US 20080207796A1

(19) United States

(12) Patent Application Publication

(10) Pub. No.: US 2008/0207796 A1

(43) Pub. Date: Aug. 28, 2008

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(54) FURANIC RESIN AGGREGATE BINDERS AND METHOD

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(21) Appl. No.: 11/865,404

(22) Filed: Oct. 1, 2007

Related U.S. Application Data

(60) Provisional application No. 60/848,279, filed on Sep. 29, 2006.

Publication Classification

(51) Int. Cl.
*B22C 1/22* (2006.01)

(52) U.S. Cl. ........................................................ 523/144

(57) ABSTRACT

Broadly, the invention provides for newly available bio-derived formaldehyde free furanic materials for aggregate binding. The specific example case is aggregate binding for forms used in the metal casting process. The new materials make possible higher productivity and lower phenol, formaldehyde, urea, and/or furfuryl alcohol content in the metal casting form-making process. It is expected that the formulations will work well in other aggregate binding situations as well.

# FURANIC RESIN AGGREGATE BINDERS AND METHOD

[0001] This application claims the benefits of U.S. Provisional Application No. 60/848,279, filed Sep. 29, 2006. The entire disclosure of the provisional application is incorporated by reference herein.

## FIELD OF THE INVENTION

[0002] The present invention provides plant-based compositions for use as binder materials in applications such as acid-cured aggregate binders. Such compositions can be used in a range of composites, adhesives, coatings and other applications. For example, such compositions are used in the metal casting industry for making self-hardenable forms for shaping cast metal parts. These forms are composites of aggregate (for example, sand) with an acidic curing agent and an acid-curable composition. In the Furan No-Bake process, the aggregate is coated sequentially by the added catalyst, then the add hardenable composition, and the mixture is then charged into a pattern. The composition then cures over a period of time at ambient conditions and the hardened forms are removed from the pattern. Furanic acid-cured compositions can also cure in the presence of heat in which case the process is referred as the Furan Hot Box or Furan Warm Box process depending on the amount of heat and the type of catalyst. Furanic acid-cured compositions can also be cured by means of an acidic gas or vapor, such as $SO_2$ (sulfur dioxide) instead of a liquid acid catalyst, in which case the process is referred to as a Furan Cold-Box process. Furanic acid-cured compositions can furthermore be used as a "blown" sand/binder mixture that is rapidly cured by composite acid catalysts (i.e.; ABC Process), a hybrid core making process). The invention includes components and formulations for use in aggregate binding that are based on plant-derived materials as binder components.

[0003] The specific composition type used as in the examples herein is based on "furanic acid-cured no-bake binders" after referred to as FNB binders. In most cases, the binders utilized in metal casting operations require either formaldehyde or phenolic derived resins in the compositions. The present invention will focus on the use of materials capable of formulating FNB binders. An FNB binder is an organic chemical resin solution that is mixed onto an aggregate, such as sand in metal casting, which has already been coated with an acid catalyst solution. To the inventors' knowledge the prior art formulations typically incorporate formaldehyde, phenol, and/or amine-containing ingredients such as ureas for greater strength and/or faster cure development. The present invention discloses formulations that do not require such additives to achieve good strength within reasonable time frames.

[0004] The typical acid catalysts used in previous processes are sulfonic acids such as toluene sulfonic acid, benzene sulfonic acid, xylene sulfonic acid and others. The problems with sulfur containing catalysts are the release of potentially harmful aromatic species into the work environment (EP 1531018) and sulfur contamination of sensitive metal alloys (Gieniec). In some instances phosphoric acid and other weaker acids have reportedly been utilized in combination with the stronger sulfonic acids (JP 19970478840). Lewis acids, such as zinc chloride, are also reported to be useful as third part cure boosters (U.S. Pat. No. 4,543,374; U.S. Pat. No. 4,543,373; WO 0181024). Using only phosphoric acid with cold-blended furanic resins (those not containing a "reacted" base resin) typically show slow cure rates and reduced core and mold physical property characteristics. Furanic formulations can also be cured with gaseous Lewis acids, such as sulfur dioxide in processes termed "cold-box". Cold-box processes are highly productive, but require the use of highly specialized equipment.

[0005] Furanic materials can also be used in hot box processes, where the binder is heat cured at 200-250° C., and warm box processes, where the binder is cure with latent catalysts that are triggered at 130-225° C. Alternative energy sources for binder cure can include microwave, warm air, electromagnetic radiation, ultrasound, electron beam, and others.

[0006] Furanic materials can also be used in the "ABC" Process, where the furanic binder is premixed onto an aggregate along with a moderate acid catalyst in one mixing trough. Another mixing trough blends a stronger acid catalyst with aggregate. The two premixes are then blended in a common high-speed, high-retention mixer and "blown" by air pressure into a pattern or core box, providing a high-production No-Bake core making process.

## BACKGROUND OF THE INVENTION

[0007] Briefly, there is an increasing need to replace petrochemically-derived materials with bio-derived materials due to the gradual decrease in the world supply of petrochemical supplies and the rising costs associated with this decline.

[0008] There is also a need to reduce harmful emissions in the workplace and into the environment. Many composite applications involve resinous binder compositions that are cured with reinforcing materials (fibers, aggregates, and other fillers) to form various functional shapes. One such composite example is bound aggregate shapes; solidified forms that can serve various functions including cores and molds for metal casting operations. Specifically, single-use metal casting forms are made by shaping and curing a resinous aggregate mix. This mix includes aggregate (typically sand) and an organic or inorganic binder. The binder is used to strengthen the forms and can be cured at ambient conditions, heat cured, catalytically cured (gas or liquid), or cured with a combination of heat and a catalyst.

[0009] Metal casting applications were selected for the introduction of these newly available binding materials due to the size and importance of the metal casting marketplace.

[0010] Furanic acid-cured binder compositions for metal casting applications are comprised primarily of furfuryl alcohol, a bio-derived material. However, furfuryl alcohol is typically an imported raw material in North America and therefore subject to trade and economic issues. Fillers, both organic and inorganic, are commonly used in furanic binder formulations to decrease the use of furfuryl alcohol and to impart additional properties (see, for example, U.S. Pat. No. 5,856,375).

[0011] In the near future, the furfuryl alcohol supply is likely to become more restricted as the world economy grows and the overseas use of furfuryl alcohol increases. Thus, there is also a continuing need to find alternatives to replace all or part of the furfuryl alcohol as a component in metal casting no-bake (room temperature cured), gas-cured, and thermally-cured binders. The examples in this invention focus upon the use of newly available materials in furanic acid-cured no-bake binder systems; however those skilled in the art will recognize the potential applicability of the examples to replacement of phenolic acid-cured, phenolic and furanic thermally cured processes, and gas-cured furanic formulations. Likewise alternative energy sources such as microwave, ultrasound, electron beam, warm-air, electromagnetic radiation, and others can be considered as energy sources for curing formulations containing the newly available materials emitted to the environment and into the workplace.

[0012] There is also a need to decrease the hazardous materials, such as hazardous air pollutants used in aggregate binders, including phenol and formaldehyde. There is also a need to decrease leachates from landfills, such as those from phenol-formaldehyde resins, that can be washed from the spent aggregate into ground water. Decreasing the phenol and formaldehyde content of foundry binders is central to conformance to state and federal environmental guidelines. A reduction in the amount of the acid-containing components used or the use of a less aggressive acid, such as a phosphoric acid is also beneficial. A less aggressive acid would decrease wear and tear on the equipment in the factory. The typical aggressive acids of the aromatic sulfonic kind can also release aromatic molecules into the work area after a metal casting is made.

[0013] A common perception among those practiced in the art is that formaldehyde is essential to the development of strength in metal casting forms, particularly the overall speed of cure and the through-cure (cure in the interior of the metal casting form) and the bonding strength. Efforts have been made to reduce the formaldehyde used in the formulation of these binders, such as the effort described in EP 0698432. Surprisingly, the present inventive approach to these formulations eliminates the formaldehyde, urea and the phenols from the formulations while maintaining acceptable strength development and reactivity.

[0014] Efforts have also been made to find alternative resins to improve acid cured binder performance. U.S. Pat. No. 6,559,203, for example discusses the use of alternative resorcinol resins to boost metal casting form strength. The inventive formulations boost metal casting strengths with minimal use of resorcinol.

## BRIEF DESCRIPTION OF THE INVENTION

[0015] The present invention relates to the use of bio-derived furanic materials as components of binder compositions for aggregates while minimizing or, preferably, eliminating formaldehyde as a binder component. In particular, the invention relates to the use of materials derived from agricultural waste streams which have been converted into a form suitable for their use in organic binders. These materials can be utilized to reduce the need for or, preferably, replace phenol-formaldehyde resins, furan-formaldehyde resins, urea-formaldehyde resins, resorcinol, and/or furfuryl alcohol in various acid-cured, thermally-cured, and gas-cured binders.

[0016] Examples of materials so derived include:

- [0017] 5-hydroxymethyl furfural (HMF);
- [0018] 2,5-furan dimethylol (FDM);
- [0019] 2,5-furan dicarboxylic acid (FDCA); and
- [0020] 2,5-diformyl furan (DFF).
- [0021] HMF-ethers such as ethoxymethylfurfural or butoxymethylfurfural
- [0022] FDM-ethers
- [0023] FDCA Monoalkyl Esters (Hemiesters)

[0024] The application of the inventive compositions to other binders, such as furanic and phenolic acid cured, thermally cured and gas-cured binders, as well as to other composites, adhesives, and coatings will be recognized by those skilled in the art.

[0025] One broad aspect of the invention provides for a furanic acid-cured resin composition including a substantially phenol, nitrogen, and formaldehyde-free formulation of furfuryl alcohol mixed with about 1 to about 45 wt % 5-hydroxymethyl furfural; or about 1 to about 60 wt % 2,5-furan dimethylol; or about 1 to about 40 wt % 2,5-furan dicarboxylic acid; or about 1 to about 60 wt % 2,5-diformyl furan; or about 1 to about 20 wt % polyester polyol; or mixtures of two or more selected from the above.

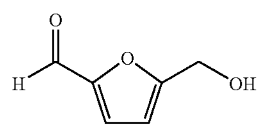
[0026] Another broad aspect of the invention provides for a furanic acid-cured resin composition including a substantially phenol, nitrogen, and formaldehyde-free formulation of furfuryl alcohol mixed with about 1 to about 20 wt % 5-hydroxymethyl furfural; or about 1 to about 30 wt % 2,5-furan dimethylol; or about 1 to about 10 wt % 2,5-furan dicarboxylic acid, or about 1 to about 25 wt % 2,5-diformyl furan; or mixtures of two selected from the above. In some embodiments about 1 weight % and 90 weight % of furfuryl alcohol is replaced with blends of 5-hydroxymethyl furfural and 2,5-furan dimethylol at wt % ratios between the two components of about 5 to about 955-hydroxymethyl furfural to 2,5-furan dimethylol, to about 95 to about 55-hydroxymethyl furfural to 2,5-furan dimethylol.

[0027] A further broad embodiment of the invention provides for a furanic acid-cured resin composition including a substantially phenol, nitrogen, and formaldehyde-free formulation of furfuryl alcohol mixed with about 1 to about 20 wt % 5-hydroxymethyl furfural; and about 1 to about 30 wt % 2,5-furan dimethylol.

## DETAILED DESCRIPTION OF THE INVENTION AND BEST MODE

[0028] The present invention provides for formulations which function as acid-cured binders for sand-based cores and molds used within the metal casting industry and are partly comprised of components derived from agricultural waste streams. Precursor materials are the result of acid catalyzed digestion of hexoses, such as fructose, and include 5-hydroxymethyl furfural (Formula 1) as a major product (U.S. Pat. No. 4,740,605 and Lewkowski). A good general discussion of possible uses of furanic materials from cellulosic feedstocks is found in the Gandini reference.

Formula 1:



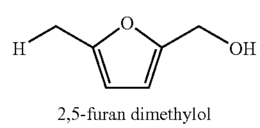

5-hydroxymethyl furfural

[0029] 5-hydroxymethyl furfural is a primary product of the acid digestion of carbohydrate materials and, as such, is of great interest in the discovery of new applications as it requires relatively few steps to produce.

[0030] 5-hydroxymethyl furfural has been reported as an intermediate in thermally cured binders being first reacted to form an $\alpha,\beta$ unsaturated molecule, then incorporated into a thermal cure formulation (JP 04327336).

[0031] 2,5-furan dimethylol (Formula 2) can be obtained from 5-hydroxymethyl furfural by a simple reduction of the aldehyde group (Lewkowski).

Formula 2:




2,5-furan dimethylol

[0032] 2,5-furan dimethylol is known as an accelerator for furanic acid-cured binder processes (JP 2000246391; JP 2000225437; JP 09047840; WO 9605925) in the metal casting industry when a formaldehyde containing material is used. 2,5-furan dimethylol in the previous process typically is synthesized by the treatment of furfuryl alcohol or furan with formaldehyde (See EP 1531018 and U.S. Pat. No. 6,479,567). Thus 2,5-furan dimethylol, oligomers of 2,5-furan dimethylol, and varying amounts of free formaldehyde are present in a furanic acid-cured binder formulation. Even in a case where 2,5-furan dimethylol was used without added formaldehyde in its formation (EP 0698432), the binder formulation included both 2,5-furan dimethylol and formaldehyde-containing resins. It is commonly believed among those practiced in the art that some formaldehyde is needed for rapid through-cure and deep-set properties. It is an intent of this invention to achieve acceptable foundry core and mold form properties with minimal or, preferably, no formaldehyde.

**[0033]** The 2,5-furan dimethylol in this invention is derived from the reduction of 5-hydroxymethyl furfural to 2,5-furan dimethylol (Lewkowski). The elimination of formaldehyde from the production improves process safety of these formulations by decreasing potential worker exposure to formaldehyde. Surprisingly, the rate of cure with the 2,5-furan dimethylol thus derived is apparently at least as fast as the "reactive resin" co-polymers such as urea-formaldehyde. This enables either higher productivity using the typical sulfur-based strong acid catalysts or typical productivity using weaker phosphorous-based catalysts when compared to currently known furanic acid-cured formulations. The use of the phosphorous catalyst is preferred for some alloys, when curing cores and molds using ambient or heated aggregates, to lower acid catalyst cost and reduce the amounts of corrosive ingredients from the foundry environment. Some castings from certain alloys are negatively impacted by the incorporation of sulfur from the conventional sulfur-based catalysts (See, for example JP 1997047840, JP 09047840, and EP 1531018). Further, the aromatic component from sulfonic acid catalysts can sometimes escape into the workplace atmosphere, creating a hazardous condition (see, for example Gieniec). Heated aggregates containing sulfonic acid catalysts can accelerate cure causing premature hardening of the sand mix and be detrimental to metallic-based tooling and patterns (due to corrosion) used within the foundry. Phosphoric acid can be used in these cases to prevent premature cure and reduce corrosion.

**[0034]** Advantages of the present invention are the replacement of petrochemical materials in some metal casting applications, replacement of furfuryl alcohol in furanic acid-cured type binders, replacement of reacted base resins, very fast cure response, elimination of formaldehyde from the process and the formulations utilized in making metal casting binders, reduction in amounts of required sulfonic acid catalysts and/or replacement of the sulfonic acids with phosphoric acid.

**[0035]** The data shows that in many inventive formulations, the speed of the reaction is increased by the use of the bio-derived materials. The speed of reaction increases in some cases to the point that weaker catalysts such as, for example, phosphoric acid can be utilized in place of sulfonic acids while maintaining acceptable cure speeds. Some references (for example JP 09047840 and EP 0698432) teach the use of 2,5-furan dimethylol being used with a blend of sulfonic and phosphoric acids. In all literature articles known to the inventors, however, some sulfonic acid and/or some formaldehyde is used.

**[0036]** In addition to furanic materials, these formulations may include phenolic resins, phenolic resoles, urea resins, urea-formaldehyde resins as cure-enhancing resins. Incorporation of these materials into the binder compositions is not necessarily preferred; however, especially since free formaldehyde is typically added to the formulation as a consequence of their inclusion.

**[0037]** Molds and cores made by the acid-cure process can be quite large, weighing several tons. Consequently, it is important to formulate a metal casting mix which will provide sufficient work-time to allow time to shape the metal casting mix in the pattern. "Work-time" is defined within these evaluations as the time interval after mixing the binder components and aggregate in a pattern, and the time when the metal casting form reaches a level of 60 on the "Model #473 Green Hardness B-Scale Gauge" sold by Harry W. Dietert Co., Detroit, Mich. "Strip-time" is the time interval after mixing the binder components and aggregate in a pattern, and the time when the metal casting form reaches a level of 90 on the Model #473 Green Hardness B-Scale Gauge (American Foundry Society Method 3180-03-S). The work time and strip time levels may vary depending in a foundry depending on the resin system employed and the size and configuration of a particular core or mold as well as the foundry climate (temperature and humidity).

**[0038]** The strip-time for removing the form from the pattern should be minimized for higher productivity aggregate forms. A typically desired work-time may range from 1 minute to 1.5 hours and typically desired strip-times range from 3 minutes to 8 hours. The forms produced must be strong enough so they can be handled after the strip-time has elapsed. They should also be easily removable from the pattern. The forms must also produce useful castings, i.e., castings that do not have or have allowable levels of defects such as veining, porosity, lustrous carbon, penetration, or erosion defects and still maintain other desirable characteristics; such as, for example, shake-out or surface finish. The improved cure from the inventive formulations should eliminate mobile molecular species, which should result in clean removal of the metal casting form from the mold in which it was cured, leaving little or no residue.

**[0039]** The metal-casting industry continues to be interested in acid-cure binder compositions that do not contain free formaldehyde and phenol; which have useful work-times and strip-times for high production operations; and that produce forms with sufficiently high tensile strengths that can be used to make casting with few or no defects. Consequently, there is an interest in developing aggregate binders with lower levels of volatile organic compound emissions, free phenol, and free formaldehyde that do not have unpleasant odors and generate little smoke during the form-making and casting processes.

**[0040]** Acid-cured furanic binder compositions are generally recognized as attractive alternatives to phenolic-based acid-cured binders because they, preferably, do not contain free phenol, free formaldehyde, do not have high levels of relatively volatile organic compound emission, result in unpleasant odors, and generally generate less smoke during the form-making and casting processes. It is also desirable to have no free formaldehyde in the process to make such binders and in the binders themselves. Typically, faster-reacting higher productivity furanic acid-cured binders are comprised in part of "reactive furan resins" made from the reaction of furfuryl alcohol or furan with formaldehyde or urea-formaldehyde, thus introducing formaldehyde into the process and into the binder. Faster-reacting furanic acid-cured binder compositions may also typically contain higher levels of monomeric furfuryl alcohol, increasing their cost and lowering emissions, but requiring stronger sulfonic acid catalysts. Furan binders are also modified to increase their reactivity by incorporating other polymer or reactive monomers into the furan binder, e.g. urea formaldehyde resins, phenol formaldehyde resins, resole resins, resorcinol, bisphenol A tar, polyols, etc. Nevertheless, these modifications may or may not provide the cure speed and/or immediate tensile strengths that are needed for true high productivity. The inventive formulations can lead to formaldehyde free, volatile organic compound free, nitrogen free and phenol free formulations.

[0041] In addition to increasing the cure rate of the binder, it is desirable to identify binder components that impart improved mechanical properties to the forms. These binder components are also desirable for improved humidity and temperature resistance in the core and mold making process.

[0042] Additionally, binder components that lower free formaldehyde by reacting with it, are desirable; especially in conventional formulations.

[0043] The use of 2,5-furan dimethylol modified furanic materials can be an environmentally friendly alternative to current phenol formaldehyde-urethane systems in that the work times/strip times are equivalent to those systems without the use of phenols, formaldehydes, amines or isocyanates.

[0044] Further, the use of fast, acid cured 2,5-furan dimethylol-modified furanic binders in place of polyurethane no-bake binders affords better compatibility of reclaimed aggregates at mixed-binder facilities, where furanic binders are currently used in the same facility as polyurethane no-bake binders. The polyurethane no-bake binders are used in the industry due to their fast cure speed. The base catalyst used to cure them can remain on the spent sand and can inhibit the acid-based furanic cure due to the higher pH of the sand after the re-claiming process.

[0045] Conventional furanic acid-cured formulations rely on furfuryl alcohol and often on additional resinous materials to enhance certain properties. These resinous materials include phenolic polymers with formaldehyde and/or urea formaldehyde, such as resoles (see U.S. Pat. No. 3,676,392 for PEP, or polyether phenol, resole resins), used at 0-50 weight %, and furfuryl alcohol polymers with formaldehyde and/or urea formaldehyde (for example Beetle® 65 resin from Cytec) copolymers at 0-95 weight %. Other candidate constituents include resorcinol or bis-phenol A (between about 0 and about 15 weight %) which are used to increase the rate of cure, an alcohol such as methanol (between about 0 and 10 weight %), silanes (between about 0 and about 4 weight %), and fillers (between about 0 and about 75 weight %).

[0046] Fillers, typically soluble resinous materials, are used to replace furfuryl alcohol, to lower resin cost and to enhance mechanical properties. For example, some fillers are used to plasticize the binder improving the flexibility when compared to the relatively brittle furanic binder. Typical filler/plasticizers are resorcinol pitch and bis-phenol A tar (by-products from the manufacture of resorcinol and bisphenol A; residues or bottoms from the production of azelaic acid by the ozone oxidation process (Henkel Corporation, Emery Group); by-products (mixed esters) from the production of terephthalic acid and its esters; lignins and lignosulfonates from the paper industry; various rosins from the forest industry, and the like. Purified commercial products may also be used as fillers, such as Terol® 250 and 256, Terate® 203 (Oxid), and Phenrez® 178 (Invista). These all may be utilized as fillers by themselves or even mixtures thereof. Such fillers need be compatible with the acid-cured furan formulations and are used to reduce the amount of furfuryl alcohol, adding plasticity to the formulation and reducing the formula cost.

[0047] Such conventional fillers and/or plasticizers are at least partially, if not fully, compatible and can be replaced by or blended with 5-hydroxymethyl furfural (Formula 1) and/or 2,5-furan dimethylol (Formula 2) in accordance with the present invention. Further, furfuryl alcohol can be replaced in formulations that currently do not contain fillers with no loss of performance properties.

[0048] Examples of some commercially available silanes are γ-aminopropyl-methyldiethoxy silane (Dow Corning D1505, from Aldrich, USA); 3-(diethoxymethylsilyl)propylamine (Aldrich); γ-glycidoxy propyltrimethoxy silane (Dow Corning Z6040 and Union Carbide A-187); γ-aminopropyltriethoxy silane (Union Carbide A-1100); N-beta(aminoethyl)-γ-amino-propyltrimethoxy silane (Union Carbide A 1120); γ-ureidopropyltriethoxy silane (Union Carbide A-1160); and many others.

[0049] Further information on these formulations can be found by reference to Langer, et al., "Foundry Resins", Encyclopedia of Polymer Science and Engineering, Vol. 7, Second Edition, pages 290-298, John Wiley & Sons, Inc. (1987). See also Solomon, The Chemistry of Organic Film Formers, Second Edition, pages 253 et seq., Robert E. Krieger Publishing Company, Huntington, N.Y. (1977). The disclosures of these references are expressly incorporated herein by reference.

[0050] The 5-hydroxymethyl furfural can be utilized as a filler replacement in accordance with the teachings of the present invention. The amount of 5-hydroxymethyl furfural can range up to about 75 weight % and advantageously it ranges from about 1 to 30 weight %. Please refer to Example 1.

[0051] The 2,5-furan dimethylol can be utilized as a replacement for furfuryl alcohol or for fillers and plasticizers in accordance with the teachings of the present invention. The 2,5-furan dimethylol can also enhance the reactivity of formulations in which it is utilized. The amount of 2,5-furan dimethylol can range up to about 90 weight % and advantageously it ranges from about 1 to 75 weight %. Caution needs to be exercised above 30% 2,5-furan dimethylol, however, as the typical sulfonic catalyzed reaction becomes extremely fast and some ingredients may affect the solubility levels of the 2,5-furan dimethylol in the binder solution.

[0052] Unexpectedly, it was determined that with the use of 2,5-furan dimethylol in a furanic acid-cured metal casting binder formulation, faster strip times were realized than in conventional formulations despite the absence of formaldehyde-derived resins and free formaldehyde. Faster strip-times can translate into higher productivity and/or lower catalyst usage in the production of meta casting forms. Please refer to Example 1.

[0053] 2,5-furan dimethylol formulations also show faster strip times, but also show high mold strengths initially and, unexpectedly, after 24 hours aging compared to a conventional formulation while using a typical strong acid catalyst. Faster strip times and initial tensile strengths were also seen with the use of bis-phenol A tar filler compared to conventional filler (U.S. Pat. No. 5,856,375), but aged strengths were of conventional magnitude. These results infer that 2,5-furan dimethylol-based formulation will reduce the need for expensive accelerator additives, such as resorcinol, and can reduce catalyst usage and cost. Please refer to Example 2.

[0054] 2,5-furan dimethylol formulations cured with weak acid catalysts show competitive strength development as well. This allows for formulations using a less corrosive and less polluting acid catalyst. Please refer to Example 3.

[0055] As used herein the term weak acid refers to an acid having a $pK_a$ between about 2 to about 6, and preferably between about 2 and about 4. Typical weak acids useful in the invention include weak acids such as phosphoric acid, nitrous acid, citric acid, formic acid, and the like, polyacrylic acid, alone or in combination. Thus a strong acid has a $pK_a$ of 2.0 or less. A typical strong acid is sulfonic acid.

[0056] 5-hydroxymethyl furfural and 2,5-furan dimethylol were also tested together and with typical binder components to demonstrate their compatibility in various combinations with current state of the art ingredients. These formulations were subjected to a wide variety of tests and were at least comparable to conventional controls in terms of overall performance. Please refer to Example 4.

[0057] The fast early strength development in several inventive formulations could translate into cost savings owing to decreased breakage and waste in the core and mold production of the metal casting operation. Alternatively, the metal caster may choose to use less acid catalyst, a less expensive catalyst, or a non-sulfur containing catalyst, such as phosphoric acid, saving money and achieving equal performance as compared to conventional formulations. Lower binder levels are also a possibility, likewise saving cost.

[0058] The results described herein also imply that a high-productivity acid-cure process is technically possible from the use of 2,5-furan dimethylol or 2,5-furan dimethylol/5-hydroxymethyl furfural blends especially. Such a process may react so quickly that there will be essentially zero strip time—the catalyst and binder will then need to be mixed separately on separate portions of the aggregate, the two premixes are then either "blown" together through a common high-speed mixer into a mold with a compressed gas, plunger, or some other means of rapid integration and mixing, such as a high-speed mixing head commonly used on commercially available foundry floor mixers. Once the aggregates are mixed and compressed, the cure will proceed rapidly. This offers the metal caster the possibility of using a furanic no-bake resin system as a replacement to the commonly employed phenolic-urethane resin system allowing less resin and having more flowable (less "sticky") resin coated aggregate, and a zero formaldehyde, zero phenol and zero amines for a high-speed core-making process. The strategy is also applicable to ambient, thermal, or gas cured forms.

[0059] The examples contained herein were tested on conventional silica aggregate. If desired, other aggregate materials can also be used. The bound form needs not be limited to the metal casting form application. Other potential applications include filters, catalyst surfaces, mortars, cements, and other bound aggregate applications.

[0060] Additives can be added to the aggregate for improvement of various casting properties. These include, for example, iron oxides (red and black), Lewis acids, ground flax fibers, flour, cellulosics, and the like.

[0061] The following examples show how the invention has been practiced, but should not be construed as limiting. All percentages and proportions herein are by weight and all citations are expressly incorporated herein by reference.

[0062] A description of the acid-cured laboratory test procedures (a sub-set of binders generally referred to as "no-bake") used to determine the cure rate and final properties of cured aggregate metal casting forms can be found in the American Foundry Society "Mold and Core Test Handbook Third Edition" and in the American Foundry Society "Chemically bonded Cores and Molds—An Operator's Manual", Section 7—Self-setting Chemical Binder Systems.

[0063] The following examples are meant to be merely illustrative of various aspects of the invention and are not meant to limit the scope of the invention in any way. The formulations disclosed in Examples 1 through 4 were used to evaluate 5-hydroxymethyl furfural and 2,5-furan dimethylol as reactive fillers in furanic acid-cured binder formulations as partial or complete replacements of furfuryl alcohol.

## EXAMPLE 1

[0064] This example illustrates the use of 5-hydroxymethyl furfural in a furanic acid-cured binder formulation. Table 1 shows formulations with 5-hydroxymethyl furfural as a binder element.

TABLE 1

Formulations with HMF binder

| | Test Number | | | |
|---|---|---|---|---|
| | Control | 1 | 2 | 3 |
| Furfuryl Alcohol (pph[1]) | 96.0 | 91.0 | 86.0 | 76.0 |
| Resorcinol (pph[1]) | 3.85 | 3.85 | 3.85 | 3.85 |
| Silane[2] (pph[1]) | 0.15 | 0.15 | 0.15 | 0.15 |
| 5-hydroxymethyl furfural (pph[1]) | 0 | 5.0 | 10.0 | 20.0 |

[1]pph = parts per hundred (weight)
[2]3-(diethoxymethylsilyl) propylamine

[0065] The ingredients in each of the Table 1 formulations were added to an 8 oz jar and shaken until dissolved to a clear amber solution.

[0066] The catalyst solution was comprised of 38% tap water, 2% methanol, and 60% para-toluene sulfonic acid (Aldrich).

[0067] To 4000 grams of Wedron 540™ sand, 20 grams of an aromatic sulfonic acid catalyst solution was added and mixed for one minute in a Hobart N50 mixer. This aggregate mixture then was manually flipped and mixed for another minute. Each formulation (50 grams) was added to the aggregate mix and the mix procedure repeated. The final mix was immediately placed into a 15-cavity core making box, the cavities structured to make standard American Foundry Society "dog-bone" test forms and pressed firmly into place. The remainder of the tests (1, 2, 3) were similarly done but with a weak acid, a solution of 85 wt % phosphoric acid.

[0068] The time recorded for the "work time/strip time" measurement began after the mix was complete. "Work time" is defined as the time it takes for the mix to reach 60 hardness on a Model #473 Green Hardness "B" Scale Tester (Dietert Co., Detroit, Mich.) and is a measure of cure speed. "Strip time" is the time at which the molds are hard enough to remove and handle, as measured by the time it takes the mix to reach 90 on the same scale, and is a measure of processing speed.

[0069] The dog bones from the Table 2 tests were stripped and timing for the tensile testing begun. Tensile strengths were run on a Thwing-Albert QC-3A™ tensile tester equipped with a 454 kilogram load cell at 5.1 centimeter per minute.

[0070] Strip times and tensiles for these are shown on Table 2.

TABLE 2

Strip times and Tensile Strengths

| | Test No. | | | |
|---|---|---|---|---|
| | Control | 1 | 2 | 3 |
| Work time (minutes) | 34 | 28 | 25 | 23 |
| Strip time (minutes) | 51 | 42 | 38 | 34 |
| Tensile Strength: Kg/cm$^2$ (average of 3 runs) | | | | |
| 1 Hour after strip | 4.4 | 6.5 | 4.6 | 4.1 |
| 3 Hours | 18.6 | 15.0 | 12.4 | 7.7 |
| 24 Hours | 21.2 | 17.3 | 12.8 | 8.7 |

[0071] The Table 2 data show that the speed of surface cure and the speed to stripping is increased as the level of 5-hydroxymethyl furfural is increased. This occurs in the absence of formaldehyde addition and infers a faster processing time for the 5-hydroxymethyl furfural-filled formulations. Ultimate tensile strengths are decreased as the 5-hydroxymethyl furfural loading increases, but this is not necessarily a disadvantage if the strengths and productivity values in Table 2 are sufficient. A metal casting operation often requires higher speed in production and for such situations these 5-hydroxymethyl furfural filled formulations may be a significant improvement over their current binders despite the absence of free added formaldehyde. With regard to furfuryl alcohol replacement by 5-hydroxymethyl furfural, up to at least 20% of the furfuryl alcohol can potentially be replaced and maintain full performance. Higher levels can be replaced, but only at the sacrifice of strength or productivity values.

## EXAMPLE 2

[0072] This example illustrates the use of 2,5-furan dimethylol as a filler and replacement for a portion of the furfuryl alcohol in furanic acid-cured binder formulations. Table 3 shows formulations utilizing 2,5-furan dimethylol in furanic acid-cured binder formulations. The acid in this case is the standard p-toluene sulfonic acid described in Example 1. The Example illustrates that the 2,5-furan dimethylol can be used as an accelerator/filler despite the absence of added free formaldehyde.

TABLE 3

| | Test No. | | | | | |
|---|---|---|---|---|---|---|
| | Control | 1 | 2 | 3 | 4 | 5 |
| Furfuryl Alcohol (pph[1]) | 96.0 | 91.0 | 86.0 | 76.0 | 66.0 | 56.0 |
| Resorcinol[2] (pph[1]) | 3.85 | 3.85 | 3.85 | 3.85 | 3.85 | 3.85 |
| Silane[3] (pph[1]) | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 |
| 2,5-Furan Dimethylol (pph[1]) | 0 | 5.0 | 10.0 | 20.0 | 30.0 | 40.0 |

[1]pph = parts per hundred (weight)
[2]Resorcinol, 98% (Sigma-Aldrich)
[3]3-(diethoxymethylsilyl) propylamine (Aldrich)

[0073] Each Table 3 formula was compounded and tested as in Example 1, the test results are shown in Table 4.

TABLE 4

| | Test | | | | | |
|---|---|---|---|---|---|---|
| | Control | 1 | 2 | 3 | 4 | 5 |
| Work time (minutes) | 29 | 22 | 22 | 19 | 15 | 12 |
| Strip time (minutes) | 45 | 38 | 33 | 25 | 19 | 16 |
| Tensile Strength: Kg/cm[2] (average of 3 runs) | | | | | | |
| 1 Hour after Strip | 6.0 | 6.4 | 7.9 | 8.3 | 7.9 | 17.8 |
| 3 Hours | 7.9 | 19.8 | 23.5 | 21.8 | 23.1 | 24.5 |
| 24 Hours | 23.8 | 25.8 | 24.8 | 25.0 | 25.0 | 22.7 |

Conditions:
Wedron 540 sand at 17° C.;
Binder at 1.25% and 40 catalyst based upon binder;
Ambient - 19° C., 60% relative humidity (RH)

[0074] The Table 4 data show that, as with the 5-hydroxymethyl furfural results in Table 2, the speed of surface cure and the speed to stripping increases as the level of 2,5-furan dimethylol is increased. This infers a faster processing time for the 2,5-furan dimethylol containing formulations. Up to 40% of the furfuryl alcohol is replaced in the Example 2 formulations.

[0075] The Table 4 tensile data shows that, unlike 5-hydroxymethyl furfural, The 2,5-furan dimethylol formulations continue to grow in tensile strength throughout a 24 hour period. The strength at one hour for Formulation 5 of Table 4 is particularly interesting as the high strength indicates, unexpectedly, the potential for a higher productivity furanic acid-cure binder system. This represents a major new type of binder for metal casting applications in terms of cure speed with standard acids and no added formaldehyde.

[0076] Formulations above 30% 2,5-furan dimethylol are stable in furfuryl alcohol solutions, but marginally stable in cold-blended solutions that include various typical filler materials. To displace more furfuryl alcohol, it may be necessary to utilize other materials in order to get compatible solutions at lower furfuryl alcohol. This is discussed in Examples 3 and 4.

## EXAMPLE 3

[0077] This example illustrates the use of 2,5-furan dimethylol as a component of a filler package and replacement for a portion of the furfuryl alcohol in furanic acid-cured binder formulations using weak acid catalyst. Table 5 shows formulations utilizing 2,5-furan dimethylol in furanic acid-cured binder formulations. The acid is 85% phosphoric at 50% based upon resin. The Example illustrates that the 2,5-furan dimethylol can be used as an accelerator/filler despite the absence of added free formaldehyde and even with a weak acid catalyst. Table 5 shows 2,5-furan dimethylol in various combinations of typical furanic additives at up to 30% replacement of furfuryl alcohol.

TABLE 5

| | Test | | | |
|---|---|---|---|---|
| | Control | 1 | 2 | 3 |
| Furfuryl Alcohol (pph[1]) | 96.0 | 78.5 | 68.5 | 69.85 |
| Resorcinol[2] (pph[1]) | 3.85 | 3.85 | 3.85 | 0.0 |
| Silane[3] (pph[1]) | 0.15 | 0.15 | 0.15 | 0.15 |
| Phenrez 178 | 0 | 7.5 | 7.5 | 0 |
| 2,5-Furan Dimethylol (pph[1]) | 0 | 10.0 | 20.0 | 30.0 |

[1]pph = parts per hundred (weight)
[2]Resorcinol, 98% (Sigma-Aldrich)
[3]3-(diethoxymethylsilyl) propylamine (Aldrich)

[0078] Each Table 3 formula was compounded and tested as in Example 1, the test results are shown in Table 4.

TABLE 6

| | Test | | | |
|---|---|---|---|---|
| | Control | 1 | 2 | 3 |
| Work time (minutes) | 2 | 2 | 2 | 3 |
| Strip time (minutes) | 3 | 3 | 3 | 5 |

TABLE 6-continued

| | Test | | | |
|---|---|---|---|---|
| | Control | 1 | 2 | 3 |
| Tensile Strength: $Kg/cm^2$ (average of 3 runs) | | | | |
| 1 Hour after Strip | 3.7 | 3.7 | 4.8 | 0.7 |
| 3 Hours | 5.2 | 4.4 | 5.9 | 7.9 |
| 24 Hours | 6.6 | 5.6 | 6.3 | 9.5 |

Conditions: Wedron 540 ™ sand at 17° C.; Binder at 1.25% and 40 catalyst based upon binder; Ambient - 19° C., 60% relative humidity (RH)

**[0079]** The Table 6 data show that the 2,5 furan dimethylol formulations are equal to or stronger than the control formulation in the presence of a weak acid. This drastically decreases the demand for furfuryl alcohol in these binders and.

**[0080]** Formulations above 30% 2,5-furan dimethylol are stable in furfuryl alcohol solutions, but marginally stable in solutions that include various typical filler materials. The last formulation on Table 3 has no additional filler for that reason. To displace more furfuryl alcohol, it may be necessary to utilize other materials in order to get compatible solutions at lower furfuryl alcohol. This is discussed in Example 4.

## EXAMPLE 4

**[0081]** This example illustrates the displacement of furfuryl alcohol with alternative materials. There are a number of materials well known in the art that are used to formulate no-bake aggregate binders. Example 4 uses several of these materials in various combinations to assess the performance of the 2,5-furan dimethylol and 5-hydroxymethyl furfural with these commonly used materials. One of these materials is a urea formaldehyde, which likely introduces some formaldehyde and nitrogen into the formulations, but is included in the Example for completeness. Another of these materials is a typical polyester polyol filler. These are used with the 2,5-furan dimethylol and 5-hydroxymethyl furfural to determine the compatibility and property consequences of these materials.

**[0082]** Example 4 also includes additional tests: scratch hardness, transversal strength, and thermal burn-out as a "shake-out" simulation. The tests are added in this Example to provide a more complete understanding of the likely performance of these formulations as binders for metal-casting forms.

**[0083]** The scratch hardness test measures the surface hardness of the bound aggregate by determining the resistance to marring, sold by Harry W. Dietert Co., Detroit, Mich. "Model $\#_{674}$™ Scratch Hardness Tester" (see American Foundry Society 3318-00-S).

**[0084]** Transversal strength tests are run using 2.54 cm×2.54 cm×20.32 cm bars on the same tensile tester as is utilized for the tensile tests, but with a specialized fixture (tooling) to hold and break the test specimen. The tooling is three-point with 15.24 cm between the points. Two measurements are simultaneously taken:

**[0085]** 1. Elongation—The distance the bar bends before breaking.

**[0086]** 2. Strength—The peak strength at break.

**[0087]** The Thermal Degradation Procedure described below is a simulation of "Shake-out" performance. Shake-out is an essential quality for a binder in metal casting operations. This involves the removal of the aggregate from the interior (cores) and around the exterior (molds) of the cooled castings. This property is particularly important for aluminum castings, as the lower temperature of the molten metal does not decompose the binder as much as in iron or steel castings. Most aluminum castings are poured at around 670 to 790° C., brass and bronze are poured around 900 to 1065° C., most irons are poured in the ranges of 1150 to 1320° C., and steels are poured around 1540 to 1650° C. Internal core/mold temperature generally do not reach the temperature of the poured metal, therefore very little binder breakdown occurs inside these forms past the first few millimeters from the molten metal, making the residual bond aggregate a challenge to remove. Shake-out is a difficult quality to measure in the laboratory, but the relative performance of a binder can be predicted by a thermal treatment following the procedure described as follows;

Shake-Out Simulation Procedure:

**[0088]** This method covers the determination of the laboratory aggregate core shake-out properties of an acid-catalyzed furan no-bake (furfuryl alcohol-based) binder system sample using a water-based sulfonic acid catalyst.
Materials and sample preparation were as follows.
Core Samples Test core samples are comprised of intact cured aggregate forms. Often, half-sections from tensile or transversal test specimens with a minimal 25 mm cross section are utilized.

Test Procedure:

**[0089]** 1. Set a muffle furnace to 427° C.
2. Select a test sample with at least 24 hours aging (all test specimens having the same aging).
3. Determine the sample weight in grams on a high temperature crucible or steel pan.
4. Using a long pair of steel tongs and heat resistant gloves, place the sample in the muffle furnace for 5 minutes.
5. Remove the sample and cool for at least 5 minutes.
6. Gently brush away the loose aggregate from the sample.
7. Weight the remaining solidified sample. The loosened aggregate weight is the "thermally reclaimed" aggregate. The difference between the original sample weight minus the "thermally reclaimed" weight is the remaining core or "mechanically reclaimed" aggregate weight.
8. The weight of the thermally reclaimed aggregate divided by the original sample weight multiplied by 100 is the final percent "shake-out".
9. Repeat these steps but now with the oven dwell time set at 10 minutes, followed by another sample at 15 minutes and then again at 20 minutes for the % shake-out versus time profile.

**[0090]** The formulations listed on Table 7 were used to evaluate 2,5-furan dimethylol as a reactive filler, or co-filler, in furanic acid-cured binder formulations. The control was a straight furfuryl alcohol formulation, test Formulation 1 was a furfuryl alcohol formulation with a typical filler. The rest of the formulations were according to the invention, with combinations of 5-hydroxymethyl furfural, 2,5-furan dimethylol, filler and a well-known formaldehyde-containing reactive resin. The well-known formaldehyde resin is included for completeness and for comparison purposes; since such resins are commonly utilized in the art. Preferably, no added formaldehyde or formaldehyde-containing resin is used with the invention.

TABLE 7

| Ingredient | Control | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| Furfuryl Alcohol (FA) (pph) | 96.00 | 88.50 | 82.85 | 73.50 | 63.50 | 63.50 | 78.50 | 73.50 | 58.50 |
| Resorcinol | 3.85 | 3.85 | 2.00 | 3.85 | 3.85 | 3.85 | 3.85 | 3.85 | 3.85 |
| Silane | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 |
| Terol 256 ™[1] | — | 7.50 | — | 7.50 | 7.50 | 7.50 | 7.50 | 7.50 | 7.50 |
| 5-hydroxymethyl Furfural | — | — | — | — | 10.00 | — | — | 5.00 | 5.00 |
| 2,5-furan Dimethylol | — | — | 15.00 | 15.00 | 15.00 | 15.00 | — | — | 15.00 |
| Urea Formaldehyde Resin[2] | — | — | — | — | — | 10.00 | 10.00 | 10.00 | 10.00 |

Notes:
[1]Terol 256 ™ - polyester polyol;
[2]methylated urea-formaldehyde resin

[0091] Each Table 7 formula was compounded and tested as in Example 1 (conventional acid catalyst) and the results are shown in Table 8. Note that results can be construed as "good" or "bad" differently, depending upon the needs of a given metal casting operation. An important consideration in the present invention is obtaining competitive performance at decreased furfuryl alcohol levels.

[0092] Conditions for the tests in Table 8 were: Wedron 540™ sand at 15-16° C.; Binder at 1.25% and 40% conventional catalyst based upon Binder; ambient temperature at 20-21° C., and 20% relative humidity (RH).

[0093] The 5-hydroxymethyl furfural and 2,5-furan dimethylol replaced 5 to 25% of the furfuryl alcohol in these tests, with conventional binder elements replacing another 7.5 to

TABLE 8

| | Test | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Control | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Work time (minutes) | 27 | 28 | 19 | 24 | 32 | 39 | 34 | 21 | 14 |
| Strip time (minutes) | 40 | 42 | 30 | 33 | 44 | 58 | 45 | 30 | 22 |
| Tensile Strength - Kg/cm$^2$ (average of 3 runs) | | | | | | | | | |
| 1 Hour | 5.4 | 4.9 | 5.3 | 5.2 | 8.3 | 5.1 | 9.6 | 8.9 | 6.3 |
| 3 Hours | 16.5 | 15.6 | 18.7 | 17.9 | 24.7 | 25.4 | 28.5 | 27.5 | 22.4 |
| 24 Hours | 23.6 | 20.5 | 24.3 | 21.7 | 30.4 | 30.5 | 28.4 | 30.1 | 30.0 |
| 24 Hours (+1 hr at 90% RH) | 18.3 | 19.1 | 17.8 | 18.0 | 22.1 | 20.0 | 21.6 | 20.5 | 18.2 |
| Scratch Hardness at 24 hours | | | | | | | | | |
| | 56 | 53 | 48 | 50 | 71 | 68 | 71 | 72 | 74 |
| Transversal Strength - Kg/cm$^2$ (average of 3 runs) | | | | | | | | | |
| 1 Hour | 4.7 | 3.2 | 2.7 | 2.3 | 1.4 | 1.7 | 2.4 | 5.0 | 3.6 |
| 3 Hours | 7.0 | 5.9 | 6.3 | 5.2 | 6.0 | 6.0 | 6.8 | 7.1 | 6.2 |
| 24 Hours | 7.3 | 5.8 | 6.6 | 6.6 | 6.8 | 7.5 | 7.9 | 7.9 | 7.2 |
| 24 Hours (+1 hr at 90% RH) | 4.3 | 3.6 | 4.7 | 4.2 | 5.0 | 5.5 | 5.1 | 5.3 | 4.3 |
| 2 Hr. Recovery (percent strength recovery after humidity test) | 84 | 85 | 92 | 86 | 100 | 85 | 78 | 87 | 84 |
| Thermal breakdown (percent aggregate removed at 427° C.) | | | | | | | | | |
| 5 minutes | 3.2 | 3.7 | 5.4 | 4.3 | 2.3 | 2.5 | 3.6 | 4.7 | 7.6 |
| 10 Minutes | 21.2 | 21.9 | 26.8 | 31.9 | 44.7 | 38.4 | 48.8 | 51.8 | 44.0 |
| 15 minutes | 70.2 | 73.3 | 77.9 | 62.9 | 80.0 | 76.0 | 75.8 | 80.4 | 79.4 |
| 30 minutes | 99.2 | 99.0 | 99.0 | 99.1 | 98.4 | 99.0 | 98.5 | 99.0 | 99.1 |

17.5%, significantly reducing the furfuryl alcohol levels required. Besides the furfuryl alcohol control, there are two formulations with only conventional additives representing more fully formulated materials such as are likely to be in use commercially: Formulation 1 with just the polyester polyol, and Formulation 6 with the polyester polyol and the urea formaldehyde accelerator resin. Overall, the performances are reasonable, with several performance trends that are evident.

**[0094]** The work time/strip time results show four formulations, Formulations 2, 3, 7, and 8, having faster work time/strip time numbers than the control and therefore may be desirable in metal casting facilities where productivity is a primary concern. 2,5-furan dimethylol is used in all but Formulation 7, which utilizes 5-hydroxymethyl furfural, the polyester polyol, and the urea formaldehyde resin.

**[0095]** The tensile strength results show that the modified formulations have very good strength development, especially during the first three through 24 hours of cure. The humidity resistance is likewise very good. The 24 hour strengths are particularly improved by the presence of the 2,5-furan dimethylol and 5-hydroxymethyl furfural (Formulations 4, 5, 7, 8), especially where the urea formaldehyde resin is also present (Formulations 5, 7, 8). Thus, formulations incorporating the 5-hydroxymethyl furfural and 2,5-furan dimethylol may be useful in metal casting operations where high tensile strength is a primary concern.

**[0096]** The scratch hardness numbers were significantly improved by the presence of the 2,5-furan dimethylol and 5-hydroxymethyl furfural (Formulation 4, 5, 7, 8). The formaldehyde-containing urea formaldehyde resin appeared to contribute to scratch hardness (Formulations 5, 7, 8), but Formulation 4 demonstrated that the formaldehyde-containing resin was not necessary for scratch hardness where both the 5-hydroxymethyl furfural and 2,5-furan dimethylol were present. Thus, formulations incorporating the 5-hydroxymethyl furfural and 2,5-furan dimethylol may be useful in metal casting operations where high scratch hardness is a primary concern.

**[0097]** The transversal strength results show that the control and Formulation 7 have significantly higher initial transversal strength numbers than the remaining formulations. Most of the formulations catch up to the control by 24 hours. 5-hydroxymethyl furfural combined with the polyester polyol and the urea formaldehyde resin (Formulation 7) shows very good transversal strength. All the formulations had good humidity resistance and recovery of strength after humidity testing.

**[0098]** The thermal breakdown results show Formulations 4, 5, 7, and 8 to have significantly faster thermal breakdown in the first 15 minutes of burn-off than the control and therefore may be desirable in metal casting facilities where thermal breakdown is a primary concern, aluminum casting operations, for example. These data should indicate the relative ease of removing the spent aggregate from the casting and could lead to significant process cost savings to the metal casting operation.

**[0099]** Resorcinol is a relatively expensive material utilized in foundry no-bake formulations to enhance the speed of cure. Formulation 2 has about half the resorcinol as the control formulation, with 15 weight % 2,5-furan dimethylol replacing furfuryl alcohol. The formulation has faster work time/strip time, tensile development, and thermal breakdown than the control.

**[0100]** In summary, the data in these examples show that 2,5-furan dimethylol and 5-hydroxymethyl furfural formulations can replace or reduce the amount of furfuryl alcohol and other ingredients, such as resorcinol, while at least maintaining, if not improving, performance of the resulting metal casting binders. It is likely that 2,5-furan dimethylol and 5-hydroxymethyl furfural may be viable options for replacement in part or whole of a typical "reacted" base-resin, commonly used in furan resins. This can reduce or eliminate binder manufacturing time, and reduce ingredient inventory and cost, since a binder manufacturing step could be eliminated.

**[0101]** While the forms of the invention herein disclosed constitute presently preferred embodiments, many others are possible. It is not intended herein to mention all of the possible equivalent forms or ramifications of the invention. It is to be understood that the terms used herein are merely descriptive, rather than limiting, and that various changes may be made without departing from the spirit of the scope of the invention.

We claim:

**1**. A furanic acid-cured resin composition comprising:

a. a substantially phenol, nitrogen, and formaldehyde-free formulation of furfuryl alcohol mixed with;

b. (1) about 1 to about 45 wt % 5-hydroxymethyl furfural; or

(2) about 1 to about 60 wt % 2,5-furan dimethylol; or

(3) about 1 to about 40 wt % 2,5-furan dicarboxylic acid; or

(4) about 1 to about 60 wt % 2,5-diformyl furan; or

(5) about 1 to about 20 wt % polyester polyol;

or mixtures of two or more selected from b(1) through b(5).

**2**. The composition according to claim **1**, further comprising a catalyst in contact with the composition.

**3**. The composition according to claim **2**, wherein the catalyst is a weak acid.

**4**. The composition according to claim **3**, wherein the $pK_a$ of the weak acid is between about 2 to about 6.

**5**. The composition according to claim **4**, wherein the $pK_a$ of the weak acid is selected from the group consisting of phosphoric acid, nitrous acid, citric acid, formic acid, and the like, polyacrylic acid, and mixtures thereof.

**6**. The composition according to claim **1**, further comprising resorcinol accelerator.

**7**. The composition according to claim **1**, further comprising an aggregate coated catalyst in contact with the composition.

**8**. The composition according to claim **1**, wherein about 1 weight % and 90 weight % of furfuryl alcohol is replaced with blends of 5-hydroxymethyl furfural and 2,5-furan dimethylol at wt % ratios between the two components of about 5 to about 955-hydroxymethyl furfural to 2,5-furan dimethylol, to about 95 to about 55-hydroxymethyl furfural to 2,5-furan dimethylol.

**9**. A furanic acid-cured resin composition comprising:

a. a substantially phenol, nitrogen, and formaldehyde-free formulation of furfuryl alcohol mixed with;

b. (1) about 1 to about 20 wt % 5-hydroxymethyl furfural; or

(2) about 1 to about 30 wt % 2,5-furan dimethylol; or

(3) about 1 to about 10 wt % 2,5-furan dicarboxylic acid, or

(4) about 1 to about 25 wt % 2,5-diformyl furan; or mixtures of two selected from b(1) through b(4).

**10**. The composition according to claim **9**, further comprising a catalyst in contact with the composition.

**11**. The composition according to claim **10**, wherein the catalyst is a weak acid.

**12**. The composition according to claim **11**, wherein the $pK_a$ of the weak acid is between about 2 to about 6.

**13**. The composition according to claim **12**, wherein the $pK_a$ of the weak acid is selected from the group consisting of phosphoric acid, nitrous acid, citric acid, formic acid, and the like, polyacrylic acid, and mixtures thereof.

**14**. The composition according to claim **9**, further comprising resorcinol accelerator.

**15**. The composition according to claim **9**, further comprising an aggregate coated catalyst in contact with the composition.

**16**. The composition according to claim **9**, wherein about 1 weight % and 90 weight % of furfuryl alcohol is replaced with blends of 5-hydroxymethyl furfural and 2,5-furan dimethylol at wt % ratios between the two components of about 5 to about 955-hydroxymethyl furfural to 2,5-furan dimethylol, to about 95 to about 55-hydroxymethyl furfural to 2,5-furan dimethylol.

**17**. A furanic acid-cured resin composition comprising:

a. a substantially phenol, nitrogen, and formaldehyde-free formulation of furfuryl alcohol mixed with;

b. (1) about 1 to about 20 wt % 5-hydroxymethyl furfural; and

(2) about 1 to about 30 wt % 2,5-furan dimethylol.

**18**. The composition according to claim **17**, further comprising a catalyst in contact with the composition.

**19**. The composition according to claim **18**, wherein the catalyst is a weak acid.

**20**. The composition according to claim **19**, wherein the $pK_a$ of the weak acid is between about 2 to about 6.

* * * * *