitable for the production of substantially pinhole-free nodular iron and steel castings.

Another object of this invention is to provide a method for production of said cores and molds which requires a very short dwell time, thereby providing for correspond-

2

ingly high rate of production in terms of units produced per core box or pattern per unit time.

A further object of this invention is to provide a method which utilizes a binder which is stable at ordinary room temperatures, yet is extremely reactive and fast curing when used in accordance with the process of this invention, and yet is not sensitive to over- or under-cure.

A still further object of this invention is to provide a method which leads to sand cores or molds which have a high degree of cold strength, and moreover have a high degree of strength at pour temperatures.

Another object of this invention is to provide a method for making cores and molds which is readily adaptable to the increasingly important high-speed, automatic, mechanized foundry operations.

A further object of this invention is to provide a method for high-speed manufacture of cores and molds which is readily applicable to a wide variety of foundry sands, despite the wide range of alkalinity and acidity which can normally be encountered in these materials.

Another object of this invention is to provide a method which does not require the use of curing ovens.

These and other objects which will become apparent from the description following are accomplished by the method of this invention. The special binder employed by the method of this invention is a substantially anhydrous, nitrogen-free mixture comprising a boron-containing component in an amount between 5% and 40% by weight based on the weight of the binder, and a second component which is either (a) a mixture of acid catalyst in an amount between 0.5% and 15% by weight based on the weight of said mixture, and a liquid furfuryl alcohol-formaldehyde composition in an amount between 99.5% and 85% by weight based on the weight of said mixture, said composition containing at least 15% by weight furfuryl alcohol monomer, and having between about 2% and 30% formaldehyde level, as defined hereinafter, or (b) a liquid furfuryl alcohol-formaldehyde composition containing at least 15% by weight furfuryl alcohol monomer and having between about 12 and about 30% by weight formaldehyde level.

The method of this invention comprises the following steps:

(1) mixing foundry sand in an amount between 94 and 99.5 parts by weight with the aforescribed special binder of this invention, said binder being in an amount between 0.5 and 6.0 parts by weight, said mixing continuing until said binder is substantially uniformly distributed on said foundry sand, thereby providing a hardenable, shapable foundry mix;

(2) applying foundry mix provided by step 1 to a shaped, heated surface, such as that of a core box or pattern, said surface being at a temperature between 350° and 600° F.;

(3) permitting the foundry mix to dwell in contact with said surface for a period of time sufficient to allow the foundry mix to become a self-supporting foundry shape,

(4) separating the self-supporting foundry shape from said surface, and

(5) curing the self-supporting foundry shape at ambient room temperature conditions.

Although 0.5% to 6.0% by weight of binder on the sand is entirely satisfactory, 1.5% to 4.0% is preferred.

The term "boron-containing component" herein refers to either single compounds or mixtures of compounds including boron oxides, such as the anhydride B_2O_3 , the various acids which reflect the various degrees of hydration of boron oxides, and the lower oxy acids of boron. Boron oxide (B_2O_3) and boric acid (H_3BO_3) are commercially available and are eminently satisfactory boron-containing components in the binder of this invention.

The special binders of this invention containing between 15% and 25% (by weight based on the weight of the binder) of boron oxide, or of boric acid, or of a mixture of boron oxide and boric acid, are preferred.

The term "acid catalyst" herein refers to relatively strongly acidic materials which are capable of catalyzing the polymerization of the special binder of this invention. Strong mineral acids, such as phosphoric acid, hydrochloric acid and many organic acids, and anhydrides, such as citric acid and maleic anhydride, are suitable catalysts. Weak acids, such as boric acid, are not to be considered catalysts. In fact, experimental work indicates that the presence of boric acid in the binder of this invention may cause polymerization of the binder on the sand to be slower than if no boric acid were present. Other acidic materials, such as BCl_3 , FeCl_3 , AlCl_3 , etc., also have some utility as catalysts. Phosphoric acid and citric acid are the preferred acid catalysts. When an acid catalyst is used, it is preferred that it be used in an amount between 3% and 9% by weight based on the weight of the mixture of the catalyst and furfuryl alcohol-formaldehyde composition used therewith. Primary or secondary amine salts, e.g., $\text{NH}_2\text{OH}\cdot\text{HCl}$, are also useful catalysts. Since the catalysts are present in low concentrations, the binders utilizing the amine salts are considered "substantially nitrogen-free."

The term "liquid furfuryl alcohol-formaldehyde composition" herein refers to a mixture containing at least 15% furfuryl alcohol monomer by weight and also free formaldehyde or furfuryl alcohol-formaldehyde resin, or both. A preferred liquid furfuryl alcohol-formaldehyde composition contains between 30% and 60% furfuryl alcohol by weight based on the weight of the composition. The formaldehyde ingredient may be supplied by dissolved anhydrous formaldehyde or trioxane. Although paraform is a less desirable source of free formaldehyde since it contains some water of hydration, it can be used for this purpose provided it does not raise the water content of the binder over 5% by weight. Aqueous solutions of formaldehyde, such as formalin, should not be used directly as an ingredient of the furfuryl alcohol-formaldehyde composition because of the water present but, of course, may be used in the preparation of the substantially anhydrous furfuryl alcohol-formaldehyde resins. Substantially anhydrous, nonnitrogen-containing formaldehyde polymers and/or furfuryl alcohol polymer may also be included in the liquid furfuryl alcohol-formaldehyde composition employed in this invention.

The term "furfuryl alcohol-formaldehyde resin" herein refers to any of the substantially anhydrous nonnitrogen-containing furfuryl alcohol-formaldehyde resins well known to the art. These resins are generally prepared by the steps: (1) catalyzed condensation of furfuryl alcohol and formaldehyde, (2) deactivation of the catalyst, and (3) distillation to remove ingredient water and water of reaction. Any of the nonnitrogen-containing sources of formaldehyde may be utilized in preparation of the resin, e.g., paraform, trioxane, anhydrous formaldehyde, and aqueous solutions, such as formalin. Substantially all of the water added by way of ingredients, as well as water formed during preparation of the resin, should be removed. Furfuryl alcohol-formaldehyde resins, such as those produced in accordance with procedures comparable to those disclosed in U.S. Patent No. 2,874,148 and in U.S. Patent No. 2,343,972, are commercially available today and are eminently satisfactory in the special binder of this invention. Of course if the resinification reaction is terminated at early stages, much of the unreacted furfuryl alcohol monomer will still be present. In general, if the reactions are terminated before the viscosity reaches about 2000 centipoises (cps.) sufficient furfuryl alcohol monomer will remain unreacted to provide more than the 15% furfuryl alcohol monomer required by the special binder of this invention. Hence, it is obvious that if the resinification reaction is cut short in this manner, the ma-

terial coming from the kettle is equivalent to a mixture of furfuryl alcohol monomer, and furfuryl alcohol-formaldehyde resin (and consequently is equivalent to the liquid furfuryl alcohol-formaldehyde composition of this invention). It is likewise considered obvious that no additional furfuryl alcohol need be added to provide the special binder of this invention under these circumstances (see Example 6). An advantage to carrying the resinification to a high degree of advancement and then diluting the highly viscous resin with furfuryl alcohol is the fact that this embodiment leads to decidedly less odor than those embodiments which employ a binder containing formaldehyde incorporated into resins carried to a low degree of advancement. These three types of embodiments lead to equivalent process and core or mold characteristics, odor considerations excepted. Because of odor considerations, furfuryl alcohol-formaldehyde compositions are preferred which contain less than 0.5% unreacted formaldehyde by weight based on the weight of the composition. Such compositions containing furfuryl alcohol-formaldehyde resin in an amount between about 20% and 60% by weight are preferred.

By "substantially anhydrous" is meant that the water content is preferably as low as possible, and should not exceed about 5%, based on the weight of the binder. In this connection it is important to note that the foundry sand must be substantially dry. Use of wet sand leads to undesirable gas formation during pouring but also has a decidedly detrimental effect on the strength of the cores or molds.

The "formaldehyde level" of a composition or mixture as used herein is defined as the total weight of formaldehyde added at any time as an ingredient per 100 parts by weight of the composition or mixture. In this definition the "weight of formaldehyde" includes formaldehyde equivalent added in the form of trioxane, paraform, formalin, furfuryl alcohol-formaldehyde resin, etc. Hence, the term "formaldehyde level" is obviously empirical in that the formaldehyde may not be present as such in some of the binders of this invention. The formaldehyde may be free, of course, but as hereinbefore indicated, it is preferred that the formaldehyde be incorporated into furfuryl alcohol-formaldehyde resin. To illustrate this definition of the "formaldehyde level" term, it is seen in Example 1 below that 6 parts of formaldehyde were used as an ingredient to produce 73.2 parts of furfuryl alcohol-formaldehyde resin. Hence, the formaldehyde level of the resin is 8.2% based on the weight of the resin. When this resin is diluted 50—50 with furfuryl alcohol, the resulting mixture has a formaldehyde level of 4.1% based on the weight of the mixture. To continue the illustration, it is in accord with the above definition that if five parts of anhydrous formaldehyde gas or trioxane were dissolved in 100 parts of the above mixture, the formaldehyde level would become approximately $(4.1+5.0)$ or 9.1%, but more precisely

$$\left(\frac{4.1+5.0}{100+5.0} \right)$$

or 8.6%.

Furfuryl alcohol-formaldehyde resins having formaldehyde levels substantially above 30% are very difficult to prepare. Further, formaldehyde may be forced into a composition, e.g., by adding paraform, but we have found that this formaldehyde is lost rapidly and leads to severe odor problems.

It is noted that the special binder of the method of this invention does not rapidly achieve the high degree of strength or its suitability for this method merely because of the presence of the acid catalysts. As is disclosed herein, the acid catalyst is not required if the formaldehyde level is above about 12%. FIGURE 1 shows the tensile strength of cured cores (produced in accordance with this invention), plotted against the dwell times utilized in two series of tests. Each series utilized a different embodiment of the special binder of this invention

5

in an amount of 2% by weight based on the weight of the sand. Both embodiments of the special binder contained 20% boric acid by weight based on the weight of the binder.

The embodiment of the special binder of this invention utilized in series A of FIGURE 1 contained no catalyst, but had a formaldehyde level of about 16%. The furfuryl alcohol-formaldehyde composition of this binder contained 70% furfuryl alcohol-formaldehyde resins and 30% furfuryl alcohol monomer. The embodiment of the special binder of this invention utilized in series B of FIGURE 1 contained phosphoric acid in the amount of 5% by weight based on the weight of the binder, had a formaldehyde level of about 3%, and the furfuryl alcohol-formaldehyde composition utilized therein had 50% furfuryl alcohol-formaldehyde resin and 50% furfuryl alcohol monomer. The curves presented in FIG. 1 illustrate that slightly better results were obtained from the method of this invention by employing a binder having 16% formaldehyde level and no catalyst than by employing a binder having 3% formaldehyde level and 5% phosphoric acid catalyst based on the weight of the binder. Both binders are entirely suitable for the high-speed process of this invention, and both are within the scope of the definition of the special binder employed by the process of this invention.

FIG. 2 illustrates the relationship between formaldehyde level and dwell time required in order that the cured core (produced in accordance with this invention) achieve a tensile strength of 200 p.s.i. The latter tensile strength is chosen merely for the purpose of illustration in that it appears to be a minimal tensile strength which is suitable for many foundry purposes. It is obvious from the data herein that strengths amounting to twice this value are commonly obtained and can be reproducibly obtained by the process of this invention (see Example 6). The cores tested to provide the information summarized in FIG. 2 were produced in accordance with this invention, and utilized 2% binder, based on the weight of the sand, 20% boric acid, based on the weight of the binder, and were prepared in a 450° F. core box. Where a catalyst was employed, 85% aqueous phosphoric acid was used, and the percent catalyst refers to percent by weight based on the weight of the binder. FIG. 2 further shows that the presence of the acid in the special binder does speed up the rate of strength formation but that excellent results were achieved with no catalyst at all. However, the eminent success of the method of this invention can be assured only if the special binder, as defined herein, is utilized. It is seen from Table VI below that, even in the presence of 5% acid catalyst, the binder consisting essentially of highly reactive furfuryl alcohol monomer-polymer mixture having zero formaldehyde level leads to a tensile strength of only 120 p.s.i. when utilizing a 30-second dwell time and other conditions of the process of this invention. An acid catalyzed binder consisting essentially of furfuryl alcohol monomer-free polymer, also having zero formaldehyde level, provides zero tensile strength in a parallel test.

The method of this invention is readily applicable to a wide variety of sands despite the wide range of acidity and alkalinity normally encountered thereon. However, sands contaminated with highly alkaline substances should be washed before use in this invention. Normally alkaline sands, such as Juniata sand, need not be treated before use in the process of this invention.

The binder ingredients may be mixed prior to addition to the sand with the exception of the acid catalyst ingredient, if employed, or the ingredients may be mixed after addition of the individual ingredients to the sand. Hence, in one embodiment proper quantities of boric acid, furfuryl alcohol monomer, and furfuryl alcohol formaldehyde resin are mixed prior to their addition to the sand. In another embodiment the same materials are added individually to the sand and mixed thereon by mulling.

6

Likewise in those embodiments utilizing free forms of formaldehyde, such as anhydrous gas, trioxane, etc., these ingredients may either be premixed with the other ingredients or added to the sand individually with the other ingredients and mixed thereon. If utilized, the acid catalyst ingredient should be added only to the sand—before, during or after the addition of the other binder ingredients to the sand. The mixing action provided by commercial mullers is satisfactory. The advantages of continuing mixing until the binder is substantially uniformly distributed on the sand are considered obvious.

As used herein, the term "wet" as applied to sand mixes indicates that a liquid binder is employed. It has been emphasized elsewhere herein that the special binder of this invention is substantially anhydrous. The "wet," shapable, hardenable sand mix provided by step 1 of the process of this invention may be applied to a pattern or core box or the like in any suitable manner. Conventional sand slingers and sand blowers are very satisfactory. In the process of this invention the core box or pattern is heated by any convenient means to provide temperatures at their sand-contacting surfaces between about 350° F. and about 600° F. Temperatures between about 400° and 500° F. are preferred. The method of this invention is particularly suited to the production of cores, shell cores, and shell molds. The preferred method of producing shell molds by the method of this invention utilizes the "matched patterns" technique familiar to the art. Hence, in one preferred embodiment of the invention, foundry mix provided by step 1 of this invention is (a) blown between heated, matched patterns, the sand-contacting surfaces of the patterns having a temperature between 350° F. and 600° F., (b) the foundry mix is permitted to dwell between the matched patterns for a period of time sufficient to allow the foundry mix to become a self-supporting foundry shape, (c) the foundry shape is separated from the patterns, and (d) the foundry shape is cured at ambient room temperatures for at least 30 minutes.

Similarly, in one preferred method of producing cores by the method of this invention the foundry mix provided by step 1 is (a) blown onto a shaped, heated surface in a core box, the surface having a temperature between 350° F. and 600° F., (b) the foundry mix is permitted to dwell in the core box for a time not less than about 10 seconds nor more than about 40 seconds, during which time the mix becomes a nonshapable, handleable, self-supporting foundry core, (c) the core is separated from the core box, and (d) the core is cured at ambient room temperatures for at least 30 minutes. By "handleable" is meant capable of being handled without damage to shape.

In the process of this invention the sand mix is allowed to dwell in contact with the shaped, heated surface for a period of time between 5 and 45 seconds if the shell has cross sections amounting to about two inches or less. Thicker, and consequently heavier, shells or molds may require longer times, up to about three minutes. The vast majority of cores and molds made by the high-speed mechanized processes appear to have cross sections of about two inches or less.

The term "dwell time" herein refers to the duration of time in which the sand mix is allowed to remain in contact with the heated surface of the core box, pattern, etc. For example, the dwell time values reported herein in connection with the sand-blowing embodiments indicate the time lapse between the termination of the sand injection and the ejection of the hardened sand shape from the core box or pattern. Using the information disclosed herein, one with ordinary skill in the art can adapt the process of this invention to provide satisfactory strengths either by employing short dwell times, e.g., 5 to 15 seconds, by utilizing compositions having a high formaldehyde level or higher catalyst levels, or both, or by employing longer dwell times, e.g., 30 to 45 seconds, by using compositions having a lower formaldehyde level and low acid catalyst level. Dwell times between 5 and 45 seconds are

eminently satisfactory for the vast majority of cores and molds produced. In most preferred embodiments dwell times between 10 and 40 seconds are utilized. Dwell times of up to three minutes may be required for very heavy molds or cores, such as those having cross sections of three inches or more. The inherent acidity or alkalinity of the sand can increase or decrease, respectively, the speed with which strength develops.

It is considered obvious to one skilled in the art that a wet sand mix is not ideally suited to the "dump" shell method of forming molds. The "dump" shell forming methods usually employ dry (i.e., solid, not liquid) resin binders. In the "dump" method an excess quantity of sand-resin mix is dumped onto the heated pattern surface and allowed to dwell thereon until a sand shell hardens. Thereafter the filled heated pattern is inverted and the nonhardened sand resin mix falls out, leaving a sand shell mold attached to the pattern.

A wet sand mix may have sufficient green strength to be self supporting in the sense that a child's sand castle on the beach is self supporting. Such a structure or sand shape is not handleable, however, as is evidenced by the disastrous consequences of an attempt to lift or tip over the sand castle. Likewise, wet sand foundry shapes are generally not self supporting or handleable in the sense that they cannot be manipulated by foundry machinery after or during ejection of the shape from the core box or pattern. In the process of this invention two changes take place in the wet sand mix as a consequence of dwelling in contact with the heated pattern or core box. First, the binder "sets" sufficiently for the sand mix to become a self-supporting, handleable, unitary sand shape. This is due primarily to the hardening of the binder at the surfaces of the sand shape. Thus the unitary sand shape can then be manipulated or handled by foundry machinery during and after ejection from the core box or pattern. Secondly, the not completely understood curing reactions begin at an accelerated rate. It must be made clear that the brief dwell time does not cure the binder. The curing process is triggered by the brief dwell in contact with the heated surface, and the cure is completed after approximately one-half to one hour at ambient room temperature conditions. A one-half-hour cure is satisfactory in most cases. Hence, the curing operation requires no additional heating equipment, such as ovens or the like. Moreover, since core box and pattern costs are not negligible, the high rate of production of cores and molds in terms of units produced per core box or pattern per unit time is most advantageous.

The invention is illustrated but not limited by the following examples in which quantities stated are in parts by weight and percent by weight unless otherwise indicated. Tensile strengths were measured at room temperature.

EXAMPLE 1

Furfuryl alcohol (78.4 lbs.), 37% formalin solution (16.24 lbs.), and oxalic acid (40 grams) are charged to a jacketed kettle equipped with anchor-type stirrer and thermometer and a reflux condenser. While stirring, the temperature of the kettle contents was raised to 100° C. over a period of 45 minutes by means of steam in the jacket. At this point an exothermic reaction became obvious, and it was necessary to maintain cooling by circulating water in the jacket for 15 minutes. After another hour and a quarter it was necessary to introduce steam into the jacket to maintain reflux. During the two-hour period of reflux, the viscosities were observed by means of a Ford viscosity cup, and the times increased from 37 seconds to 64.5 seconds. The actual times are not significant since several types of cups are available, but use of a particular type and size Ford cup does provide a convenient means of following the relative increase in viscosity. Another convenient way of following the development of viscosity is the so-called "string" method. In the "string" method a portion of resin is placed on a cold plate

and stirred with the tip of one's finger. The finger is quickly withdrawn and the length of the string drawn before breaking is observed. At the end of the two-hour reflux period, a sample of the charge was tested in this manner, and gave a two-inch string. The kettle charge was then neutralized with 132 grams of triethanolamine. Water was distilled off at atmospheric pressure until the still charge reached 140° C. The viscosity of the resulting 73.7 pounds of resin was 5600 centipoises at 40° C. A 56.4-pound portion of this resin was mixed with 54 pounds 3 ounces of furfuryl alcohol monomer to give a viscosity of 180 centipoises at 25° C. This mixture was used as a binder ingredient in accord with the process of this invention and proved eminently satisfactory.

EXAMPLE 2

A portion (1.5 parts) of the mixture produced by Example 1 was mulled with silica sand (98.5 parts). Phosphoric acid (0.0011 part) and boric acid (0.015 part) were also added to the sand, and the mixture was mulled until an apparently uniform mixture was obtained. Portions of this mixture were blown into test core boxes heated to 450° F. Hardened, unitary, handleable test cores were ejected therefrom after thirty seconds dwell time. After one-half to one hour cure at ambient room temperature conditions, the cores were tested and found to have tensile strengths of 400-450 p.s.i.

EXAMPLE 3

Furfuryl alcohol (3920 parts), 37% formalin (812 parts), and oxalic acid (4.3 parts) were heated to 100° C. and maintained for three-hour reflux (pH=2.10) in equipment similar to that in Example 1. The pH was then adjusted to 5.5 with triethanolamine and the charge was distilled to remove water, until the charge temperature rose to 140° C. A portion of the resulting resin (800 parts) was admixed with 700 parts of furfuryl alcohol monomer to provide a furfuryl alcohol-formaldehyde composition as defined herein. A portion of this composition (50 parts) was mulled with silica sand (2300 parts) and 85% phosphoric acid (5 parts). No boric acid was added to this wet sand mix. A portion of this wet sand mix was blown into core boxes heated to 350° C. in a series of tests. Ten-second dwell times provided 144 p.s.i. tensile strength after cure, and 30-second dwell times provided 154 p.s.i. tensile strength after cure.

EXAMPLE 4

A sand mix was prepared by mulling 2300 parts of sand and 5 parts of aqueous 85% phosphoric acid for one minute, then mulling in 50 parts of the furfuryl alcohol-formaldehyde composition produced by Example 3 for three additional minutes. Note that no boric acid was used in the preparation of the mix. Portions of this mix were blown into core boxes heated to 350° F. Some test cores produced had been subjected to ten seconds dwell time, others to thirty seconds dwell time. After 24 hours' cure at dry ambient room temperature conditions, those having ten seconds dwell time showed an average tensile strength of 144 p.s.i. and those cores subjected to thirty seconds dwell time showed an average tensile strength of 154 p.s.i.

EXAMPLE 5

Portions of the furfuryl alcohol-formaldehyde composition produced as in Example 3 were mixed with varying amounts of sand, boric acid, and phosphoric acid. The percent boric acid, formaldehyde level, and percent catalyst indicated in Table I below are based on the weight of binder. Cores were prepared from each mix utilizing ten, twenty, and thirty second dwell times. After about 45 minutes' cure, the p.s.i. tensile strength of each was determined, and average values obtained are in Table I.

9
Table I

Percent Binder	Percent H_2BO_3	Formaldehyde Level (Percent)	Percent H_3PO_4	Tensile Strength (p.s.i.) After Cure, Dwell Time		
				10 sec.	20 sec.	30 sec.
2.0-----	25	3.0	0	0	156	335
2.0-----	20	3.0	5	64	202	368
2.0-----	20	3.0	7	106	259	398
2.0-----	20	3.0	9	201	299	396
2.0-----	20	3.0	12.7	229	309	368

EXAMPLE 6

A resin was prepared in a manner similar to Example 3 except that 1.0 mole of formaldehyde was incorporated per mole of furfuryl alcohol to provide a formaldehyde level of approximately 27% in the final substantially anhydrous mixture. The resinification reaction was terminated when a viscosity of 1000 centipoises at 25° C. was obtained. A small sample of substantially anhydrous product was subjected to low-vacuum distillation in order to remove "volatiles." The distillate was further fractionated to give quantities of furfuryl alcohol monomer, furfuryl alcohol "dimer" and difurfuryl ether which indicated that these compounds were present in the substantially anhydrous product in amounts by weight of about 25%, 15% and 5%, respectively. Hence, since the resinification reaction product already contained sufficient quantities of furfuryl alcohol monomer, it is apparent that further addition of furfuryl alcohol monomer was not necessary in order for the composition to be within the scope of the definition of furfuryl alcohol-formaldehyde composition.

Hence, the following embodiment is seen to be within the spirit and teachings of the specification and claims of this invention, even though no further furfuryl alcohol monomer is added to this composition. A portion of the substantially anhydrous resin product of this example was mixed with silica sand, boric acid, and aqueous 85% phosphoric acid in amounts sufficient to give 20% boric acid and 5% phosphoric acid based on the weight of the binder and 2% binder based on the weight of the sand. No additional furfuryl alcohol monomer was added. The mixture was mulled until apparently uniform. Cores were produced by the process of this invention by blowing this wet mix into a heated core box. Various dwell times and core box temperatures were checked in this series of tests. Tensile strengths (p.s.i.) were determined after approximately 45 minutes' cure at ambient room temperature conditions. The results are tabulated in Table II.

Table II

Core Box Temp., ° F.	Tensile Strength (p.s.i.) After 45 Min. Cure, Dwell Time		
	15 sec.	30 sec.	45 sec.
350-----	465	555	500
400-----	447	480	481
450-----	495	457	390

10
EXAMPLE 7

A furfuryl alcohol-formaldehyde resin containing 0.5 mole formaldehyde per mole furfuryl alcohol was prepared by a procedure similar to that of Example 1. The substantially anhydrous product of the resinification vessel was diluted 50-50 with furfuryl alcohol. The formaldehyde level of this furfuryl alcohol-formaldehyde composition was about 8%. A series of wet sand mixes were prepared utilizing this composition and Juniata sand, each containing varying amounts of phosphoric acid catalyst and/or other catalysts. Each mix in this series contained 20% boric acid based on weight of binder and 4% binder based on weight of mix. Cores were produced as in Example 6 employing various box temperatures and dwell times. The results are summarized in Table III.

Table III

Percent H_3PO_4	Other Catalyst	Box Temp., ° F.	Tensile Strength (p.s.i.) After Cure, Dwell Time		
			15 sec.	30 sec.	45 sec.
7.5-----		450	130	348	372
10.0-----		450	227	354	360
10.0-----	+10% H_2SO_4 -----	450	347	380	350
10.0-----	+10% H_2SO_4 -----	450	360	423	393
0-----	10% $\text{NH}_2\text{OH}\cdot\text{HCl}$ -----	450	320	310	320
0-----	10% $\text{NH}_2\text{OH}\cdot\text{HCl}$ -----	350	130	334	380
0-----	10% Maleic Anhyd-----	450	300	490	434

¹ 4-hour cure at room temperature conditions. All other cures were about 30 minutes.

EXAMPLE 8

Other portions of the furfuryl alcohol-formaldehyde composition produced and utilized in Example 7 were tested for high temperature compressive strength. A portion of the composition (1.5 parts) was admixed with silica sand (98.5 parts) and phosphoric acid (.0011 part). This admixture was divided into three portions and boric acid added to provide boric acid levels of 0%, 20% and 40% based on the weight of the binder. Test specimens 1½" in diameter were prepared by blowing mix into a box heated to 400° F. and allowing dwell time of 30 seconds. Compressive strength of cured specimens was determined at 1500° F. and 2500° F. using a Dietert No. 785 Thermolab with a hooded post. Specimens were in a helium atmosphere using flow rate of 1 liter per minute at time of test. The results are tabulated in Table IV.

Table IV

Percent Binder	Percent Catalyst	Percent Boric Acid	Compressive Strength (p.s.i.) at—	
			1,500° F.	2,500° F.
1.5-----	7.5	0	45	31
1.5-----	7.5	20	112	53
1.5-----	7.5	40	116	56

From Table IV it is obvious that little is gained in strength as a result of the addition of more than 20% boric acid.

Several additional resins, sand mixes and test structures were prepared in a manner similar to that described above and tested for room temperature tensile strength as summarized in Table V. Cure times were between one-half and one hour.

Table V

Percent Resin	Formaldehyde Level (Percent)	Percent Boric Acid	Percent Catalyst	Core Box Temp., ° F.	Tensile Strength (p.s.i.) After Cure, Dwell Times				
					15 Sec.	20 Sec.	30 Sec.	45 Sec.	60 Sec.
2-----	22	20	0	450	151	-----	402	425	421
2-----	24	20	5	450	425	-----	410	371	-----
1.5-----	8	20	7.5	450	357	310	452	433	353
1.5-----	8	20	5	450	-----	228	340	-----	-----

EXAMPLE 9

Three sand mixes utilizing binders having zero formaldehyde level were prepared to show their ineffectiveness. Each mix had 2% binder based on weight of sand, 20% boric acid and 5% phosphoric acid based on the weight of the binder. These sand mixes were blown into a test cavity which was heated to 475° F. Several dwell times were tested. One binder employed monomer-free furfuryl alcohol polymer, another binder utilized a 50-50 mixture of this polymer and furfuryl alcohol monomer. A third employed furfuryl alcohol monomer only. The results are summarized in Table VI. The symbol FA is used for furfuryl alcohol.

Table VI

	Tensile Strength (p.s.i.) After Cure, Dwell Times		
	10 Sec.	20 Sec.	30 Sec.
FA monomer-free polymer.....	0	0	0
50-50 FA monomer/polymer.....	0	43	120
FA monomer only.....	67	100	190

A similar test run, utilizing furfuryl alcohol monomer plus 3% paraform (all other variables the same as Example 9 above), gave a 258 p.s.i. tensile strength after utilizing a 30-second dwell time.

It is apparent that no one of the ingredients of the special binder of this invention accounts for the unique balance of properties which makes this high-speed method successful. As indicated earlier, the preferred embodiment of this invention utilizes binders containing formaldehyde which is incorporated into highly advanced copolymers. One practical advantage is the drastic improvement in the odor problem, both during mixing and/or mulling and blowing operations. Moreover, it is obviously a matter of considerable convenience for the foundry man to procure the liquid furfuryl alcohol-formaldehyde compositions already prepared. These compositions are quite stable, and have long life even after being mixed with boric acid. To demonstrate this, the following tests were conducted at elevated temperature (120° F.). Each of the resins referred to in Table VII was prepared by a procedure similar to that described in Example 3. Twenty parts of boric acid was added per 100 parts of binder, and two parts binder was used per 100 parts of sand in each set of tests.

Table VII.—Sand mix storage at 120° F.

Mole CH ₂ O/Mole FA in Preparation of Resin	Parts FA Added Per Part Resin	Binder Formaldehyde Level (Percent)	Observation at—	
			36 hours	48 hours
0.25.....	None.....	3.5	Usable.....	Usable.
0.50.....	One.....	3.5do.....	Not usable.
0.75.....	None.....	23.0do.....	Do.
1.00.....	None.....	30.0do.....	Do.

Furfuryl alcohol-, furfuryl alcohol-formaldehyde-boric acid mixtures, such as those utilized in the special binder of this invention, have a room temperature life far beyond the needs of most foundries. Under room temperature conditions, mixtures such as these have proven entirely satisfactory in the method of this invention even after months of time lapsed between the time they were mixed

and the time they were used in the method of this invention.

EXAMPLE 10

A furfuryl alcohol-formaldehyde resin was prepared in a manner similar to that of Example 1. A mixture containing 0.25 moles of formaldehyde (as 37% formalin) per mole of furfuryl alcohol was resinsified using 0.08% oxalic acid as a catalyst until a 56,000 cps. viscosity (40° C.) was obtained. The final substantially anhydrous resin was diluted with furfuryl alcohol until viscosity was reduced to 180 cps. at 25° C. This required 0.847 pound of furfuryl alcohol per pound of resin.

This liquid furfuryl alcohol-formaldehyde composition was tested in the method of this invention and found eminently satisfactory.

While we do not want to be bound by any theories, we believe that pinholing of steel and nodular iron castings is somehow related, at least in part, to the rate at which gas is evolved by the sand shape, as the metal is being poured in contact therewith. Ignition loss values have been found misleading in this regard, since the ignition loss of a core or mold does not necessarily give a clue as to the rate at which the core or mold evolves gas (or the rate at which the binder decomposes) at pour temperature. This was demonstrated by the following experiments.

A set of test cores was prepared using the liquid furfuryl alcohol-formaldehyde composition of Example 10, 5% phosphoric acid, and 20% boric acid based on the weight of the binder, and produced in accordance with the method of this invention, utilizing a 60-second dwell in the foundry core box at 450° F., followed by about 30-minute cure at room temperature. Five additional sets of test cores were prepared using various commercial binders and prior art methods, including the traditional cereal oil, and a phenolic binder used in the "dry" dump shell mold method. These five test samples were prepared essentially in accord with the manufacturer's recommendations and accepted art procedures. The binders are identified in the "Sample Identity" tabulation of Table VIII, in which the percent binder refers to the percent of binder based on the weight of sand mix. The percent catalyst in Table VIII refers to the percent of catalyst based on the weight of binder plus catalyst. Catalyst (A) is an aqueous solution containing 1 part ammonium chloride and 40 parts urea per 100 parts solution. Catalyst (B) is an aqueous solution containing 2.5 parts ammonium chloride and 40 parts urea per 100 parts solution. Catalyst (C) is an aqueous solution containing 4.0 parts ammonium chloride and 40 parts urea per 100 parts solution. Catalyst (D) is 85% aqueous phosphoric acid.

The "Ignition Loss" reported in Table VIII represents the percent of initial cured sample weight which is lost in two hours at 800° C. (air atmosphere). In addition, the rate of gas evolution at 2500° F. of the six sets of cured cores was determined using a modified Dietert gas determinator. Equipment modifications included means for continuously equalizing the pressure of the evolved gas, controlled heating means to all evolved gas containing surfaces to prevent condensation of moisture from the evolved gas, and camera equipment by which multiple instantaneous readings of stop watch timer, gas volume, etc., are made at predetermined time intervals. The "Gas Evolved" volumes reported in Table VIII are an indication of the rate at which gas is evolved by the cured core or mold at pour temperature. The value reported is the number of milliliters of gas evolved by a 10-gram sample of the core or mold in the first twenty seconds after the sample and its container were plunged into a zone heated to 2500° F. (nitrogen atmosphere). These values are corrected for readings changes encountered when blanks are run in the same manner using only 10 grams of dry sand and the sample container. The results obtained are summarized in Table VIII below.

Table VIII

Sample Identity	Catalyst	Dwell Time at 425° F.	Ignition Loss (2 hrs. at 800° C.), percent	Gas Evolved (20 sec. at 2,500° F.), ml.	Comparison, percent
1	-----	45 min	1.41	24	171
2	20% (A)	20 sec	1.30	22	157
3	20% (B)	20 sec	1.45	22	157
4	-----	60 sec	3.36	19	136
5	20% (C)	20 sec	1.49	18	128
6	5% (D)	60 sec. at 450° F.	1.68	14	100

Sample Identity:

1. Cereal-oil binder: 1.0% MOGUL (Corn Products Corporation) +1.25% Linseed Oil (Archer-Daniels-Midland).

2. Urea-Formaldehyde binder: 2.0% URAC 180 (American Cyanamid Corporation).

3. Urea-Formaldehyde-Furfuryl Alcohol binder: FURSET 2590 (2.0%) (The Quaker Oats Company).

4. Dry Phenolic Coated Sand (American Steel Foundry Corporation).

5. Urea-Formaldehyde-Furfuryl Alcohol binder: 2.00% FURSET 4090 (The Quaker Oats Company).

6. Example 10 binder: 2.00% binder based on the weight of sand mix. Binder contains 20% boric acid, based on weight of binder.

The "Comparison" column in Table VIII relates the volume of gas evolved during the initial 20 seconds by the sample to that evolved during the same period by cores or molds produced by the method of this invention in accordance with Example 10. The dramatic decrease in rate of gas evolution from cores and molds produced in accordance with the method of this invention is evident from the above data. Castings produced utilizing the prior art cores and molds (first five listed in Table VIII) exhibit pinholing of various degrees of severity.

Nodular iron and steel castings manufactured from the cores and molds produced by the process of this invention are substantially 100% free of pinholes as determined by X-ray examinations. In addition, by utilizing the method of this invention, production rates previously unattainable can be achieved. The quality of these cores and molds, in terms of surface soundness, handleability, cold and hot strengths, and shakeout, is most satisfactory. The invention is thus believed to constitute a significant and patentable advance in the art.

I claim:

1. A method for the high-speed production of cores and molds suitable for production of substantially pinhole-free iron and steel castings comprising the following steps:

- (1) mixing foundry sand in an amount between 94 and 99.5 parts by weight, and binder in an amount between about 0.5 and 6.0 parts by weight, said binder consisting essentially of a boron-containing component selected from the group consisting of boron oxides, boron acids reflecting the various degrees of hydration of boron oxides, and lower oxy acids of boron, said boron-containing component being present in an amount between 5 and 40% by weight based on the weight of the binder, and a second component which is a member selected from the group consisting of

- (a) a mixture of
 - an acid catalyst in an amount between 0.5 and 15% by weight based on the weight of said mixture, and
 - a liquid furfuryl alcohol-formaldehyde composition in an amount between 99.5 and 85% by weight based on the weight of said mixture, said composition containing at least 15% furfuryl alcohol monomer, and having between

about 2 and 30% formaldehyde level, and

- (b) a liquid furfuryl alcohol-formaldehyde composition containing at least 15% furfuryl alcohol monomer and having between about 12 and about 30% formaldehyde level,

said mixing continuing until said binder is substantially uniformly distributed on said foundry sand, thereby providing a hardenable, shapable foundry mix,

- (2) applying the foundry mix provided by step 1 to a shaped, heated surface, said surface being at a temperature between 350° and 600° F.,
- (3) permitting the foundry mix to dwell in contact with said surface for a period of time not less than about 10 seconds nor more than about 40 seconds sufficient to allow the foundry mix to become a self-supporting handleable foundry shape,
- (4) separating the self-supporting foundry shape from said surface, and
- (5) curing the self-supporting foundry shape at ambient room temperature conditions.

2. A method according to claim 1, in which the boron-containing component is boric acid and said second component is a mixture of

an acid catalyst in an amount between 0.5 and 15% by weight based on the weight of said mixture, and a liquid furfuryl alcohol-formaldehyde composition in an amount between 99.5 and 85% by weight based on the weight of said mixture, said composition containing at least 15% furfuryl alcohol monomer, and between about 2 and 30% formaldehyde level.

3. A method according to claim 1, in which the boron-containing component is boric acid and said second component is a liquid furfuryl alcohol-formaldehyde composition containing at least 15% furfuryl alcohol monomer and having between about 12 and about 30% formaldehyde level.

4. A method according to claim 1, in which said furfuryl alcohol-formaldehyde composition contains less than 0.5% unreacted formaldehyde by weight based on the weight of said composition.

5. A method according to claim 1, in which said binder consists essentially of:

- (1) boric acid in an amount between 15 and 25% by weight based on the weight of the binder,
- (2) acid catalyst in an amount between 3 and 9% by weight based on the weight of said mixture, and
- (3) a composition comprising
 - (a) furfuryl alcohol monomer in an amount between 30 and 60% by weight based on the weight of said mixture, and

15

- (b) furfuryl alcohol-formaldehyde resin in an amount between 20 and 60% by weight based on the weight of said composition, said composition having between 2 and 30% formaldehyde level.

6. A method for the high-speed production of cores suitable for use in production of substantially pinhole-free iron and steel castings comprising the following steps:

- (1) mixing
 - foundry sand in an amount between 94 and 99.5 parts by weight, and
 - binder in an amount between about 0.5 and 6.0 parts by weight,
 - said binder consisting essentially of a boron-containing component selected from the group consisting of boron oxides, boron acids reflecting the various degrees of hydration of boron oxides, and lower oxy acids of boron, said boron-containing component being present in an amount between 5 and 40% by weight based on the weight of the binder, and a second component which is a member selected from the group consisting of
 - (a) a mixture of
 - an acid catalyst, in an amount between 0.5 and 15% by weight based on the weight of said mixture, and
 - a liquid furfuryl alcohol-formaldehyde composition in an amount between 99.5 and 85% by weight based on the weight of said mixture, said composition containing at least 15% furfuryl alcohol monomer, and having between about 2 and 30% formaldehyde level, and
 - (b) a liquid furfuryl alcohol-formaldehyde composition containing at least 15% furfuryl alcohol monomer and having between about 12 and about 30% formaldehyde level,
 - said mixing continuing until said binder is substantially uniformly distributed on said foundry sand, thereby providing a hardenable, shapable foundry mix,
- (2) blowing the foundry mix provided by step 1 onto a shaped, heated surface in a core box, said surface having a temperature between 350° F. and 600° F.,
- (3) permitting the foundry mix to dwell in said core box for a time not less than about 10 seconds nor more than about 40 seconds, wherein said mix becomes a nonshapable, handleable, self-supporting foundry core,
- (4) separating said core from said core box, and
- (5) curing said core at ambient room temperatures for at least 30 minutes.

7. A method according to claim 6, in which the acid catalyst is phosphoric acid.

8. A method for the high-speed production of shell molds suitable for use in production of substantially pinhole-free iron and steel castings comprising the following steps:

- (1) mixing
 - foundry sand in an amount between 94 and 99.5 parts by weight, and

16

binder in an amount between about 0.5 and 6.0 parts by weight,

said binder consisting essentially of a boron-containing component selected from the group consisting of boron oxides, boron acids reflecting the various degrees of hydration of boron oxides, and lower oxy acids of boron, said boron-containing component being present in an amount between 5 and 40% by weight based on the weight of the binder, and a second component which is a member selected from the group consisting of

- (a) a mixture of
 - an acid catalyst, in an amount between 0.5 and 15% by weight based on the weight of said mixture, and
 - a liquid furfuryl alcohol-formaldehyde composition in an amount between 99.5 and 85% by weight based on the weight of said mixture, said composition containing at least 15% furfuryl alcohol monomer, and having between about 2 and 30% formaldehyde level, and
- (b) a liquid furfuryl alcohol-formaldehyde composition containing at least 15% furfuryl alcohol monomer and having between about 12 and about 30% formaldehyde level,

said mixing continuing until said binder is substantially uniformly distributed on said foundry sand, thereby providing a hardenable, shapable foundry mix,

- (2) blowing foundry mix provided by step 1 between heated matched patterns, the sand-contacting surfaces of said patterns having a temperature between 350° F. and 600° F.,
- (3) permitting the foundry mix to dwell between said matched patterns for a period of time not less than about 10 seconds nor more than about 40 seconds sufficient to allow the foundry mix to become a self-supporting handleable foundry shape,
- (4) separating the self-supporting foundry shape from said patterns, and
- (5) curing the self-supporting foundry shape at ambient room temperatures for at least 30 minutes.

9. A method according to claim 8, in which the acid catalyst is phosphoric acid.

References Cited by the Examiner

UNITED STATES PATENTS

2,874,148	2/59	Brown	260—37
2,999,829	9/61	Treat et al.	22—193
3,008,205	11/61	Blaies	22—193
3,024,215	3/62	Freeman et al.	22—193
3,145,438	8/64	Kotlke et al.	22—193

FOREIGN PATENTS

573,760	4/59	Canada.
1,039,017	5/53	France.

MARCUS U. LYONS, *Primary Examiner.*

MICHAEL V. BRINDISI, *Examiner.*