

Description**FIELD OF THE INVENTION**

5 This invention relates to the manufacture of articles such as foundry molds and cores made from sand that is mixed with an alkaline phenolic resin binder, where the sand comprises a high level of reclaimed sand. More particularly, a portion of this invention relates to novel binder solutions for use with reclaimed sand, which binder solutions provide higher tensile strengths for articles produced therefrom.

BACKGROUND OF THE INVENTION

In the manufacture of foundry molds and cores from sand using a curable binder, recycling the sand is an important economic consideration.

Sand reclamation is the physical, chemical or thermal treatment of a refractory aggregate to allow its reuse. Ideally there is no significant loss of its original useful properties as required for the application involved.

15 In typical foundry operations, the sand is collected after taking out a casting from a poured mold. This sand comprises loose sand grains, sand agglomerates and lumps of bonded sand. All these are broken down by mechanical devices into free-flowing granules. These granules are screened to produce reclaimed sand, ready for reuse. This is the simplest form of sand reclamation. The reclaimed sand from this process generally has layers of burned and partially burned binder films still adhering to it. The amount of such organic layer present can be determined by a loss-on-ignition (L.O.I.) determination.

The granular sand can be further processed to remove the binder residue layer either by mechanical means (sand scrubbers) or thermal means (a rotary kiln).

25 There are thus three treatments available for reclaiming sand. These include mechanical, wet, and thermal treatment processes. The mechanical treatment process typically involves subjecting the sand granules to grinding, scrubbing or other means of mechanical attrition to provide particles of a desired size, remove binder residues, provide new sand surfaces and/or remove fines. The equipment and process used may depend on the particle size and uniformity desired.

30 The wet treatment processes involve washing the sand granules with water, draining the wash water and drying the washed sand.

In thermal treatment processes, the sand is heated to a temperature of about 120°C or above, so that the binder residue is decomposed or burned.

35 The mechanical treatment processes and thermal treatment processes have not proven very effective in enhancing the bonding properties of reclaimed sand obtained from foundry cores and moulds wherein the binder is an ester cured alkaline phenolic resin.

It is desirable to enhance the bonding affinity and ability of used sand, reclaimed from foundry use, that has been bonded with an ester cured alkaline phenolic resin, particularly a highly alkaline phenolic resin, to the extent that usage levels of such reclaimed sand may be as high as 60% to 80% or 90% by weight in subsequent foundry operations.

40 GB 2177408 teaches a composition for and a method of making foundry moulds using an aqueous binder composition containing an alkaline phenol-aldehyde resin, an alkaline phenol-aldehyde resole and a curing agent.

SUMMARY OF THE INVENTION

45 It has now been discovered that solutions of alkaline phenolic resins with solids contents of the range from about 33% to about 47% by weight, based on the weight of the solution, provide superior bonding properties for used, reclaimed sand, when compared to those obtained by the use of similar resin binder solutions at conventional, higher solids contents, and that said lower solids content resin solutions achieve higher tensile strengths for resin-bonded sand articles such as foundry molds or cores made from reclaimed sand.

50 U.S. Patents 4,474,904 (R.I. I-1757), 4,468,359 (R.I. I-1803), and 4,426,467 (R.I. I-1804) specified several features of their respective alkaline phenolic, ester-curable resin binders that were deemed necessary for their successful usage in the foundry, including relatively high solids contents, i.e., above 50%.

55 The present invention resides in the use of solutions of alkaline phenolic resin binders that are curable by curing agents having ester functionality, for binding sand of which at least 40% by weight, and preferably from 50% to 100% by weight, and more preferably at least 60% to about 80% by weight, comprises reclaimed used sand, such as sand that has been recovered from dismantled foundry molds or cores, and reclaimed. The invention is useful for used sand that has been reclaimed and has "residual alkalinity", as described below.

The resin binder solutions of this invention comprise from about 33% up to about 47% by weight solids, based on the weight of solution, preferably about 35% to about 45%, and most preferably, about 38% to 42%. That is, the resin binder solutions that are useful in the practice of this invention have solids contents of from about 33% to about 47%, and preferably, from about 35% to about 45%. The solids contents are determined by heating a 1.5g sample at 135°C for three hours, then determining weight of the remainder. The weight of the remainder is reported as the solids content. This procedure for determining the solids content was used for all such determinations reported in this application. The binder solutions of the invention generally have Brookfield viscosity values of from 0.015 Pas to 0.150 Pas (15-150 cps), as determined utilizing a Model RVF Brookfield viscometer with a No. 1 spindle at 20 rpm and at 25°C. These alkaline phenolic resin binders can cure at room temperature with curing agents having ester functionality.

Also provided by this invention is a raw batch composition which comprises a binder solution, an ester-functional curing agent, and sand in substantially uniform admixture. This raw batch composition is useful for forming sand aggregates such as foundry moulds and cores. The sand used comprises at least 40% by weight sand which has been reclaimed from one or more mechanically dismantled foundry cores or moulds. The "effective" solids content of the binder solution in the raw batch formulation is from about 33% to about 47% by weight, based on the weight of said solution. This "effective solids" content is achieved by the use of the binder solutions of the present invention or by the use of a more concentrated binder solution (i.e. one having a higher solids content than 33% up to 47%) with dilution water, when forming the raw batch formulation.

In addition, a process is provided for using the raw batch formulations of the present invention to form foundry moulds or cores. In this process, a raw batch formulation, as described above, is shaped into the configuration desired. The binder is then allowed to cure. The phenolic resin may be an alkaline phenolic resin, in which case a curing agent with ester functionality will initiate curing under ambient conditions. Alternatively, if the phenolic resin is neutral or acidic, then the curing agent should be a mixture or solution having ester functionality and the ability to impart sufficient alkalinity to the resin upon admixture with it to bring about curing conditions. The embodiments of this process also include shaping a mixture of sand and binder solution, and gassing this mixture with an ester-functional curing agent in vapor or gaseous form, to cure the resin.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates in one preferred embodiment to the use of alkaline phenolic resin binders having relatively low solids contents, for forming foundry molds and cores from reclaimed sand.

The term "reclaimed sand" as used herein, refers to sand that has been formed into a resin-bonded shape with an alkaline resin binder, then recovered for reclamation and reuse in the form of free flowing sand granules. These free-flowing granules have residues of the alkaline binder that are adhered to their surfaces.

The invention was developed for use with used sand that had been previously bonded with an ester cured alkaline phenolic binder. Such previously bonded sand, when recovered for reclamation, can be used again as is with an ester curable alkaline phenolic resin binder, but the resin-bonded articles thus formed generally are characterized by tensile strengths that are lower than is desirable. This is believed to be caused by the presence, on the used sand grains, of a residue. This residue appears to consist of several different components, but the important one with respect to effect on tensile strength is believed to be an alkali silicate. If the alkaline phenolic resin binder previously used was a potassium phenolic resin, the residue would comprise potassium silicate. Other alkaline silicates are believed to be produced by other alkaline resins.

While the identity of the residue, which is believed to be on the surfaces of the sand grains, is not known with certainty, the present invention provides a practical means for using recovered used sand with an ester curable alkaline phenolic resin to form resin-bonded sand shapes having acceptable tensile strengths, despite the presence of such residues. The invention appears deceptively simple when known, but was not easy of development: it involves the use of ester curable alkaline phenolic resin binders in aqueous solutions at low solids contents, i.e., from about 33% to about 47%, and preferably from about 35% to about 45% by weight. For convenient reference hereafter, the recovered used sand, to which the invention is applicable, is referred to as sand recovered from a shape previously bonded with an alkaline binder or as sand granules having residual alkalinity, or as sand having on its surfaces a water-removable residue. It is also believed that at least a part of the residue on the surfaces of the sand is alkaline silicate material. Consequently the reclaimed sand could also be referred to as sand having on its surfaces residues comprising an alkaline silicate. These alternative expressions for referring to the reclaimed sand are apt because of uncertainty of the cause of the poor tensiles that are observed with recovered, previously alkaline-resin-bonded sand, although there is no uncertainty about the improvement in tensiles obtained through the use of the present invention.

Recovered used sand may be prepared for use in the practice of the invention by mechanical and thermal reclamation processes, as now known in the art. Such processes can be used to produce reclaimed sand

granules of a size corresponding to a screen distribution of about 25-140, as defined in the American Foundrymen Society's Handbook, "Molds and Cores", pp. 4.2-4.5. A vibratory mill is typically the mechanical means used to form the free flowing sand granules following shake-out of the loose sand from a mold.

5 Foundry sand or other refractory materials used in the production of foundry molds and cores is generally silica sand, quartz, chromite sand, zircon sand, or olivine sand, and may be beach sand, lake sand, bank sand, but many other such materials could be used.

10 It is important to identify the source of the binder residues that are present on the reclaimed sand to determine which reclamation and subsequent use processes will provide the best results. Binder residues that appear to have a deleterious effect on the affinity of reclaimed sand for a phenolic resin binder in particular are those residues found on sand that has been used in a mold or core bonded by ester cured alkaline phenolic resins applied in an aqueous solution after metal casting. Such binders are often hardened with curing agents that have ester-functionality, which are referred to herein as "ester curing agents". Specific examples of "ester curing agents" are described more particularly below. Where these curing agents are used, the binder typically hardens and cures under ambient conditions.

15 The recovered used sand, with which the invention is concerned, is sand that has been previously bonded with a phenolic resin obtained by the reaction of a phenol such as phenol, cresols, resorcinol, 3,5-xyleneol, bisphenol-A, other substituted phenols, or mixtures thereof, with aldehydes such as formaldehyde, acetaldehyde or furfuraldehyde. Preferred reactants are phenol and formaldehyde utilized in a molar ratio of phenol to formaldehyde in the range of about 1:1 to about 1:3 and more preferably 1:1.5 to 1:2.8.

20 Preferred alkaline materials used to condense these phenolic resins include sodium hydroxide, potassium hydroxide, lithium hydroxide, and mixtures thereof, with potassium hydroxide being the most preferred. A part of the alkaline material may be provided by substituting for a part of the alkali metal hydroxide a divalent metal hydroxide such as, for example, magnesium hydroxide and calcium hydroxide. The preferred alkaline phenolic resins have an alkali:phenol molar ratio in the range of 0.2:1 to 1.2:1.

25 The more commonly used alkaline phenolic resin binders will have a Brookfield viscosity of from 0.075 to 0.250 Pas (75-250 cps), at a concentration of 53% to 58% in water, utilizing a model RVF Brookfield viscometer with a No. 1 spindle at 20 rpm and at 25°C. The binder solutions of this invention have solids contents of about 33% to about 47% by weight, preferably by about 35% to 45% by weight, and most preferably, about 38% to about 42% by weight.

30 Suitable phenolic resins generally have a weight average molecular weight greater than about 500 and less than about 2500, more preferably greater than about 700, and most preferably within the range of about 700 to 2000, as determined by gel permeation chromatography (GPC). In the preferred GPC method, used herein, the resin sample is dissolved in tetrahydrofuran (THF), then neutralized with 1N hydrochloric acid. The salt thus formed is removed by filtration, and the filtered supernatant liquid resin solution is run on a GPC apparatus to determine Mw. The apparatus included a Waters model 6000A pump, a Waters model R401 differential refractive index detector, a Waters model 730 Data Module, PL Gel 30 μ columns, porosities 10⁴, 500 and 50 Angstrom units, respectively, and a Rheodyne model 70-10 sample loop injector fitted with a 100 μ l loop and a 0.5 μ m in-line filter situated between the injector and the first column.

To determine Mw for an aqueous alkaline resole, the procedure is as follows.

40 Dissolve 1 g resin in 10 ml methanol. Adjust the pH to 7 on a buffered pH meter using 1N hydrochloric acid. Add 10 ml unstabilized THF and continue stirring to ensure all the resin is in solution. Allow any precipitated salt to settle and transfer 500 μ l of the supernatant liquor to a 5 ml sample vial. Remove the solvent under vacuum for the minimum of time (about 5 mins) and at a temperature of 35°C. Add 1 ml mobile phase and filter.

45 Primary calibration of the columns is carried out using phenol and the oligomers formed by reaction of 2,4'-dihydroxy diphenyl methane with formaldehyde at a mol. ratio of 1-5:1 with sulphuric acid catalysts and a temperature of 120°C for 30 mins. This gives individual peaks for up to 8-ring compounds (m.wt. 850). Above this the calibration curve is extrapolated.

50 Once the columns are calibrated with primary standards, resins may be run and their weight average molecular weights obtained. One of these samples may be chosen as a secondary standard to check the day-to-day tie-up not only of retention times but of calculated molecular weight averages.

A standard resin solution should be injected each time the GPC system is started up and repeated until consistent retention times and molecular weights are obtained. If the calibration is satisfactory then samples may be run. If the results are consistent but vary from those expected, and there are no leaks or trapped air bubbles in the system, then the columns should be recalibrated with primary standards.

55 Some of the preferred phenolic resins used in the binder solution of this invention are the highly alkaline phenolic resins such as those described in U.S. Patent Nos. 4,474,904 and 4,468,359. It is noted that in these patents, the alkalinity content of the resins is expressed in terms of the molar ratio of potassium hydroxide to phenol and that potassium hydroxide is described as the most preferred alkali. The molar ratio of KOH:phenol

for the preferred potassium alkaline resins for use in the practice of this invention falls in the range of about 0.2:1 to about 1.2:1.

The binder solution useful in the practice of this invention preferably is an aqueous solution of an alkaline phenol formaldehyde resin wherein

- (i) the solids content is in the range from about 33% to about 47%, preferably 35% to 45%, and more preferably 38% to 42%,
- (ii) the weight average molecular weight (Mw) is from 500 to 2500, preferably 700 to 2000, and more preferably 800 to 1700,
- (iii) the formaldehyde:phenol molar ratio is from 1:1 to 3:1, preferably 1.2:1 to 2.6:1,
- (iv) the alkali:phenol molar ratio is from 0.2:1 to 1.2:1, preferably 0.6:1 to 1.2:1,
- (v) the alkali used comprises sodium hydroxide, potassium hydroxide, and their mixtures,
- (vi) said solution may optionally contain a silane to the extent of 0.05% to 3.0% by weight of said aqueous resin solution, and
- (vii) said resin is curable at room temperature with C₁-C₃ alkyl formates, organic esters formed from C₁-C₁₀ carboxylic acids and mono- and polyhydric alcohols and low molecular weight lactones including butyrolactone, propiolactone, caprolactone, and mixtures thereof.

However, the phenolic resin may also be an acidic or neutral resin, the aqueous solution of which is made alkaline either before or at the same time that the ester-functional curing agent is added to the resin solution. Otherwise, the parameter values (i) through (iii) and (vi) through (vii) apply, and after addition of the source of alkalinity to the resin, the parameter values (iv) and (v) also apply, for the more preferred embodiments.

Where the binder solution includes a silane, added for the purpose of improving the tensile strength of the molds or cores produced therefrom, the silane concentration may be as low as 0.05% by weight, based on the weight of the binder solution. Higher concentrations of silane provide greater improvements in strength up to quantities of about 0.6% by weight, based on the weight of the binder solution. The use of silane concentrations at higher levels, while useful, is not preferred because of the added cost. In addition, because one preferred silane often used is an aminoalkyl alkoxy silane, which contains nitrogen, the use of excess silane may increase the risk of pinhole defects in the casting and for this reason, amounts in excess of 3% by weight, based on the weight of binder solution, are not used.

A silane, if used, is generally effective in increasing the tensile strength of the foundry mold or core product. Suitable silanes include those conforming to the formula R'Si(OR)_n, wherein R' is a C₂-C₆ alkylene group, bonded to an amino, epoxy, mercapto, glycidoxy, ureido, hydroxy, hydroxy-C₁-C₆, alkyl amino, amino-C₁-C₆ alkyl amino, C₂-C₆ alkenyl or C₂-C₆ alkenyl-carboxy group, and the groups R may be the same or different and are selected from C₁-C₆ alkyl and C₁-C₆ alkoxy substituted C₁-C₆ alkyl groups.

Also included are those aminoalkyl alkoxy silanes which conform to the general formula



wherein n equals a whole number of from 2-4, R¹ is an alkyl group of from 1-4 carbon atoms and phenyl, R² is an alkyl group of 1-4 carbon atoms and x is 0 or 1. Specific examples of such silanes which conformed to either of the above formulas include:

gamma-aminopropyl trimethoxysilane,
 gamma-aminopropyl triethoxysilane (Silane A-1100)
 gamma-aminobutyl triethoxysilane,
 gamma-aminopentyl triethoxysilane,
 gamma-aminopropyl diethoxymethylsilane,
 gamma-aminopropyl diethoxyethylsilane,
 gamma-aminopropyl diethoxyphenylsilane,
 delta-aminobutyl diethoxyphenylsilane,
 delta-aminobutyl diethoxymethylsilane, and
 delta-aminobutyl diethoxyethylsilane.

The alkaline phenolic resin binder solutions that are useful in the practice of this invention are curable with ester curing agents. Those which are preferred include lactones, organic carbonates, carboxylic acid esters, and mixtures thereof. These species exhibit the ester functionality necessary for "ester cure" of the phenolic resin.

Generally, low molecular weight lactones are suitable, such as gamma-butyrolactone, valerolactone, caprolactone, beta-propiolactone, beta-butyrolactone, beta-isobutyrolactone, beta-isopentylactone, gamma-isopentylactone and delta-pentylactone. Carboxylic acid esters which are suitable include those of short and medium chain length, i.e., about C₁ to C₁₀, alkyl mono or polyhydric alcohols with short or medium length, i.e., C₁ to C₁₀ carboxylic acids. Specific carboxylic acid esters include, but are not limited to, n-butyl acetate, ethylene glycol diacetate, triacetin (glycerol triacetate), dimethyl glutarate, and dimethyl adipate.

Of the organic carbonates, those which are suitable include, but are not limited to, propylene carbonate, ethylene glycol carbonate, glycerol carbonate, 1,2-butanediol carbonate, 1,3-butanediol carbonate, 1,2-pentanediol carbonate and 1,3-pentanediol carbonate.

The binder may also be cured by gassing with an ester functional curing agent such as a low molecular weight carboxylic acid ester, preferably one of the C₁ to C₃ alkyl formates, including methyl formate and ethyl formate. The gassing curing agent is preferably dispersed in a carrier gas as a vapor or an aerosol. This carrier gas must be inert in that it should not react with the alkyl formate curing agent or have an adverse effect on the curing reaction or other property of the product. Suitable carrier gas examples include air and nitrogen.

The relative volatility of the alkyl formates facilitate their use as gassing curing agents. This is especially true of methyl formate which is a volatile liquid having a boiling point at atmospheric pressure of about 31.5°C. At ambient temperatures, it is sufficiently volatile that passing a carrier gas through the liquid methyl formate gives a concentrated methyl formate vapor. Ethyl and propyl formates are less volatile than the methyl ester, having boiling points in the range of 54°C to 82°C at atmospheric pressure.

The concentration of formate ester in the carrier gas is preferably at least 0.2% by volume. The total amount of alkyl formate used will typically be from about 10% to 110%, preferably from 15% to 35% by weight of the phenolic resin solution. The time required for adequate gassing depends on the size and complexity of the core or mold and on the particular resin used. It can be as short as 0.1 seconds but more usually is in the range of 1 second to 1 minute. The gassing procedures are described more particularly in U.S. Patent No. 4,468,359.

The binder solutions of this invention are particularly suited for bonding reclaimed sand. Reclaimed sand is distinguished from new or pristine sand in that it has been recovered from a dismantled foundry mold or core following use in a metal casting process. It is the heat experienced during the metal casting which is believed to generate the binder residues that are believed to be responsible for reducing the tensiles of resin-bonded shapes made from the reclaimed sand with ester curable alkaline phenolic resin binders, and that may be the source of residual alkalinity.

RAW BATCH FORMULATION

Also within the scope of this invention are raw batch formulations comprising a binder solution, sand, and a curing agent. At least 40% by weight of the sand used is reclaimed sand, generally 50% to 100%, and preferably 60% or more. Suitable reclaimed sand and other components for the raw batch formulation are those described above.

Thus the binder solution in these raw batch formulations preferably comprises a highly alkaline phenolic resin in solution, applied in an amount sufficient to bind the sand with the adhesive bonding necessary for use in making a foundry mold or core. The quantity of the binder solution is typically in the range of from about 0.5% to 8% by weight of resin solution, based on the weight of the sand utilized, when the solids content of the resin solution is from about 33% up to about 47%. Preferred quantities of the binder solution generally fall below about 2% by weight of the sand used.

The third component of these raw batch formulations is a curing agent selected from the group consisting of lactones, carboxylic acid esters, organic carbonates and mixtures thereof, which cure the binder at ambient temperature. The curing agent is present in an amount sufficient to cure said binder, with preferred concentrations of curing agent falling within the range of about 10% to 110% by weight, based on the weight of binder solution.

The raw batch formulation may be formed by combining and mixing these components to provide a substantially uniform mixture. This can be achieved with simple lab batch mixers, high speed continuous mixers or other conventional equipment. Alternatively, the sand and binder solution may be mixed and formed into a desired shape, and the curing agent introduced in gaseous or vapor form. When the raw batch formulation is completed by gassing a mixture of sand and curable binder with a curing agent, the curing agent is preferably a C₁-C₃ alkyl formate, used in the quantity of about 10% to 110% by weight, based on the weight of curable binder solution.

The binder solution in the raw batch formulation has an "effective" solids content of from about 33% to about 47% by weight, based on the total weight of the binder solution therein plus any solvent that is added to the raw batch formulation which dilutes the binder solution. Suitable solvents may be water or an organic solvent which is soluble in water, such as methanol, ethanol, a glycol, furfuryl alcohol, mixtures of these, and the like.

This "effective" solids concentration for the binder solution can be achieved by utilizing a low solids binder solution or by utilizing a high solids binder solution in combination with a separate solvent that is added and which will reduce the solids content of the binder solution. Once the dilution solvent and binder solution are added to the sand and mixed, an "effective" solids content of about 33% to about 47% will be realized, and an improvement in bonding properties will be realized over raw batch formulations containing reclaimed sand and

binder solutions at conventional solids contents of above 50% by weight.

PROCESS FOR PRODUCING FOUNDRY CORES AND MOLDS, MAKING EFFECTIVE USE OF RECLAIMED SAND

A raw batch formulation as described above is prepared by combining and mixing sand, a binder solution and curing agent. A dilution solvent can also be introduced so as to provide the necessary "effective" solids content for the binder solution in the raw batch formulation.

The raw batch formulation is then formed into a desired shape prior to curing. To form the desired shape, all the components of the raw batch formulation, i.e., sand, binder solution and curing agent, can be mixed and subsequently shaped. Alternatively, the sand and binder solution can be mixed, shaped, and subsequently gassed with an ester functional curing agent. The binder hardens and cures at ambient conditions.

EXAMPLES

This invention will now be demonstrated by the following examples. In these examples, and elsewhere throughout the specification, all parts and proportions are by weight, and all temperatures are in degrees Celsius, unless expressly indicated otherwise.

EXAMPLE 1

PREPARATION OF BINDER SOLUTIONS WITH LOW SOLIDS CONTENTS

In this example, binder solutions for evaluation are prepared from a commercially available ester curable alkaline phenolic resin binder solution, ALPHASET 9000 resin, sold by Borden, Inc. This binder solution is referred to in these examples as the "Standard Resin 1."

Resin solutions A through E, prepared from Standard Resin 1 by dilution, have different solids contents that are useful in the practice of the present invention. Control Resin 1 is a binder solution having a 30.2% solids content, that is below the useful range prescribed for the practice of this invention.

The ALPHASET 9000 resin binder solution used (Standard Resin 1) had a solids content of about 54% by weight. This resin is obtained by the reaction of phenol and formaldehyde at a phenol:formaldehyde molar ratio of about 1:1.8. The potassium hydroxide:phenol molar ratio for this resin is about 0.85:1. The resin solution contains gamma-aminopropyl triethoxy silane in the amount of about 0.4% by weight, based on the weight of the resin solution. The Brookfield viscosity of this resin solution fell within the range of about 0.100 to 0.150 Pas, as determined by a Model RVF Brookfield viscometer with a No. 1 spindle, at 20 rpm and at 25°C.

The quantities of Standard Resin 1 and water used to produce the binder solutions of Resin solutions A through E and Control Resin 1, respectively, are indicated below in Table 1, along with the resultant solids contents, all determined by the method described above. To make Resin C, Standard Resin 1 was further diluted with 5.3% by weight, based on the total weight of the binder solution, of a 40% solution in water of gamma-aminopropyl triethoxy silane, to achieve a final water content of 21.1%.

TABLE 1
DILUTION OF STANDARD RESIN 1

	Standard Resin 1 (wt % percent)	Dilution Water (wt percent)	% Solids Content
Standard Resin 1	100	0	54
Resin A	78.9	21.1	42.5
Resin B	83.4	16.6	45.6
Resin C	78.9	21.1*	46
Resin D	77	23	41.3
Resin E	70	30	37.6
Control Resin 1	56	44	30.2

* Solution contains 5.3 wt. % of a 40% solution of gamma-aminopropyl triethoxy silane.

These resin solutions are used in subsequent examples to produce test cores.

EXAMPLE 2

PREPARATION OF ADDITIONAL BINDER SOLUTIONS WITH LOW SOLIDS CONTENTS

In this example, a binder solution for evaluation was prepared from a different commercially available ester curable alkaline phenolic resin binder solution, BETASET 9500, sold by Borden, Inc. This resin was prepared by the reaction of phenol and formaldehyde at a molar ratio of about 1:2 and at a potassium hydroxide:phenol molar ratio for this resin of about 0.8:1. This resin binder solution contains gamma-aminopropyl triethoxy silane in the amount of about 0.4% by weight. The Brookfield viscosity of this resin binder solution fell within the range of about 0.0750, 100 Pas as determined by the method described in Example 1. This binder solution had a solids content of about 57%, and is referred to as "Standard Resin 2."

Resin F, prepared by dilution from Standard Resin 2, represents a binder solution within the scope of this invention. Resin F was prepared to contain 77.7 weight percent of Standard Resin 2 solution and 22.3 weight percent added water. The solids content for Resin F was 44.3%.

Both Resin F and Standard Resin 2 were used in the preparation of test cores in subsequent examples to illustrate some of the preferred embodiments of this invention.

EXAMPLE 3

PREPARATION OF A BINDER SOLUTION WITH A LOW SOLIDS CONTENT WHERE THE RESIN IS CONDENSED WITH MIXED ALKALIS OF SODIUM AND POTASSIUM

In this example, the binder solution was prepared as follows. About 27.3 parts by weight phenol was weighed in a three necked flask fitted with a stirrer, thermometer and condenser. To this three necked flask were added about 14.9 parts by weight of a 50% sodium hydroxide solution in water. The contents were mixed and following the addition of the sodium hydroxide, about 34.9 parts by weight of a 50% formaldehyde solution in water were added over a period of time at 65°C. Once all the formaldehyde was added, the temperature was raised to about 92°C until the viscosity reached 0.800 Pas to 1.00 Pas. The temperature was then reduced to about 72°C to 74°C and the mixture was reacted further until a viscosity of about 8.00 Pas to 9.00 Pas was obtained.

After this viscosity was obtained, the resin solution was cooled, and about 14.4 parts of water, 3.8 parts by weight ethanol, and 2 parts by weight of a 50% potassium hydroxide solution in water were added and mixed. While the solution was cooling, about 0.8% by weight of Silane A-1100 was added. This finished binder solution had a viscosity of about 0.163 Pas, as determined by the method used in Example 1, a solids content of 51%

and a gel time of about 9 minutes 40 seconds. This binder solution is identified in the Examples herein as "Control Resin 2".

Resin G was prepared by diluting Control Resin 2 to form a binder solution within the scope of this invention. Resin G was comprised of about 80% by weight of Control Resin 2 and 20% by weight of added water, and had a solids content of 37.3% by weight.

EXAMPLE 4

PREPARATION OF TEST CORES WITH RECLAIMED SAND

This example demonstrates the use of low solids content binder solutions of the present invention in forming test cores with reclaimed sand, and compares the tensile strengths of these test cores to those obtained using similar resin binder solutions having more customary solids contents.

In preparing the test cores, a quantity of sand of about 1500 to 2500 g was added to a Hobart Kitchen Aid Mixer for each Test and Control described below. The sand was brought to a temperature of about 25°C and about 1.5% by weight of a binder solution, based on sand weight, was added to the sand and mixed in for about one minute. The binder solution and sand which were utilized in each Test and Control are described more particularly below.

After the mixing in the binder solution, about 25% by weight triacetin curing agent, based on the weight of binder solution used, was added and mixed in for another 40 seconds.

After mixing, the raw batch formulation thus produced was used immediately to form standard American Foundrymen Society's 1-inch dogbone tensile briquettes in a Dietert 696 corebox. The cores were cured at room temperature and the samples were broken at the following approximate intervals: one hour, two hours, four hours, and twenty-four hours, after the cores were made. Tensile strength measurements were made using a Dietert Universal Sand Strength Machine 400-1, fitted with a Tensile Core Strength Accessory 610-N. Average values for about 3 to 4 tensile strength measurements were determined.

The reclaimed sand used in this example was recovered from foundry molds and cores that had been used in casting iron or steel. The reclaimed sand contained a binder residue derived from an ALPHASET 9000 resin that had been cured with triacetin curing agent. The foundry molds or cores, from which the reclaimed sand was obtained, were dismantled after use in a metal casting process by vibrating the mold or core to loosen sand and break up any large lumps with a vibratory mill. The free-flowing sand granules obtained were subjected to dry attrition in a unit produced by Redford Carver Foundry Products, Sherwood, Oregon. The sand obtained had particle sizes corresponding to an American Foundrymen's Society's screen distribution of about 48.7 Grain Fineness and a loss on ignition value (LOI) of 0.80.

To illustrate the processes of this invention, test cores were made utilizing the reclaimed sand with the binder solutions described in Example 1 as Resin A and Standard Resin 1, to provide Test A and Control A, respectively. Raw batch formulations and test cores were prepared as described above and the average tensile strength values for these test cores are reported below in Table 2, along with the percentage improvement observed in tensile strengths of dogbones made in accordance with the invention (i.e., Test A dogbones). The hour times reported in the table represent hours after the test cores were made.

TABLE 2

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Solids Content of the Binder		Tensiles (kPa)			
<u>Solution</u>		<u>1 hr</u>	<u>2hr</u>	<u>4hr</u>	<u>24hrs</u>
Con- trol- A	54	152 (22psi)	207 (30)	276 (40)	365 (53)
Test- A	42.5	159 (23)	290 (42)	359 (52)	434 (63)

Solids Content of the Binder		Improvement in Tensiles %			
<u>Solution</u>		<u>1hr</u>	<u>2hr</u>	<u>4hr</u>	<u>24hrs</u>
Con- trol- A	54	--	--	--	--
Test- A	42.5	4.5%	40%	30%	18%

The data in Table 2 show that the Text A binder solution, having a solids content below conventional levels, i.e., below 45%, provided improved tensile strengths for test cores made from reclaimed sand.

EXAMPLE 5

PREPARATION OF TEST CORES WITH PRISTINE SAND

This example compares the tensile strength of test cores made using (1) a conventional binder solution and (2) a binder solution having a solids content below 45% with pristine sand.

Test cores were prepared in accordance with the method described in Example 4. The pristine sand used was washed and dried and had a particle size corresponding to an American Foundrymen Society's screen distribution of about 52 Grain Fineness.

The binder solutions used were those described in Example 1 as Resin A and the Standard Resin 1. They were used to provide Test B and Control B, respectively. The test cores did not contain any reclaimed sand and as such. This example does not illustrate the present invention, but is presented for purposes of comparison. Upon obtaining the raw batch formulations in accordance with the procedures of Example 4, test cores were made and tested as described in Example 4. The average tensile strength values calculated from the observed values are reported in Table 3, with the percent changes (losses) in tensile strengths indicated for the test cores made utilizing the binder composition of the present invention.

TABLE 3

Solids Content of the Binder Solution		Tensiles (kPa)			
		1hr	2hr	4hr	24hrs
5	Con-				
	trol-	54	379 (55psi)	517 (75)	655 (95)
	2				848 (123)
10	Test-	42.5	255 (37)	345 (50)	517 (75)
	B				621 (90)

20	Solids Content of the Binder Solution	Improvement in Tensiles %				
25		1 hr	2hr	4hr	24hrs	
	Con- trol- 2	54	--	--	--	
30	Test- B	42.5	-32%	-33%	-21%	-26%

The data in Table 3 illustrate that lower solids contents in binder solutions of alkaline phenolic resin binders provide lower and less satisfactory tensile strengths for test cores produced from pristine sand.

EXAMPLE 6

PREPARING TEST CORES WITH AN ALTERNATE RECLAIMED SAND

This example illustrates that the improvement in tensile strength obtained from the binder solutions of the present invention is not limited to a particular type of reclaimed sand.

Test cores were made utilizing the binder solutions described in Example 1 as Resin B, Resin C and Standard Resin 1 to provide Test C, Test D and Control -C, respectively. These test cores were prepared and tested as described in Example 4.

The reclaimed sand was recovered and reclaimed from foundry moulds and cores used in casting metal from a different foundry than the reclaimed sand used in Example 4. The binder that had been used in making these moulds and cores was an Alphasat 9000 alkaline phenolic resin cured with triacetin.

The sand was mechanically reclaimed from the foundry moulds and cores at an American Foundrymen's Society screen size distribution of about 55.2 Grain Fineness. It had an LOI of 1.14.

The average values for the tensile strengths of the test cores made utilizing this reclaimed sand are shown below in Table 4.

TABLE 4

5	Solids Content of the Binder		Tensiles (kPa)			
10	<u>Solution</u>		<u>1hr</u>	<u>2hr</u>	<u>4hr</u>	<u>24hrs</u>
	Con- trol- C	54	103 (15psi)	159 (23)	228 (33)	207 (30)
15	Test- C	45.6	138 (20)	186 (27)	---	338 (49)
20	Test- D	46	152 (22)	186 (27)	276 (40)	345 (50)
25	Solids Content of the Binder		Improvement in Tensiles %			
30	<u>Solution</u>		<u>1hr</u>	<u>2hr</u>	<u>4hr</u>	<u>24hrs</u>
	Con- trol- C	54	--	--	--	--
35	Test- C	45.6	30%	17%	--	63%
40	Test- D	46	46%	17%	21%	60%

The data in Table 4 illustrate that improvements in tensile strength can be obtained with low solids content binder solutions with reclaimed sands from different sources.

EXAMPLE 7

Preparation of Test Cores with Reclaimed Sand/Pristine Sand Mixtures

Test cores were prepared with mixtures of reclaimed and pristine sand utilizing binder solutions at low solids contents and at conventional solids contents, to illustrate the advantages of this invention when working with a mixture of pristine sand and reclaimed sand.

Test cores were made utilizing the binder solution described in Example 1 as Resin B and Standard Resin 1 to provide Test E and Control D, respectively. The sand used was an 80:20 mixture of reclaimed:pristine sand. The pristine sand was washed and dried silica sand. These test cores were prepared and tested as described in Example 4. The reclaimed sand was obtained from a foundry different from the source of the reclaimed sand described in Examples 4 and 6. The reclaimed sand was recovered from foundry molds and cores used in casting iron or steel. These foundry molds and cores contained a binder residue from an Alphasat 9000 resin binder that had been cured with triacetin, as described in Example 4.

The foundry molds or cores were dismantled after removal of the casting and shaken to remove loose sand particles. The sand was then mechanically reclaimed. The blend of pristine sand and reclaimed sand had a size distribution corresponding to an AFS screen distribution of about 39.56 Grain Fineness and had an LOI of 0.369.

The average values for the tensile strengths and the percentage improvements obtained by using the binder solutions of this invention are reported below in Table 5.

TABLE 5

Solids Content of the Binder Solution	Tensiles (kPa)				
	1hr	2hr	4hr	24hrs	
Control-D	54	131 (19psi)	186 (27)	241 (35)	269 (39)
Test-E	45.6	193 (28)	262 (38)	303 (44)	296 (43)

Solids Content of the Binder Solution	Improvement in Tensiles %				
	1hr	2hr	4hr	24hrs	
Control-D	54	--	--	--	--
Test-E	45.6	47%	40%	25%	11%

The data in Table 5 illustrate that binder solutions of the present invention provide improved tensile strengths for foundry cores or moulds made from mixtures of reclaimed sand with pristine sand.

EXAMPLE 8

Test Cores Prepared by a Vapor Cure Method

Vapor cured test cores were prepared utilizing curable binder solutions at low solids contents and at more conventional solids contents, to illustrate that the advantages of the present invention can be realized with vapor cure methods.

To prepare the test cores, about 1500 - 2500 g of reclaimed sand, as used in Example 4, were added to a Hobart Kitchen Aid Mixer. This reclaimed sand was brought to a temperature of about 25°C. Binder solutions described in Example 2 as Resin F and Standard Resin 2 were utilized in Test-F and Control-E, respectively. For Test-F, 1.8% by weight resin solution, based on the weight of sand, was added to the sand and mixed for 2 minutes. In Control-E, 1.5% by weight, based on the weight of sand, was added to the sand and mixed for 2

minutes.

When mixing was complete, the reclaimed sand/binder solution mixture was blown with a Redford Carver Core Blower (a tradename of Dependable Foundry Equipment Company, Sherwood, Oregon) using 552 kPa air pressure for 1/2 second into a 3-cavity corebox, for producing Standard American Foundrymen Society's one-inch dogbone tensile briquettes. The corebox was then gassed for 5 seconds with methyl formate vapors generated in a CerJet Gas Generator (a tradename of Dependable Foundry Equipment, Sherwood, Oregon). Upon gassing, the cores cured under ambient conditions. Tensile strength measurements were made using a Dietert universal sand strength machine 400-1, fitted with a Tensile Core Strength Accessory 610-N.

Although the quantity of resin used in Test-F was greater than that of Control-E, the percent resin solids based on sand weight was higher for Control-E (0.855) than for Test-F (0.797).

The average values for the tensile strengths of the test cores made are indicated below in Table 6.

TABLE 6

Solution	Solids Content of the Binder	Tensiles (kPa)			
		1hr	2hr	4hr	24hrs
Control-E	57	159 (23psi)	152 (22)	179 (26)	241 (35)
Test-F	44.3	186 (27)	214 (31)	221 (32)	338 (49)

Solution	Solids Content of the Binder	Improvement in Tensiles %			
		1hr	2hr	4hr	24hrs
Control-E	57	--	--	--	--
Test-F	44.3	17.3%	40%	18%	40%

The improvement in tensile strength obtained from the low solids content binder solution indicates that the advantages of the present invention can be realized where reclaimed sand is utilized in a vapor cure manufacturing procedure.

Example 9

Preparing Test Cores Utilizing Binder Solutions at Solids Contents Below 33% by Weight

This example illustrates the lower limits for the solids content of binder solutions. A comparison is made

of tensile strengths for test cores prepared from binder solutions of the present invention and those having lower solids contents, i.e., below about 33%.

Test cores were made utilizing the binder solutions described in Example 1 as Resin D, Resin E and Control Resin 1 to provide Test G1, Test G and Control G, respectively. The raw batch formulations were prepared as described in Example 4 and cured with triacetin. The reclaimed sand used was as described in Example 4. Average values for tensile strength were obtained from 3 - 4 measured values and are reported in Table 7 below.

TABLE 7

	Solids Content of the Binder Solution	Tensiles (kPa)			
		1hr	2hr	4hr	24hrs
Test- G1	41.3	138 (20psi)	186 (27)	207 (30)	310 (45)
Test- G	37.6	138 (20)	221 (32)	290 (42)	448 (65)
Con- trol- G	30.2	90 (13)	103 (15)	172 (25)	221 (32)

	Solids Content of the Binder Solution	Improvement in Tensiles %			
		1hr	2hr	4hr	24hrs
Test- G1	41.3	--	--	--	--
Test- G	37.6	--	18.5%	90%	44.4%
Con- trol- G	30.2	-35%	-44%	-16.6%	-28.8%

The data in Table 7 illustrate that the use of binder solutions having solids contents as low as 30%31% by weight have an adverse effect on tensile properties of test cores made with 100% reclaimed sand.

EXAMPLE 10

Preparing Test Cores With Low Solids Content Binder Solutions Made With Mixed Alkalis

This example illustrates that the advantages of the present invention can be realized with binder solutions having resins condensed with a mixture of sodium and potassium alkalis. A comparison is made of tensile

strengths for test cores prepared from a binder solution of the present invention and a binder at a more conventional solids content.

Test cores were prepared with the resins defined in Example 3 as Resin G and Control Resin 2 to provide Test H and Control H, respectively. The reclaimed sand was the same sand described in Example 4. These test cores were prepared and tested as described in Example 4. Average tensile strength values were obtained from 3 or 4 measurements and are reported in Table 8 below.

TABLE 8

Solids Content of the Binder		Tensiles (kPa)			
<u>Solution</u>		<u>1hr</u>	<u>2hr</u>	<u>4hr</u>	<u>24hrs</u>
Con- trol- H	51	138 (20psi)	152 (22)	138 (20)	103 (15)
Test- H	37.3	152 (22)	159 (23)	221 (32)	193 (28)

Solids Content of the Binder		Improvement in Tensiles %			
<u>Solution</u>		<u>1hr</u>	<u>2hr</u>	<u>4hr</u>	<u>24hrs</u>
Con- trol- H	51	--	--	--	--
Test- H	37.3	10%	4%	60%	86%

The data in Table 8 illustrate that improvements in tensile strength can be obtained wherein the phenolic resin binder is made with a mixture of sodium and potassium alkalis.

EXAMPLE 11

Preparation of Test Cores With a Two Component Binder Solution

This example demonstrates the use of a two component binder solution in forming test cores and the improvements in tensile strength obtained therefrom. The reclaimed sand was the same sand described in Example 4.

The two component binder solution in this example comprised (1) Standard Resin 1 and (2) an amount of dilution water added to the sand. The tensile strengths of the cores obtained were compared against test cores obtained from the use of Standard Resin 1 without added dilution water.

The test cores were prepared and tested as described in Example 4. About 1.5 weight percent Standard Resin 1 was added to the reclaimed sand for Control I and Test I. In Test I, 0.2 weight percent water, based on the initial weight of the reclaimed sand, was added to the reclaimed sand as a separate component.

Average tensile strength values were obtained from 3 or 4 measurements made for each Control and Test and they are reported below in Table 9.

5	Solids Content of the Binder	Tensiles (kPa)				
10	<u>Solution</u>	<u>1hr</u>	<u>2hr</u>	<u>4hr</u>	<u>24hrs</u>	
	Con- trol- I	54	228 (33psi)	262 (38)	310 (45)	414 (60)
15	Test- I	46.5	276 (40)	365 (53)	448 (65)	496 (72)

20		Solids				
		Content				
		of the			Improvement in	
		Binder			Tensiles %	
25		<u>Solution</u>	<u>1hr</u>	<u>2hr</u>	<u>4hr</u>	<u>24hrs</u>
	Con-					
	trol-	54	--	--	--	--
30	I					
	Test-	46.5	21%	39%	44%	20%
	I					

The data in Table 9 show that improved tensile strengths can be obtained in test cores where the curable binder solution is comprised of two components and the solids content for the combined components falls below 50% by weight. While water was used as the second component and diluent in this example, it could as well be a silane solution that would be expected to result in a further, incremental improvement in tensile strength.

CONCLUSION

In the foregoing specification and in the examples, the binder has been an aqueous solution of an ester curable alkaline phenolic resin. Comparable results are obtainable where the binder is an acidic or neutral phenolic resin, and the curing agent and a source of alkalinity are added to the resin-sand mix either together or separately. The source of alkalinity must render the binder solution alkaline to make ester curing effective.

Claims

1. A method for producing a shaped article of a resin-bonded sand, wherein at least 40% of the sand in said article is reclaimed sand, said method comprising combining:

- sand of which at least 40% by weight is reclaimed sand,
- an aqueous solution of an alkaline phenolic resin that is curable at ambient temperature by a curing agent having ester functionality, and wherein said solution has a solids content in the range of 33% to 47% by weight; and
- a curing agent having ester functionality that can cause resin to cure at ambient temperature; and shaping and permitting said shape to cure;



Average tensile strength values were obtained from 3 or 4 measurements made for each Control and Test and they are reported below in Table 9.

	Solids Content of the Binder		Tensiles (kPa)			
	<u>Solution</u>					
			<u>1hr</u>	<u>2hr</u>	<u>4hr</u>	<u>24hrs</u>
Con-	54		228 (33psi)	262 (38)	310 (45)	414 (60)
I						
Test-	46.5		276 (40)	365 (53)	448 (65)	496 (72)
I						

	Solids Content of the Binder		Improvement in Tensiles %			
	<u>Solution</u>					
			<u>1hr</u>	<u>2hr</u>	<u>4hr</u>	<u>24hrs</u>
Con-	54		--	--	--	--
I						
Test-	46.5		21%	39%	44%	20%
I						

The data in Table 9 show that improved tensile strengths can be obtained in test cores where the curable binder solution is comprised of two components and the solids content for the combined components falls below 50% by weight. While water was used as the second component and diluent in this example, it could as well be a silane solution that would be expected to result in a further, incremental improvement in tensile strength.

CONCLUSION

In the foregoing specification and in the examples, the binder has been an aqueous solution of an ester curable alkaline phenolic resin. Comparable results are obtainable where the binder is an acidic or neutral phenolic resin, and the curing agent and a source of alkalinity are added to the resin-sand mix either together or separately. The source of alkalinity must render the binder solution alkaline to make ester curing effective.

Claims

1. A method for producing a shaped article of a resin-bonded sand, wherein at least 40% of the sand in said article is reclaimed sand, said method comprising combining:

- (a) sand of which at least 40% by weight is reclaimed sand,
- (b) an aqueous solution of an alkaline phenolic resin that is curable at ambient temperature by a curing agent having ester functionality, and wherein said solution has a solids content in the range of 33% to 47% by weight; and
- (c) a curing agent having ester functionality that can cause resin to cure at ambient temperature; and shaping and permitting said shape to cure;



said reclaimed sand containing an alkaline resin binder residue, said residue being left on the surfaces of the reclaimed sand after being previously bonded in a shape by an ester cured alkaline phenolic resin and recovered from said shape in the form of free-flowing sand granules.

5 2. A method as claimed in claim 1, wherein said resin solution comprises an aqueous solution of an alkaline phenol formaldehyde resin, said resin having

- (i) a weight average molecular weight (Mw) of from 500 to 2500,
- (ii) a formaldehyde:phenol molar ratio in the range of from 1:1 to 3:1,
- (iii) an alkali:phenol molar ratio in the range of from 0.2:1 to 1.2:1,
- (iv) an alkali content comprising sodium hydroxide, potassium hydroxide, lithium hydroxide or their mixtures,
- (v) said solution may optionally contain a silane to the extent of 0.05% to 3.0% by weight of said aqueous resin solution, and
- (vi) said resin is curable at ambient temperature with C₁-C₃ alkyl formates, organic esters formed from C₁-C₁₀ carboxylic acids and mono- and polyhydric alcohols, and low molecular weight lactones including butyrolactone, propiolactone, caprolactone, and mixtures thereof.

10 3. A method as claimed in claim 1 or claim 2, wherein at least 50% of the sand in said article is reclaimed sand.

4. A method as claimed in any of claims 1 to 3, wherein said solution of alkaline phenolic resin has a solids content in the range of about 35% to 45% by weight.

20 5. A method as claimed in claims 1 to 4, wherein said sand is characterized by residual alkalinity.

6. A method as claimed in claims 1 to 5, wherein said sand has on its surfaces a water-removable residue.

7. A method as claimed in claims 1 to 6, wherein said sand has on its said surfaces residual material comprising alkaline silicate material.

25 8. A method as claimed in any of claims 2 to 7, wherein the weight average molecular weight (Mw) of the resin is from 700 to 2000.

9. A method as claimed in any of claims 2 to 8, wherein the formaldehyde:phenol molar ratio in the resin is in the range of from 1.2:1 to 2.6:1.

30 10. A method as claimed in any of claims 1 to 9, wherein at least 60% of the sand in said article is reclaimed sand.

11. A method as claimed in any of claims 1 to 10, wherein said shaped article is for use in casting molten metal where the molten metal makes contact with said shaped article and from 40% to 100% of said sand in said shaped article is reclaimed sand.

35 12. A method as claimed in claims 2 to 11, wherein the alkali:phenol molar ratio in the resin is in the range of from 0.6:1 to 1.2:1.

13. A method as claimed in any of claims 1 to 12, wherein said aqueous solution is made by adding an amount of water to a second aqueous solution of alkaline phenolic resin having a solids content of alkaline phenolic resin in the range of 50% to 75% by weight.

40 14. A method as claimed in any of claims 1 to 13, wherein the product obtained by combining said (a), (b) and (c) is a raw batch formulation and the amount of said curing agent (c) in said raw batch formulation is at least about 10% by weight based on the weight of binder solution (b).

15. A method as claimed in any of claims 1 to 14, wherein the sand is reclaimed from dismantled foundry moulds or cores and the cured binder in the foundry cores and moulds from which the sand is obtained is (a) cured at ambient temperature with a curing agent selected from the group consisting of lactones, carboxylic acid esters, organic carbonates and mixtures thereof, and

45 (b) the ester cured alkaline phenol formaldehyde resin is the reaction product of a phenol and formaldehyde at a phenol formaldehyde molar ratio within the range of about 1:1 to 1:3 condensed with an alkali comprising potassium hydroxide, sodium hydroxide, lithium hydroxide or mixtures thereof.

16. A method as claimed in claim 15, wherein said curable binder solution comprises a silane wherein the concentration of silane may be as low as 0.05% by weight, based on the weight of the binder solution.

50 17. A method as claimed in any of claims 1 to 16, wherein the solids concentration of said aqueous solution is determined by heating a 1.5 g sample at 135°C for 3 hours and measuring the weight of the residue as the weight of solids.

18. A method as claimed in any of claims 1 to 17, wherein said aqueous solution has a Brookfield viscosity within the range of 0.015 to 0.150 Pas, and the Brookfield viscosity is determined utilizing a Model RVF Brookfield Viscometer with a No. 1 spindle at 20 rpm at 25°C.

55 19. A method as claimed in any of claims 1 to 17, wherein 50% to 100% by weight of said sand comprises sand reclaimed from mechanically dismantled foundry moulds or cores following use in casting metals, said reclaimed sand having a size corresponding to an American Foundrymen's Society's screen dis-



tribution of 25 to 140 Grain Fineness;

said foundry moulds or cores being made with an alkaline phenolic resin, cured with a curing agent selected from the group consisting of lactones, carboxylic acid esters, organic carbonates and mixtures thereof; and

said solids comprising a potassium alkali phenolic resin, wherein the molar ratio of potassium hydroxide:phenol falls within the range of 0.2:1 to 1.2:1, said potassium alkali phenol and formaldehyde being obtained by the reaction of phenol and formaldehyde at a ratio of about 1:1 to 1:3.0, said curable binder solution having a Brookfield viscosity of 0.075 to 0.250 Pas, as determined by a Model RVF Brookfield viscometer with a No. 1 spindle at 20 rpm at 25°C, at a 53% to 58% solids content.

20. A raw batch composition for use in making foundry moulds and cores comprising a mixture of

(a) sand,

(b) a curable binder solution comprising solvent and alkaline phenolic resin solids, said binder solution having an alkaline phenolic resin solids content of 33% to 47% by weight, and

(c) a curing agent having ester functionality that can cause said resin to cure under ambient conditions in an amount of at least 10% by weight based on the weight of binder solution;

wherein said sand is comprised of at least 40% by weight reclaimed sand obtained from dismantled foundry moulds or cores following use in a metal casting process; and

said reclaimed sand contains an alkaline resin binder residue, said residue being left on the surfaces of the reclaimed sand after being previously bonded in a shape by an ester cured alkaline phenolic resin and recovered from said shape in the form of free-flowing sand granules.

21. A raw batch formulation as claimed in claim 20, wherein said sand comprises 50% to 100% by weight reclaimed sand, based on the total weight of sand.

22. A raw batch formulation as claimed in claim 20 or claim 21, wherein the curable binder composition comprises two separate components, said first separate component is said alkaline phenolic resin and a solvent and said second separate component is a solvent wherein the two separate components when combined have solids content within the range of 33% to 47% based on the combined weight of said two separate components.

23. A raw batch formulation as claimed in claim 22, wherein said two components of the curable binder solution comprise

(1) a solution of alkaline phenolic resin having a solids content of above 50% by weight, and

(2) an amount of water sufficient to provide a solids content for said components, when combined, in the range from about 33% to about 47% by weight.

24. A raw batch formulation as claimed in claims 20 to 23, wherein the curable binder solution further comprises silane, wherein the concentration of the silane being as low as 0.05% by weight based on the weight of binder solution.

Patentansprüche

1. Verfahren zur Herstellung eines geformten Gegenstandes aus mit Kunstharz gebundenem Sand, wobei der in dem Gegenstand enthaltene Sand zu wenigstens 40% aus wiedergewonnenem Sand besteht, welches das Zusammengeben von

(a) Sand, der zu wenigstens 40% aus wiedergewonnenem Sand besteht,

(b) einer wässrigen Lösung eines alkalischen Phenolharzes, das bei Umgebungstemperatur mit einem Estergruppen enthaltenden Härtungsmittel aus gehärtet werden kann, wobei die Lösung einen Feststoffgehalt im Bereich von 33 Gew.% bis 47 Gew.% hat, und

(c) einem Estergruppen enthaltenden Härtungsmittel, das befähigt ist, die Aushärtung des Harzes bei Umgebungstemperatur zu bewirken, und das Formen und das Aushärtenlassen des geformten Gegenstandes umfaßt,

wobei der zurückgewonnene Sand einen Rückstand des als Bindemittel verwendeten alkalischen Harzes enthält, der sich auf der Oberfläche des zurückgewonnenen Sandes befindet, nachdem dieser Sand vorher durch ein mit einem Ester gehärtetes alkalisches Phenolharz in einen Formkörper eingebunden war und aus diesem Formkörper in Form freifließender Sandkörner zurückgewonnen wurde.

2. Ein Verfahren nach Anspruch 1, worin die Lösung des Harzes eine wässrige Lösung eines alkalischen Phenol-Formaldehyd-Harzes darstellt, welches

(i) ein durchschnittliches Molekulargewicht (MG) von 200-500,

(ii) ein Molverhältnis von Formaldehyd zu Phenol im Bereich von 1:1 bis 3:1,

(iii) ein Molverhältnis von Alkali zu Phenol im Bereich von 0,2:1 bis 1,2:1,

(iv) einen Gehalt an Alkali bestehend aus Natriumhydroxid, Kaliumhydroxid, Lithiumhydroxid oder Mischungen dieser Hydroxide hat, und



(v) die Lösung gewünschtenfalls ein Silan in einer Menge von 0,05 Gew% bis 3 Gew% enthalten kann und
(vi) dieses Harz bei Umgebungstemperatur mit C₁-C₃ Alkylformiaten, mit aus C₁-C₁₀ Carbonsäuren und ein- und mehrwertigen Alkoholen gebildeten Estern und mit niedermolekularen Lactonen, wie Butyrolacton, Propiolacton, Caprolacton, und Mischungen davon härtbar ist.

3. Ein Verfahren nach Anspruch 1 oder 2, worin wenigstens 50% des in dem geformten Gegenstand enthaltenen Sandes wiedergewonnener Sand sind.

4. Ein Verfahren nach einem der Ansprüche 1 bis 3, worin die Lösung des alkalischen Phenolharzes einen Feststoffgehalt im Bereich von etwa 35 Gew% bis 45 Gew% hat.

5. Ein Verfahren nach einem der Ansprüche 1 bis 4, worin der Sand einen Rest von Alkalität besitzt.

6. Ein Verfahren nach einem der Ansprüche 1 bis 5, worin der Sand auf seiner Oberfläche einen durch Wasser entfernbaren Rückstand hat.

7. Ein Verfahren nach einem der Ansprüche 1 bis 6, worin der Rückstand auf der Oberfläche des Sandes Alkalisilikat enthält.

8. Ein Verfahren nach einem der Ansprüche 2 bis 7, worin das durchschnittliche Molekulargewicht (MG) des Harzes 700-2000 beträgt.

9. Ein Verfahren nach einem der Ansprüche 2 bis 8, worin das Molverhältnis von Formaldehyd zu Phenol im Harz im Bereich von 1,2:1 bis 2,6:1 liegt.

10. Ein Verfahren nach einem der Ansprüche 1 bis 9, worin wenigstens 60% des in dem geformten Gegenstand enthaltenen Sandes wiedergewonnener Sand sind.

11. Ein Verfahren nach einem der Ansprüche 1 bis 10, worin der geformte Gegenstand für das Gießen von geschmolzenem Metall verwendet wird, wobei das geschmolzene Metall mit dem geformten Gegenstand in Kontakt kommt und bis zu 60% des in dem geformten Gegenstand enthaltenen Sandes wiedergewonnener Sand sind.

12. Ein Verfahren nach einem der Ansprüche 1 bis 11, worin das Molverhältnis von Alkali zu Phenol im Bereich von 0,6:1 bis 1,2:1 liegt.

13. Ein Verfahren nach einem der Ansprüche 1 bis 12, worin die wässrige Lösung durch Zugabe von Wasser zu einer zweiten wässrigen Lösung von alkalischem Phenolharz hergestellt wird, die einen Feststoffgehalt an alkalischem Phenolharz im Bereich von 50 Gew% bis 75 Gew% hat.

14. Ein Verfahren nach einem der Ansprüche 1 bis 13, worin das durch Zusammengeben der Komponenten (a), (b) und (c) erhaltene Produkt eine in einem Arbeitsgang erzeugte ungehärtete Formulierung ist und die Menge des Härtungsmittels (c) in dieser ungehärteten Zusammensetzung wenigstens etwa 10% bezogen auf das Gewicht der Lösung (b) des Bindemittels ist.

15. Ein Verfahren nach einem der Ansprüche 1 bis 14, worin der Sand von zerkleinerten Gießformen oder Gießformkernen zurückgewonnen wurde, und das gehärtete Bindemittel in den Gießformen und Gießformkernen, aus denen der Sand erhalten wurde,

(a) bei Umgebungstemperatur mit einem Härtungsmittel ausgewählt aus der Gruppe bestehend aus Lactonen, Carbonsäureestern, organischen Carbonaten und Mischungen davon gehärtet und

(b) das mit dem Ester ausgehärtete Phenol-Formaldehyd-Harz das Reaktionsprodukt eines Phenols mit Formaldehyd mit einem Molverhältnis von Phenol zu Formaldehyd im Bereich von 1:1 bis 1:3 ist, das mit einem alkalischen Kondensationsmittel, welches Kaliumhydroxid, Natriumhydroxid, Lithiumhydroxid und Mischungen davon umfaßt, kondensiert ist.

16. Ein Verfahren gemäß Anspruch 15, worin die Lösung des härtbaren Bindemittels ein Silan umfaßt, wobei die Konzentration des Silans so niedrig wie 0,05 Gew% bezogen auf das Gewicht der Lösung des Bindemittels sein kann.

17. Ein Verfahren nach einem der Ansprüche 1 bis 16, worin der Feststoffgehalt der wässrigen Lösung 3-stündiges Erhitzen einer Probe von 1,5 g auf 135°C und Auswiegen des Rückstandes bestimmt wird.

18. Ein Verfahren nach einem der Ansprüche 1 bis 17, worin die wässrige Lösung des Bindemittels eine nach Brookfield gemessene Viskosität im Bereich von 0,015 bis 0,150 Pas hat und die Viskosität mit einem RVF-Brookfield-Viscosimeter mit Spindel Nr. 1 und 20 Umdrehungen pro Minute bei 25°C bestimmt wird.

19. Ein Verfahren nach einem der Ansprüche 1 bis 17, worin 50 Gew% bis 100 Gew% des verwendeten Sandes aus einem Sand bestehen, der aus mechanisch zerkleinerten Gießformen oder Gießformkernen nach deren Verwendung zum Gießen von Metall wiedergewonnen ist,

wobei der wiedergewonnene Sand eine Korngröße besitzt, die gemäss der Norm der American Foundrymen's Society einer Korngrößenverteilung von 25-140 entspricht,

die Gießformen und Gießformkerne unter Verwendung eines alkalischen Phenolharzes hergestellt sind, das mit einem Härtungsmittel ausgewählt aus der Gruppe bestehend aus Lactonen, Carbonsäureestern, organischen Carbonaten und Mischungen davon, gehärtet ist, und

die festen Bestandteile ein Kaliumhydroxid enthaltendes Phenolharz umfassen, in dem das Molverhält-



nis von Kaliumhydroxid zu Phenol in dem Bereich von 0,2:1 bis 1,2:1 fällt und das Kaliumhydroxid enthaltende Phenolharz durch Umsetzung von Phenol und Formaldehyd im Molverhältnis von etwa 1:1 bis 1:3,0 hergestellt ist und die Lösung des härtbaren Bindemittels bei einem Feststoffgehalt von 53% bis 58% eine nach Brookfield in einem RVF-Brookfield-Viscosimeter mit Spindel Nr. 1 bei 20 Umdrehungen pro Minute und 25°C gemessene Viskosität von 0,075 bis 0,250 Pas besitzt.

20. Eine in einem Arbeitsgang hergestellte ungehärtete Zusammensetzung zur Verwendung für die Herstellung von Gießformen und Gießformkernen, die

(a) Sand,

(b) eine Lösung eines härtbaren Binders, die ein Lösungsmittel und ein alkalisches Phenolharz als Feststoff enthält, wobei die Lösung einen Feststoffgehalt an alkalischem Phenolharz von 33 Gew% bis 47 Gew% hat und

(c) ein Estergruppen enthaltendes Härtungsmittel, das befähigt ist die Aushärtung des Harzes bei Umgebungstemperatur zu bewirken und das in einer Menge von wenigstens 10 Gew% bezogen auf das Gewicht der Lösung des Bindemittels eingesetzt wird,

wobei der Sand zu wenigstens 40 Gew% aus wiedergewonnenem Sand besteht, der aus zerkleinerten Gießformen oder Gießformkernen nach deren Verwendung zum Gießen von Metall gewonnen wurde und

der einen Rückstand des als Bindemittel verwendeten alkalischen Harzes enthält der sich auf der Oberfläche des zurückgewonnenen Sandes befindet, nachdem dieser Sand vorher durch ein mit einem Ester gehärtetes alkalisches Phenolharz in einen Formkörper eingebunden war und aus diesem Formkörper in Form freifließender Sandkörner zurückgewonnen wurde.

21. Eine in einem Arbeitsgang hergestellte ungehärtete Zusammensetzung nach Anspruch 20, worin der Sand zu 50 Gew% bis 100 Gew% bezogen auf das Gesamtgewicht des Sandes aus wiedergewonnenem Sand besteht.

22. Eine in einem Arbeitsgang hergestellte ungehärtete Zusammensetzung nach einem der Ansprüche 20 oder 21, worin die härtbare Bindemittelzusammensetzung zwei separate Komponenten umfasst, wobei die erste Komponente das alkalische Phenolharz und ein Lösungsmittel und die zweite Komponente ein Lösungsmittel ist in welchem die zwei separaten Komponenten nach ihrer Vereinigung einen Feststoffgehalt im Bereich von 33% bis 47% bezogen auf das Gesamtgewicht der beiden Einzelkomponenten ergeben.

23. Eine in einem Arbeitsgang hergestellte ungehärtete Zusammensetzung nach Anspruch 22, worin die zwei Komponenten der Lösung des härtbaren Bindemittels

(1) eine Lösung eines alkalischen Phenolharzes mit einem Feststoffgehalt von über 50 Gew% und

(2) eine Menge Wasser, die ausreicht um bei der Vereinigung der beiden Komponenten einen Feststoffgehalt im Bereich von etwa 33 Gew% bis etwa 47 Gew% zu ergeben, darstellen.

24. Eine in einem Arbeitsgang hergestellte ungehärtete Zusammensetzung nach einem der Ansprüche 20 bis 23, worin die Lösung des härtbaren Binders zusätzlich ein Silan enthält, wobei die Konzentration des Silans so niedrig wie 0,05 Gew% bezogen auf das Gewicht der Lösung des Bindemittels ist.

Revendications

1. Procédé pour produire un article de forme en un sable lié par une résine, dans lequel au moins 40% du sable dans l'article est du sable régénéré, ce procédé consistant à combiner :

(a) un sable dont au moins 40% en poids est du sable régénéré;

(b) une solution aqueuse d'une résine phénolique alcaline qui peut prendre à la température ambiante sous l'action d'un agent de prise ayant une fonctionnalité ester, cette solution ayant une teneur en solides comprise entre 33 et 47% en poids; et

(c) un agent de prise ayant une fonctionnalité ester qui peut faire prendre la résine à la température ambiante, et à former et à permettre à cet article formé de durcir;

ce sable régénéré contenant un résidu de liant à base de résine alcaline, ce résidu étant laissé sur les surfaces du sable régénéré après avoir été précédemment lié en un moule par une résine phénolique alcaline durcie par un ester et récupéré de cet moule sous la forme de granules de sable s'écoulant librement.

2. Procédé selon la revendication 1, dans lequel la solution de résine est une solution aqueuse d'une résine phénol-formaldéhyde alcaline, cette résine ayant :

(i) un poids moléculaire moyen en poids (Mw) compris entre 500 et 2500;

(ii) un rapport molaire du formaldéhyde au phénol compris entre 1:1 et 3:1,

(iii) un rapport molaire de l'alcali au phénol compris entre 0,2:1 et 1,2:1,

(iv) un contenu d'alcali comprenant de l'hydroxyde de sodium, de l'hydroxyde de potassium, de l'hydroxyde



de lithium ou leurs mélanges,

(v) cette solution pouvant facultativement contenir une quantité de silane comprise entre 0,05 et 3,0% en poids de la solution de résine aqueuse, et

(vi) cette résine pouvant prendre à la température ambiante avec des formates d'alcoyle à 1 à 3 atomes de carbone, des esters organiques formés à partir d'acides carboxyliques à 1 à 10 atomes de carbone et de monoalcools ou de polyols, et des lactones à faible poids moléculaire, comprenant le butyrolactone, le propiolactone, le caprolactone et leurs mélanges.

3. Procédé selon la revendication 1 ou la revendication 2, dans lequel au moins 50% du sable dans l'article est du sable régénéré.

4. Procédé selon l'une des revendications 1 à 3, dans lequel la solution de résine phénolique alcaline a une teneur en solides comprise entre environ 35 et 45% en poids.

5. Procédé selon les revendications 1 à 4, dans lequel le sable est caractérisé par une alcalinité résiduelle.

6. Procédé selon les revendications 1 à 5, dans lequel le sable a sur ses surfaces un résidu pouvant être enlevé à l'eau.

7. Procédé selon les revendications 1 à 6, dans lequel le sable a sur ses surfaces un matériau résiduel constitué par un silicate alcalin.

8. Procédé selon l'une des revendications 2 à 7, dans lequel le poids moléculaire moyen en poids (Mw) de la résine est compris entre 700 et 2000.

9. Procédé selon l'une des revendications 2 à 8, dans lequel le rapport molaire du formaldéhyde au phénol dans la résine est compris entre 1,2:1 et 2,6:1.

10. Procédé selon l'une des revendications 1 à 9, dans lequel au moins 60% du sable dans l'article est du sable régénéré.

11. Procédé selon l'une des revendications 1 à 10, dans lequel l'article de forme est destiné à être utilisé pour couler du métal fondu, le métal fondu entrant en contact avec l'article de forme et 40 à 100% du sable dans l'article formé étant du sable régénéré.

12. Procédé selon les revendications 2 à 11, dans lequel le rapport molaire de l'alcali au phénol dans la résine est compris entre 0,6:1 et 1,2:1.

13. Procédé selon l'une des revendications 1 à 12, dans lequel la solution aqueuse est préparée en ajoutant une quantité d'eau à une deuxième solution aqueuse de résine phénolique alcaline, celle-ci ayant une teneur en solides comprise entre 50 et 75% en poids.

14. Procédé selon l'une des revendications 1 à 13, dans lequel le produit obtenu en combinant (a), (b) et (c) est une composition de mélange brute et dans lequel la quantité de l'agent de prise (c) dans cette composition de mélange brute est au moins environ 10% en poids sur la base du poids de la solution de liant (b).

15. Procédé selon l'une des revendications 1 à 14, dans lequel le sable est récupéré de moules ou de noyaux de fonderie désagregés et dans lequel le liant durci dans les noyaux et moules de fonderie dont le sable est obtenu est :

(a) durci à la température ambiante avec un agent de prise sélectionné dans le groupe constitué par des lactones, des esters d'acides carboxyliques, des carbonates organiques et leurs mélanges, et

(b) la résine phénol-formaldéhyde alcaline durcie par ester est le produit de réaction d'un phénol et d'un formaldéhyde avec un rapport molaire du phénol au formaldéhyde comprise entre environ 1:1 et 1:3 condensé avec un alcali contenant de l'hydroxyde de potassium, de l'hydroxyde de sodium, de l'hydroxyde de lithium ou leurs mélanges.

16. Procédé selon la revendication 15, caractérisé en ce que la solution de liant durcissable contient un silane, la concentration de silane pouvant être aussi faible que 0,05% en poids, sur la base du poids de la solution de liant.

17. Procédé selon l'une des revendications 1 à 16, dans lequel la teneur en solides de la solution aqueuse est déterminée en chauffant un échantillon de 1,5 g à 135°C pendant 3 heures et en mesurant le poids du résidu comme poids de solides.

18. Procédé selon l'une des revendications 1 à 17, dans lequel la solution aqueuse a une viscosité Brookfield comprise entre 0,015 et 0,150 Pa.s, et dans lequel la viscosité Brookfield est déterminée en utilisant un viscosimètre Brookfield Modèle RVF avec une aiguille No 1, à 20 tpm et à 25°C.

19. Procédé selon l'une des revendications 1 à 17, dans lequel 50 à 100% en poids du sable est du sable régénéré en provenance de moules ou de noyaux de fonderie désagregés, après utilisation pour couler des métaux,

ce sable régénéré ayant une dimension correspondant à une granulométrie selon la norme de l'American Foundrymen's Society avec une finesse de grain de 25 à 140,

ces moules ou noyaux de fonderie étant fabriqués avec une résine phénolique alcaline, durcie avec un agent de prise sélectionné dans le groupe comprenant des lactones, des esters d'acides carboxyliques, des



carbonates organiques et leurs mélanges, et

ces solides comprenant une résine phénolique alcaline de potassium, dans laquelle le rapport molaire de l'hydroxyde de potassium au phénol est compris entre 0,2:1 et 1,2:1, ce phénol alcalin de potassium et le formaldéhyde étant obtenus par la réaction du phénol et du formaldéhyde à un rapport molaire d'environ 1:1 à 1:3,0, la solution de liant durcissable ayant une viscosité Brookfield comprise entre 0,075 et 0,250 Pa.s, comme déterminé par un viscosimètre Brookfield Modèle RVF, avec une aiguille No 1, à 20 ppm et 25°C, pour une teneur en solides de 53 à 58%.

20. Composition de mélange brute destinée à être utilisée pour fabriquer des moules et noyaux de fonderie, comprenant un mélange :

(a) de sable,

(b) d'une solution de liant durcissable contenant un solvant et des solides à base de résine phénolique alcaline, cette solution de liant ayant une teneur en solides à base de résine phénolique alcaline de 33 à 47% en poids, et

(c) d'un agent de prise ayant une fonctionnalité ester qui peut faire prendre la résine dans les conditions ambiantes en une quantité d'au moins 10% en poids sur la base du poids de la solution de liant,

dans laquelle le sable comprend au moins 40% en poids de sable régénéré obtenu de moules ou de noyaux de fonderie désagregés après utilisation dans un processus de coulée de métal, et

ce sable régénéré contient un résidu de liant à base de résine alcaline, ce résidu étant laissé sur les surfaces du sable régénéré après avoir été précédemment lié en un moule par une résine phénolique alcaline durcie par un ester et récupéré de ce moule sous la forme de granules de sable s'écoulant librement.

21. Composition de mélange brute selon la revendication 20, dans laquelle le sable contient 50 à 100% en poids de sable régénéré, sur la base du poids total de sable.

22. Composition de mélange brute selon la revendication 20 ou la revendication 21, dans laquelle la composition de liant durcissable comprend deux composants séparés, le premier composant est une résine phénolique alcaline et un solvant et le deuxième composant est un solvant dans lequel les deux composants séparés, lorsqu'ils sont combinés, ont une teneur en solides comprise entre 33 et 47%, sur la base du poids combiné des deux composants séparés.

23. Composition de mélange brute selon la revendication 22, dans laquelle les deux composants de la solution de liant durcissable sont :

(1) une solution de résine phénolique alcaline ayant une teneur en solides supérieure à 50% en poids, et

(2) une quantité d'eau suffisante pour procurer une teneur en solides pour ces composants, lorsqu'ils sont combinés, comprise entre environ 33 et 47% en poids.

24. Composition de mélange brute selon les revendications 20 à 23, dans laquelle la solution de liant durcissable comprend en outre du silane, la concentration du silane étant aussi faible que 0,05% en poids sur la base du poids de la solution de liant.