

**Description****FIELD OF THE INVENTION**

5 This invention relates to the manufacture of foundry molds and cores with alkaline phenolic resin binders and reclaimed sand. More particularly, this invention relates to methods for treating the reclaimed sand so as to improve the tensile strength of articles produced from the reclaimed sand and an alkaline phenolic resin binder.

**10 BACKGROUND OF THE INVENTION**

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

15 To reclaim sand from a foundry mold or core, the used mold or core is shaken, vibrated or dismantled mechanically subsequent to removal of the casting, to loosen the sand and break up any lumps or agglomerates. The bonding properties of reclaimed sand are generally poorer than those of pristine sand, requiring further processing for effective use. There are three generally recognized treatment methods for reclaiming sand, mechanical, wet and thermal.

20 Mechanical treatment processes are the most commonly employed by the foundry industry because they are the most economical. Thermal treatment processes are undesirable in comparison because of their high energy costs. Wet treatment processes are undesirable in comparison because of disposal problems associated with the wash water and energy costs for drying the sand.

25 Because of limitations in the mechanical and thermal treatment processes, reclaimed sands so treated, particularly those recovered from foundry molds or cores wherein the cured binder was an ester cured alkaline phenolic resin, have bonding properties inferior to those of pristine sand. These inferior bonding properties limit the usage level of reclaimed sand in many cases to about 50 weight percent of the total sand when forming foundry cores and molds. Reclaimed sand levels of up to 90 weight percent are needed to achieve the desired economics and minimize disposal costs.

30 EP-A-0085512 discloses a foundry moulding composition comprising a mixture of a granular refractory material, a potassium alkali phenol-formaldehyde resin solution, at least one silane and, as curing agent, an ester.

**SUMMARY OF THE INVENTION**

35 It has now been discovered that the ability of reclaimed sand to form bonded articles of satisfactory tensile strength can be enhanced by treatment of the reclaimed sand with a silane solution. This treatment is generally useful for used sand that has been recovered for reuse and subjected to a mechanical or thermal reclamation treatment. It is also useful, but generally is not needed, for a used sand that has been subjected to a wet reclamation treatment.

40 The present invention provides a method for forming a resin bonded article from reclaimed sand that has previously been used by forming it into a resin-bonded shape with a binder of an ester cured alkaline phenolic resin comprising:

(i) treating the reclaimed sand by placing it in contact with from 0.05% to 1.0% by weight based on the weight of the reclaimed sand of a silane solution having a concentration of silane of from 1% to 100% based on the weight of the silane solution, wherein:

45 (a) the solvent in said solution is selected from polar organic solvents, aqueous liquids and mixtures thereof; and

(b) the silane has the formula: (1)  $R'Si(OR)_3$  where  $R'$  is a  $C_2$ - $C_6$  alkylene group bonded to an amino, epoxy, mercapto, glycidoxy, ureido, hydroxy, hydroxy- $C_1$ - $C_6$  alkylamino, amino- $C_1$ - $C_6$  alkylamino,  $C_2$ - $C_6$  alkenyl or  $C_2$ - $C_6$  alkenyl-carboxy group and  $R$  may be the same or different and are selected from  $C_1$ - $C_6$  alkyl and  $C_1$ - $C_6$  alkoxy-substituted  $C_1$ - $C_6$  alkyl groups; or

(2)  $H_2N(CH_2)_nSi(OR^1)_{3-x}(R^2)_x$  where  $n$  equals a whole number of from 2 to 4,  $R^1$  is a  $C_1$ - $C_4$  alkyl group and  $R^2$  is a  $C_1$ - $C_4$  alkyl or phenyl group and  $x$  is 0 or 1; or

(3)  $H_2N(CH_2)_m-NH-(CH_2)_nSi(OR^1)_{3-x}R^2_x$  where  $n$  is a whole number of from 2 to 4,  $m$  is 2 or 3,  $R^1$  is a  $C_1$ - $C_4$  alkyl group,  $R^2$  is a  $C_1$ - $C_4$  alkyl group and  $x$  is 0 or 1; and

55 (ii) mixing the treated reclaimed sand with a resin.

The resin-bonded article, such as a foundry mold or core is produced from the reclaimed, silane-treated sand, using an ester curable, alkaline phenolic resin.

This invention provides methods for producing resin-bonded sand shapes, such as foundry molds or cores, wherein at least 20% by weight of the sand used is reclaimed sand. In fact, the amount of reclaimed sand preferably is 50%, 60%, 80% or even 100%, of the sand used. For many foundries, economics dictate that a reclaimed sand level of 60% to 80%, at least, be used.

5 These methods comprise the steps of mixing a binder solution, a curing agent, and silane-treated reclaimed sand, in a raw batch formulation, forming the desired shape from this formulation, and allowing the binder to cure. The silane solution is applied to the reclaimed sand before preparation of the raw batch formulation.

10 The quantities of silane solution for application to reclaimed sand falls within the range from 0.05% to 1.0% by weight, based on the weight of reclaimed sand, and the preferred concentrations of the silane solution fall within the range of about 5% to 90% by weight, preferably 10% to 50%, based on the weight of the silane solution.

15 Treatment of reclaimed sand with a silane solution in accordance with this invention has been found to be more efficient than treatment of reclaimed sand with undiluted silane or by the addition of silane or a silane solution to a solution of an alkaline phenolic resin binder.

20 This invention additionally provides a composition for mixing with a resin in the process of the invention comprising granular foundry sand that has been formed into a resin-bonded shape with an ester cured alkaline phenolic resin binder, then separated from said shape into free-flowing granules, said granules having applied thereto from 0.05% to 1.0% by weight based on the weight of the reclaimed sand of a silane solution having a concentration of silane of from 1% to 100% based on the weight of the silane solution wherein

(a) the solvent in said solution is selected from polar organic solvents, aqueous liquids and mixtures thereof; and

25 (b) the silane has the formula: (1)  $R'Si(OR)_3$  where  $R'$  is a  $C_2$ - $C_6$  alkylene group bonded to an amino, epoxy, mercapto, glycidoxy, ureido, hydroxy, hydroxy- $C_1$ - $C_6$  alkylamino, amino- $C_1$ - $C_6$  alkylamino,  $C_2$ - $C_6$  alkenyl or  $C_2$ - $C_6$  alkenyl-carboxy group and  $R$  may be the same or different and are selected from  $C_1$ - $C_6$  alkyl and  $C_1$ - $C_6$  alkoxy-substituted  $C_1$ - $C_6$  alkyl groups; or

(2)  $H_2N(CH_2)_nSi(OR^1)_{3-x}(R^2)_x$  where  $n$  equals a whole number of from 2 to 4,  $R^1$  is a  $C_1$ - $C_4$  alkyl group and  $R^2$  is a  $C_1$ - $C_4$  alkyl or phenyl group; or

30 (3)  $H_2N-(CH_2)_m-NH-(CH_2)_nSi(OR^1)_{3-x}R^2_x$  where  $n$  is a whole number of from 2 to 4,  $m$  is 2 or 3,  $R^1$  is a  $C_1$ - $C_4$  alkyl group,  $R^2$  is a  $C_1$ - $C_4$  alkyl group and  $x$  is 0 or 1.

The invention also provides a raw batch formulation comprising the composition of the invention or a mixture of the composition and reclaimed sand and a solution of a curable binder, comprising an aqueous solution of a phenolic resin which aqueous solution is curable at ambient temperature with a curing agent 35 selected from the group consisting of lactones, carboxylic acid esters, organic carbonates and mixtures thereof. The phenolic resin may be an alkaline phenolic resin, in which case a curing agent with ester functionality will initiate curing at ambient temperature.

Alternatively, if the phenolic resin is neutral or acidic, then the curing agent may be, preferably, 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. It is also possible to use separate additions of curing agent and of an alkaline source, to such a resin. This binder system can be added to sand, whether the sand is 100% reclaimed or is a mixture of pristine and reclaimed, to provide resin-bonded shapes such as foundry molds and cores with useful tensile strengths.

#### 45 DETAILED DESCRIPTION OF THE INVENTION

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 granules. 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 50 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 water removable 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 55 produced by other alkaline resins.

The surface residue on the recovered used sand would also be expected to include a film or particles of cured resin binder, carbon, partially carbonized resin binder, and dust, as well as any alkaline silicate present. Some of these materials can be removed by water washing, and some by thermal or attrition treatments. Use of the present invention has the advantage of eliminating concerns over the nature of the residue and the cause of poor tensile strengths, since the use of the present invention leads to the production of resin-bonded sand articles that have satisfactory tensiles.

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 application of a silane solution to the recovered, used sand.

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. These alternative expressions are used 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 25 to 140 Grain Fineness, as defined in the American Foundrymen's Society's "Mold and Core Test Handbook", pp. 4.2-4.5. The most preferred grain sizes for pristine sand have a screen distribution of about 30 to 80 and the most preferred grain sizes for reclaimed sand follow a similar size pattern and distribution.

The sand commonly employed in the foundry industry includes silica sand, quartz, chromite sand, zircon sand and olivine sand, but many other materials could be used.

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, including phenol, a cresol, resorcinol, 3,5-xyleneol, bisphenol-A, other substituted phenols, and mixtures thereof, with an aldehyde such as, for example, formaldehyde, acetaldehyde, furfuraldehyde, and aldehyde mixtures. 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.

Suitable alkaline materials used to condense these phenolic resins include sodium hydroxide, potassium hydroxide, lithium hydroxide, and mixtures thereof, with potassium hydroxide being 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 alkali:phenol molar ratio for these phenolic resins preferably is in the range from about 0.2:1 to 1.2:1.

The more commonly useful phenolic resins generally are those having a weight average molecular weight preferably greater than 500, more preferably greater than 700 and most preferably within the range of about 1000 to about 2500, 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 cm 10 $\mu$  columns, porosities 10 $\mu$ , 500, and 50 Angstrom units, respectively, and a Rheodyne model 70-10 sample loop injector fitted with a 100 $\mu$ l loop and a 0.5  $\mu$ 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. 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 $\mu$ 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.

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 catalyst 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.

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.

- 5 The useful aqueous solutions of the phenolic resin binder should have solids contents in the range from about 40% to 75% by weight, and preferably about 50% to 60% by weight. The Brookfield viscosity of such solutions is generally in the range from about 50 to about 750 cps. The Brookfield viscosity of such solutions at a solids content in the range of 53% to 58% by weight, as measured after standing at 135 °C for 3 hours, is generally in the range of about 75 cps to 250 cps, preferably, 100 to 150 cps, using an RVF  
10 Model Brookfield viscometer with a No. 1 spindle at 20 r.p.m., at 25 °C.

- Some of the preferred phenolic resins are the more highly alkaline phenolic resins described in U.S. Patent Nos. 4,474,904 and 4,468,359. It is noted that for these resins, alkalinity content 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 ratios of KOH:phenol for the preferred potassium alkali condensed phenolic  
15 resins of this invention fall within the range of about 0.2:1 to about 1.2:1.

- The cured binder within the foundry molds or cores from which the used sand is obtained may include a silane originally added to the aqueous solution of alkaline phenolic resin. Certain silanes are commonly added to phenolic resin solutions to improve the tensile strengths of the molds and cores produced therefrom. Amounts as low as 0.05% by weight, based on the weight of the phenolic resin solution, have  
20 been found to provide significant improvements in tensile strength. Higher levels of silane give greater improvements in strength up to quantities of about 0.6% by weight, based on the weight of the phenolic resin solution. The use of silane concentrations at higher levels is not preferred because of the added cost. In addition, because the silane typically used is an aminoalkyl silane, which contains nitrogen, use of excess silane may increase the risk of pinhole defects in the casting and for this reason, amounts in excess of 3%  
25 by weight, based on the weight of the binder, are not used.

Preferred curing agents include lactones, organic carbonates, carboxylic acid esters, and mixtures thereof. These species exhibit the ester functionality necessary for "ester cure" of the alkaline 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 C<sub>1</sub> to C<sub>10</sub>, alkyl mono- or polyhydric alcohols with short or medium length, i.e., C<sub>1</sub> to C<sub>10</sub> carboxylic acids. Specific carboxylic acid esters include, but are not limited to, n-butyl acetate, ethylene glycol diacetate, and triacetin (glycerol triacetate), dimethyl glutarate, and dimethyl  
30 adipate.  
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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 foundry molds or cores from which the used sands are obtained may also have been cured by  
40 gassing with low molecular weight carboxylic acid esters, such as C<sub>1</sub> to C<sub>3</sub> alkyl formates, including methyl formate and ethyl formate. The gassing catalyst 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 examples of carrier gases include air and nitrogen.

- 45 The relative volatility of these alkyl formates enables their use as gassing catalysts. 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 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 ° to 82 °C at atmospheric pressure.

- 50 The concentration of formate catalysts in the carrier gas is preferably at least 0.2% by volume and most preferably from 30% to 80% 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. These gassing  
55 procedures are described more particularly in U.S. Patent No. 4,468,359.

In further identifying the reclaimed used sand useful in foundry applications of this invention, the foundry mold or core from which the sand is obtained generally has been used in a metal casting process. It is the heat experienced during the metal casting process which is believed to generate the residues that

inhibit or limit the tensiles of resin-bonded articles made from the sand upon reuse.

In reclaiming foundry sand, the casting is first removed from the mold or core. Any sand which adheres to the casting is typically disposed of. The mold or core is then shaken or vibrated to remove any loose sand particulates and break up any lumps to provide free flowing sand granules. In some cases, this may be all that is necessary to recover the used sand. If large clumps persist, they may be broken up by kneaders, mixers, lump crushers, and the like.

Where the reclaimed sand is of a desirable particle size, a silane solution is applied in a quantity sufficient to increase the tensile strength of foundry cores and molds or other resin-bonded articles made from such silane-treated sand. The amounts of silane solution fall within the range of 0.05% to less than 1% by weight, based on the weight of the reclaimed sand. Preferably, the quantity of silane solution falls within the range of about 0.1% to 0.5% based on the weight of reclaimed sand.

Although undiluted silane, i.e., silane concentrations of about 100% by weight, will provide the improvements in tensile strength desired for the molds and cores obtained from reclaimed used sand, it is preferred to utilize silane more efficiently by diluting the silane in a solvent, to facilitate application of the solution to the sand.

The silane solution used has a concentration of silane of at least 1% by weight, based on the total weight of the solution. Preferably, the silane concentration falls within the range of about 5 to 90 weight percent and most preferably about 10 to 50 weight percent, based on the total weight of solution, i.e., solvent and silane solute.

The degree of agitation used in mixing the reclaimed sand and the silane solution is significant in obtaining high tensile strengths for the molds and cores produced. High speed continuous mixers have been found to be very effective. While low speed equipment will provide the necessary agitation and the improved results desired of the present invention, high speed mixers provide even better results.

In treating the reclaimed used sand, the silane solution is added to the sand before adding the addition of the binder solution and the curing agent.

The silane in the silane solution should be effective in enhancing the tensile strength of foundry cores and molds obtained from reclaimed sand when bonded with a resin binder. Such silanes are well known.

Suitable silanes include those conforming to the formula  $R'Si(OR)_3$ , wherein  $R'$  is a  $C_2-C_6$  alkylene group bonded to an amino, epoxy, mercapto, glycidoxy, ureido, hydroxy, hydroxy- $C_1-C_6$  alkylamino, amino- $C_1-C_6$  alkylamino,  $C_2-C_6$  alkenyl or  $C_2-C_6$  alkenyl-carboxy group and the groups  $R$  may be the same or different and are selected from  $C_1-C_6$  alkyl and  $C_1-C_6$  alkoxy-substituted  $C_1-C_6$  alkyl groups. Such silanes include:

gamma-hydroxypropyl trimethoxysilane,  
hydroxymethyl diethoxymethylsilane,  
N-(gamma-aminopropyl)-gamma-aminopropyl trimethoxysilane,  
N-(beta-aminoethyl)-gamma-aminopropyl trimethoxysilane,  
gamma-carboxypropyl triethoxysilane,  
delta-aminobutyl trimethoxysilane,  
gamma-mercaptopropyl trimethoxysilane,  
gamma-aminopropyl triethoxysilane,  
gamma-ureidopropyl triethoxysilane and  
gamma-glycidoxypentyl triethoxysilane.

Suitable silanes are not limited to those described above. United Kingdom patent specification 876,033 describes suitable silanes that do not conform to the formula above. They include, for example,

p-aminophenyl triphenoxysilane,  
p-hydroxyphenyl trichlorosilane,  
di-p-hydroxyphenyl diethoxysilane, and  
p-aminophenylmethyl triethoxysilane.

The most commonly used silanes are the amino silanes. Those amino silanes which are preferred comprise aminoalkyl alkoxysilanes which conform to the general formula  $H_2N(CH_2)_nSi(OR^1)_{3-x}(R^2)_x$ , wherein  $n$  equals a whole number of from 2 to 4,  $R^1$  is an alkyl group of from 1 to 4 carbon atoms,  $R^2$  is an alkyl group of from 1 to 4 carbon atoms or phenyl and  $x$  is 0 or 1. Specific examples of such silanes, which have not been described earlier, include

gamma-aminopropyl trimethoxysilane,  
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.

Also suitable are diaminosilanes, also referred to as N-(aminoalkyl) aminoalkyl silanes, of the formula,  $H_2N-(CH_2)_m-NH-(CH_2)_n-Si(OR^1)_{3-x}R^2_x$ , wherein n is a whole number of from 2 to 4, m is a whole number of from 2 to 3, R<sup>1</sup> is alkyl group of from 1 to 4 carbon atoms, R<sup>2</sup> is an alkyl group of from 1 to 4 carbon atoms and x is 0 or 1. Specific examples of such silanes include:

N-(gamma-aminopropyl)-gamma-aminopropyl triethoxysilane,  
N-(gamma-aminopropyl)-gamma-aminopropyl trimethoxysilane,  
N-(beta-aminoethyl)-gamma-aminopropyl dimethoxymethylsilane.

U.S. Patent No. 4,256,623 describes suitable alkyl substituted species of the aminoalkyl alkoxy silanes and diaminosilanes. These more particularly include:

N-methyl-gamma-aminopropyl triethoxysilane,  
N-ethyl-gamma-aminopropyl trimethoxysilane,  
N-methyl-gamma-aminopropyl dimethoxymethylsilane, and  
N-(N-methyl-beta-aminoethyl)-gamma-aminopropyl dimethoxymethylsilane, and  
N-(gamma-aminopropyl)-N-methyl-gamma-aminopropyl dimethoxymethylsilane.

Suitable solvents for the silanes may be selected from water-compatible organic solvents, preferably polar organic solvents, aqueous liquids such as water, and mixtures thereof. Aqueous liquids are the preferred solvents in that water is inexpensive and higher tensile strengths are often obtained from silanes dissolved in water. The solvent selected is principally determined by the solubility of the silane. Those silanes which are most preferred are the aminoalkylsilanes available in aqueous solution typically at 40% by weight silane concentration. It is preferable for any organic solvent used to be water soluble so that it is compatible with the binder solution, which is an aqueous solution. Suitable organic solvents include alcohols and glycols of from 1 to 6 carbon atoms such as methanol and ethanol. The alcohols are suitable solvents for the ureidosilanes and glycidoxy silanes described above. Water is the preferred solvent for aminosilanes.

### Foundry Molds and Cores

Also provided by this invention are methods for producing foundry molds and cores from a curable binder system and sand, of which at least 20% by weight is used sand that has been reclaimed, generally from dismantled foundry molds or cores which have been used and that were made with an ester cured alkaline phenolic resin.

These methods comprise forming a raw batch formulation comprised of reclaimed sand, a solution of a resin binder, and a curing agent, wherein at least 20%, preferably from 50% to 100%, by weight of the sand is used, reclaimed sand from articles such as foundry molds or cores, which sand has had applied to it a silane solution in sufficient quantity to increase the tensile strength of articles produced from the raw batch formulation.

The silane solution and reclaimed sand are mixed prior to forming the desired shape.

The binder solution used in this raw batch formulation comprises an aqueous solution of a phenolic resin that can cure at room temperature with a curing agent having ester functionality. Most preferably, the phenolic binder is an aqueous solution of an alkaline phenol formaldehyde resin wherein

- (i) the solids content is in the range from 40% to 75%,
- (ii) the weight average molecular weight (Mw) is from 500 to 2500, preferably 700 to 2000, and more preferably from 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 C<sub>1</sub>-C<sub>3</sub> alkyl formates, organic esters formed from C<sub>1</sub>-C<sub>10</sub> 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.

The amount of alkaline phenolic resin in the binder solution must be sufficient to provide the necessary adhesive bond between sand particles. Quantities of the resin solution, in the range of about 0.5% to 8% by weight, based on the weight of sand, are preferred and amounts below 2% by weight are most preferred, where the phenolic resin solution is at a solids content of about 40% to 75% by weight and preferably about 50% to 60% by weight. The Brookfield viscosity for these resin solutions ranges from about 50 to 750 cps, at a solids content of about 40% to 75%, and is preferably 75 to 250 cps, at a solids content of 53% to 58%, as measured on a RVF Model Brookfield viscometer, with a No. 1 spindle at 20 r.p.m., at 25 °C.

Binder solutions with a solids content below 50% have not been preferred for use with pristine sand. Binder solutions with a solids content above 75% by weight have not been used because the viscosity of such solutions is too high.

The third component of the raw batch formulation is a curing agent for curing the binder. The preferred curing agents are the lactones, organic carbonates, and carboxylic acid esters, or mixtures of such agents.

The methods for producing foundry molds or cores which comprise this invention include those methods wherein the curable binder solution is cured by gassing with an alkyl formate, either directly or with a carrier gas. These methods have been described more particularly above and in U.S. Patent No. 4,468,359.

The amount of curing agent used should be sufficient to cure said binder under curing conditions, which is generally at ambient temperature and pressure. Where the curing agent is mixed with the sand and the binder solution to provide the raw batch formulation, concentrations of curing agent of from about 10% to 110%, based on the weight of binder solution, are preferred.

An optional ingredient in the curable binder solution, which is often a preferred ingredient, is a silane which is effective in increasing the tensile strength of the foundry mold or core product. Suitable silanes are those described above. The quantity of silane added to the binder solution is that which provides an increase in tensile strength for the article produced. Such quantities generally fall within the range of about 0.05% to 3% by weight, based on the weight of the binder solution.

In addition to forming the raw batch formulation, steps must be taken to form this raw batch formulation in the shape desired, which generally will be a foundry core or mold. This can be accomplished by mixing all the components of the raw batch formulation together and then forming this mixture in the desired shape. Alternatively, sand and a binder solution may be mixed and formed into the desired shape, then gassed with an alkyl formate of from 1 to 3 carbon atoms.

The silane solution is mixed with the reclaimed sand prior to the formation of the raw batch formulation. A suitable amount of silane solution for admixture with reclaimed sand is that which is sufficient to increase the tensile strength of the foundry cores and molds produced, as compared to similar articles prepared from untreated sand. Preferred quantities of silane solution and preferred concentrations of silane solution are as described above.

Preferred reclaimed sand for use in this invention is obtained from used, resin bonded foundry molds or cores which (1) were made with a cured, alkaline phenolic resin binder, (2) have been exposed to a metal casting process and (3) have been dismantled mechanically. The preferred particles for the reclaimed sand have an AFS screen distribution size of 0.71 to 0.105 mm (25 to 140 Grain Fineness).

#### Raw Batch Formulations

The raw batch formulations used in the methods described above comprise sand, of which at least 20% by weight is reclaimed, generally from dismantled foundry molds and cores which have been used in a metal casting process.

The reclaimed sand is mixed with a silane solution in an amount sufficient to increase the tensile strength of molds and cores obtained therefrom, as compared to similar articles made from reclaimed sand that has not been treated with silane solution. Preferred silane solutions are as described above.

The raw batch formulations also include a solution of a resin binder, preferably an alkaline phenol formaldehyde resin which is used in an amount sufficient to bind the sand with the strength necessary for use as foundry molds and cores. Preferred binder solutions and amounts thereof are as described above.

The third component of the raw batch formulation is a curing agent selected from the group consisting of lactones, carboxylic acid esters, organic carbonates, and mixtures of these agents, which cause the binder to cure at ambient temperature and pressure. The curing agent is present in an amount sufficient to cure said binder solution. Preferred curing agent solution concentrations fall within the range of about 10% to 110% of the curing agent by weight, based on the weight of resin solution, which is at a concentration of

40% to 75% or so solids, by weight.

The components of this raw batch formulation are uniformly mixed so as to permit a uniform cure of the binder. This can be achieved with simple lab batch mixers, with high speed, continuous mixers, or with any other type of mixer commonly used for foundry sand.

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#### Binder System

Also provided by this invention is a binder system which can be used for producing foundry molds and cores. This system comprises three separate components. The first component is a solution of an alkaline phenolic resin binder as described previously. Preferred binder solutions are those alkaline phenolic resin solutions identified above.

The second component in the binder system is a curing agent suitable for curing said binder at ambient temperature. Suitable curing agents are selected from lactones, organic carbonates, carboxylic acid esters, and mixtures thereof.

The third component is a silane solution which can either be an aqueous solution, an organic solution or mixtures thereof. The silane applied preferably is a solution that is compatible with the aqueous solution of the binder. Methanol and ethanol are suitable solvents. Suitable silanes are those described in detail above.

To utilize the binder system, amounts of the resin solution and silane solution necessary to provide a foundry core or mold of adequate strength are added to the sand and mixed. A portion of the sand is preferably reclaimed sand. Quantities of binder solution preferably range from about 0.5% to 8% by weight based on the weight of the sand. Preferred quantities of curing agent typically range from 10% to 110% based on the weight of the binder solution at 40% to 75% solids content. The quantity of silane solution utilized is dependent on the proportion of reclaimed sand within the sand utilized and preferably is from 0.05% to 0.5% by weight, based on the weight of reclaimed sand.

The resin and silane components of this binder system can be mixed with sand in any order and should provide superior tensile strengths in the articles produced. Where only small amounts of reclaimed sand is used, i.e., below about 40% by weight of the total sand, it may be desirable to treat the reclaimed sand prior to admixture with the pristine sand so as to economize on the silane solution used.

This invention will be demonstrated by the following examples and in these examples, and elsewhere throughout the specification, parts and percentages are by weight and temperatures are in °C unless expressly indicated to be otherwise.

#### EXAMPLE 1

##### Pretreatment of Reclaimed Sand With Aqueous Solutions of Gamma-Aminopropyl Triethoxysilane

In this example, reclaimed sand was treated with an aqueous solution of gamma-aminopropyl triethoxysilane and used to form test cores. These test cores were compared against test cores obtained from untreated sand.

Test cores were made from reclaimed sand as treated below.

Control 1 - The reclaimed sand was not treated.

Test A - The reclaimed sand was treated at 25°C with 0.024 weight percent, based on the weight of sand, of a 40% solution in water of gamma-aminopropyl triethoxysilane diluted with 0.096 weight percent water, based on the weight of sand.

Test B - The reclaimed sand was treated at 25°C with 0.048 weight percent, based on the weight of sand, of a 40% solution in water of gamma-aminopropyl triethoxysilane diluted with 0.072 weight percent water, based on the weight of sand.

Test C - The reclaimed sand was treated at 25°C with 0.12 weight percent, based on the weight of sand, of a 40% gamma-aminopropyl triethoxysilane in water.

The sand used was a mixture of reclaimed sand obtained from foundry cores and molds that had been used in casting molten iron or steel. The cured binder in the molds and cores from which this sand was obtained was ALPHASET 9000® potassium alkali phenol-formaldehyde resin binder from Borden, Inc. having a Brookfield viscosity of from 100 - 150 cps, as determined by a RVF Model Brookfield viscometer with a No. 1 spindle at 20 r.p.m., at 25°C. This resin binder has a solids content of about 54% by weight, a phenol:formaldehyde molar ratio of about 1:1.8 and a KOH:phenol molar ratio of about 0.85:1. This resin binder also contained gamma aminopropyl triethoxy silane in an amount of about 0.4% by weight, based on the weight of the binder solution. This resin was cured with triacetin.

In reclaiming the sand, the used molds and cores were shaken within a vibratory mill (Vibramill of General Kinematics Corp., Barrington, Ill.) to remove loose particulates and break up any lumps. The sand grains were treated mechanically in a Thermal/Mechanical unit (Eirch Machines, Maple, Ontario, Canada) at ambient temperature. The reclaimed sand has a size of about 0.43 mm (an AFS screen distribution of about 39.1 Grain Fineness). The L.O.I. of the reclaimed sand was about 0.450.

In performing the processes of this invention, the reclaimed sand was added to a Hobart Kitchen Aid Mixer, brought to 25 °C, and mixed with added silane solution for about 1 minute.

To produce the test cores, from 1500 - 2500 grams of the sand for each test and control were added to a Hobart Kitchen Aid mixer. This sand was brought to a temperature of about 25 °C, the silane solution was applied, and about 1.5% by weight of an aqueous solution of ALPHASET 9000® potassium alkali condensed phenol-formaldehyde resin, having a solids content of about 54% by weight, was added to the sand. This resin binder solution had a Brookfield viscosity in the range of 100-150 cps utilizing a Model RVF Brookfield viscometer with a No. 1 spindle at 20 r.p.m. and 25 °C. The weight percent of resin was based on the weight of sand. The phenol:formaldehyde molar ratio for the resin was 1:1.8. The KOH:phenol molar ratio for the resin was 0.85:1. The resin binder solution additionally contained the silane gamma-aminopropyl triethoxy silane in an amount of about 0.4% by weight, based on the weight of binder solution.

The resin and sand were mixed for about 1 minute then about 25% by weight of triacetin, based on the weight of the resin solution, was added to the Hobart Kitchen Aid mixer and mixed for about another 40 seconds.

After mixing, the sand was used immediately to form Standard American Foundrymen Society's 25.4 mm (1-inch) dogbone tensile briquettes in a Dietert 696 corebox. The cores cured at room temperature and were broken at the following time intervals: 1 hour, 2 hours, 4 hours and 24 hours, after the mix was made.

Tensile strength measurements were made using a Dietert Universal Sand Strength Machine 400-1 fitted with a Tensile Core Strength Accessory 610-N.

The tensile strengths of 3-4 cores obtained for each test and control were measured at the intervals indicated above and averaged. The average values are reported in Table 1 with the percent improvement in tensile strength also indicated.

TABLE 1

| Test      | Total Silane Solution<br>% Based on Sand Wt. |                | Tensiles kPa (psi) |          | % Improvement<br>In Tensile Strength |          |       |       |
|-----------|----------------------------------------------|----------------|--------------------|----------|--------------------------------------|----------|-------|-------|
|           | Silane<br>(wt%)                              | Water<br>(wt%) | Hrs:1              | 2        | 4                                    | 24       | Hrs:1 | 2     |
|           |                                              |                |                    |          |                                      |          |       |       |
| Control-1 | ---                                          | ---            | 158 (23)           | 227 (33) | 241 (35)                             | 241 (35) | ---   | ---   |
| Test A    | 0.024                                        | 0.096          | 289 (42)           | 345 (50) | 365 (53)                             | 365 (53) | 82.6  | 51.5  |
| Test B    | 0.048                                        | 0.072          | 282 (41)           | 400 (58) | 434 (63)                             | 413 (60) | 78.2  | 75.7  |
| Test C    | 0.120                                        | ---            | 289 (42)           | 400 (58) | 469 (68)                             | 482 (70) | 82.6  | 75.7  |
|           |                                              |                |                    |          |                                      |          | 94.0  | 100.0 |

The data in Table 1 illustrate the progressive improvements in tensile strength that can be achieved by pretreating the sand with a silane solution. The effectiveness and economy in diluting the silane with water is also shown in that the initial tensile strength of cores obtained from Test A and those of Test C are equivalent, wherein Test C utilized five times more silane when compared to Test A. Cores obtained from Test B show equivalent tensile strengths to those of Test C at later intervals, although less silane was

utilized.

## EXAMPLE 2

### 5 Pre-Treatment With Silane Solutions vs. Silane in the Binder

This example compares the tensile strength of test cores obtained utilizing the processes of this invention with test cores obtained where additional silane was added to the binder solution.

Test cores were made from reclaimed sand as treated below.

10 Control-2 - The reclaimed sand was untreated.

Control-3 - The reclaimed sand was untreated, but 0.02 weight percent of a 40% solution in water of gamma-aminopropyl triethoxysilane, based on the weight of sand, was added to the binder solution.

Test-D - The reclaimed sand was treated at 25°C with 0.02 weight percent, based on the weight of sand, of a 40% silane solution as described in Control 3, diluted with 0.18 weight percent water, based on  
15 the weight of sand.

In treating these different lots of treated reclaimed sand, the silane solution was directly added to sand at 25°C in a Hobart Kitchen Aid Mixer and mixed for about 1 minute.

The sand used in this example was reclaimed from foundry molds and cores that had been used in casting molten iron or steel. These molds and cores were made using as the binder an ALPHASET 9000®  
20 potassium alkali phenol-formaldehyde resin binder as described in Example 1. These resins were cured with triacetin as the curing agent.

In reclaiming the sand, the used molds and cores were shaken within a vibratory mill as described in Example 1 to remove loose particulates and break up any remaining lumps.

To prepare the test cores, from 1500-2500 gms of sand for each test and control were added to a  
25 Hobart Kitchen Aid Mixer. This sand was brought to a temperature of about 25°C, the silane solution was applied, and about 1.5% by weight of an aqueous solution of the resin, based on weight of sand, was added to the sand and mixed for about 1 minute. This resin binder was as described in Example 1 for making the test cores.

Then, 25% by weight of triacetin curing agent, based on the weight of resin solution, was added to the  
30 Hobart Kitchen Aid Mixer and mixed for another 40 seconds. After mixing, the sand was used immediately to form Standard American Foundrymen's Society's 25.4 mm (1 inch) dogbone tensile briquettes on a Dietert 696 corebox.

The cores were cured at room temperature and broken at the following time intervals, 1 hour, 2 hours, 4 hours, and 24 hours after the mix was made. Tensile strength measurements were made using a Dietert  
35 Universal Sand Strength Machine 400-1, fitted with a Tensile Core Strength Accessory 610-N. From 3 to 4 tensile strength measurements were determined and averaged for each test and control. The average tensile strength values for Control-2, Control-3, and Test D, are given in Table 2.

TABLE 2

| Total Silane Solution |              |             |          |                    |          |          |               |      |       |
|-----------------------|--------------|-------------|----------|--------------------|----------|----------|---------------|------|-------|
| % Based on Sand Wt.   |              |             |          |                    |          |          |               |      |       |
| Test                  | Silane (wt%) | Water (wt%) | Hrs:1    | Tensiles kPa (psi) |          |          | % Improvement |      |       |
|                       |              |             |          | 2                  | 4        | 24       | Hrs:1         | 2    | 4     |
| Control-2             | 0            | 0           | 69 (10)  | 83 (12)            | 152 (22) | 172 (25) | --            | --   | --    |
| Control-3             | 0.02         | ---         | 103 (15) | 179 (26)           | 220 (32) | 207 (30) | 50%           | 100% | 95.4% |
| Test-D                | 0.02         | 0.18        | 207 (30) | 255 (37)           | 303 (44) | 324 (47) | 200%          | 208% | 100%  |
|                       |              |             |          |                    |          |          |               |      | 88%   |

The data in Table 2 show that the addition of extra silane to the resin binder is less effective than using silane solutions to pretreat the reclaimed sand in accordance with the present invention. The improvement in tensile strength for Test D is initially 4 times that obtained in Control-3 and generally shows twice the improvement in tensile strength over a 24-hour period.

**EXAMPLE 3****Treatment With Silane Solution vs. Silane Added to the Binder With Different Reclaimed Sands**

5 Example 3 serves to provide another comparison of the tensile strength of test cores obtained utilizing the present invention with test cores obtained where additional silane was added to the binder solution.

Test cores were made from reclaimed sand as treated below.

10 Test E - The reclaimed sand at 25°C was treated with 0.02 weight percent, based on the weight of sand, of a 40% solution in water of gamma-aminopropyl triethoxysilane diluted with 0.18 weight percent water, based on the weight of sand, by mixing in a Hobart Kitchen Aid Mixer for about 1 minute.

Control-4 - The reclaimed sand was untreated.

Control-5 - The reclaimed sand was untreated, but 0.02 weight percent, based on the weight of reclaimed sand, of a 40% gamma-aminopropyl triethoxysilane solution in water was added to the binder solution.

15 The reclaimed sand used in this example was obtained from foundry cores or molds that had been used in casting steel or iron. The sand came from a different foundry than those of Example 2 yet the cured binder in these molds and cores was derived from an ALPHASET 9000 potassium alkali phenolic resin as described in Example 1.

20 This binder was cured using triacetin and contained about 0.4% by weight gamma-aminopropyl triethoxy silane, based on the weight of the binder solution. In reclaiming the sand, the used molds and cores were shaken to remove any loose particles and break up any lumps with a vibratory mill. These sand granules were thermally treated at about 750°C in an indirectly heated rotary kiln type thermal reclaimer manufactured by Coreco, Inc., Germantown, Wi., to obtain granules having a size of about 0.26 mm (an AFS screen distribution of about 57.1 Grain Fineness).

25 To prepare the test cores, from 1500 - 2500 gms of sand were added to a Hobart Kitchen Aid Mixer for each test and control. This sand was brought to a temperature of about 25°C in the Hobart Kitchen Aid mixer, the silane solution was applied, and about 1.5% by weight of a phenol-formaldehyde resin solution, as described in Example 1, was added and mixed for about 1 minute. The amount of resin solution was based on the weight of sand.

30 Then about 25% by weight of triacetin as the curing agent, based on the weight of resin solution, was added and mixed for another 40 seconds in the Hobart Kitchen Aid mixer.

After mixing, the sand was used immediately to form Standard American Foundrymen's Society's 25.4 mm (1 inch) dogbone tensile briquettes in a Dietert 696 corebox. The cores were cured at room temperature and broken at intervals of 1 hour, 2 hours, 4 hours and 24 hours, after the mix was made.

35 Tensile strengths were measured using a Dietert Universal Sand Strength Machine 400-1, fitted with a Tensile Core Strength Accessory 610-N. From about 3 to 4 tensile strength measurements were made and averaged for each test and control. The average tensile strength values are given for Controls 4 and 5 and Test E in Table 3. The tensile strength of Test D is also reported in Table 3 for comparison purposes.

TABLE 3

| Test      | Total Silane Solution<br>% Based on Sand Wt. |                | Tensiles kPa (psi) |          | % Improvement<br>In Tensile Strength |           |       |       |
|-----------|----------------------------------------------|----------------|--------------------|----------|--------------------------------------|-----------|-------|-------|
|           | Silane<br>(wt%)                              | Water<br>(wt%) | Hrs:1              | 2        | 4                                    | 24        | Hrs:1 | 2     |
|           |                                              |                |                    |          |                                      |           |       |       |
| Control-4 | ---                                          | ---            | 138 (20)           | 193 (28) | 255 (37)                             | 310 (45)  | --    | --    |
| Control-5 | 0.02                                         | ---            | 255 (37)           | 372 (54) | 531 (77)                             | 620 (90)  | 85%   | 92.8% |
| Test-E    | 0.02                                         | 0.18           | 296 (43)           | 420 (61) | 613 (89)                             | 861 (125) | 115%  | 117%  |
|           |                                              |                |                    |          |                                      |           |       | 108%  |
|           |                                              |                |                    |          |                                      |           |       | 140%  |
|           |                                              |                |                    |          |                                      |           |       | 177%  |

The data in Table 3 show that the use of the silane solution provides superior results over the use of additional silane in the binder solution. It is clear that the tensile strengths for molds made from reclaimed sand are dependent on the treatments applied to such sands when comparing the tensile strengths reported in Table 2 and Table 3.

Example 4Aqueous/Organic Silane Solutions

5 This example demonstrates the superior tensile strengths of test cores obtained where the reclaimed sand is treated with aqueous/organic solution of silane.

Test cores were made from reclaimed sand as treated below.

Control-6 - The reclaimed sand was untreated.

10 Test-F - The reclaimed sand at 25°C was treated with 0.04 weight percent, based on the weight of sand, of a 40% gamma aminopropyl triethoxy silane solution in water diluted with 0.16 weight percent water, based on the weight of sand.

Test G - The reclaimed sand at 25°C was treated with 0.04 weight percent, based on the weight of sand, of a 40% gamma aminopropyl triethoxy silane solution in water diluted with 0.16 weight percent methanol, based on the weight of sand.

15 In treating the reclaimed sand, the silane solution was directly added to reclaimed sand at 25°C in a Hobart Kitchen Aid Mixer and mixed for about one minute. The reclaimed sand used in this example was as described in Example 3.

To prepare the test cores, from 1500 to 2500 gms of sand were added to a Hobart Kitchen Aid Mixer for each test and control. Following any silane treatment of the reclaimed sand, about 1.5% by weight resin solution, based on the weight of sand, was added to the reclaimed sand in the Hobart Kitchen Aid Mixer and mixed for about one minute. The resin used was as described in Example 1.

Subsequently, about 25% by weight of triacetin, based on the weight of binder solution, was added and mixed for about 40 seconds.

After mixing, the sand was immediately used to form the tensile briquettes as described in Example 1.  
25 The cores were cured at room temperature and broken at intervals of 1 hour, 2 hours, 4 hours and 24 hours, after the mix was made. Tensile measurements were made as reported in Example 1. The average values for the tensile strength data for Control 6 and Tests F and G, are given in Table 4.

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TABLE 4

| Total Silane Solution<br>% Based on Sand Wt. |       | Tensiles kPa (psi) |          | In Tensile Strength |          | % Improvement |                     |
|----------------------------------------------|-------|--------------------|----------|---------------------|----------|---------------|---------------------|
| Silane                                       | Water |                    |          |                     |          |               |                     |
| (wt%)                                        | (wt%) | Hrs:1              | 2        | 4                   | 24       | Hrs:1         | 2 4 24              |
| Test                                         |       |                    |          |                     |          |               |                     |
| Control-6                                    | ---   | ---                | 138 (20) | 193 (28)            | 255 (37) | 310 (45)      | -- -- --            |
|                                              |       |                    | Water    |                     |          |               |                     |
| Test-F                                       | 0.04  | 0.16               | 469 (68) | 537 (78)            | 744(108) | 944 (137)     | 240% 178% 186% 204% |
|                                              |       |                    | Methanol |                     |          |               |                     |
| Test-G                                       | 0.04  | 0.16               | 358 (52) | 365 (53)            | 586 (85) | 779 (113)     | 160% 89% 129% 151%  |

The data in Table 4 demonstrate that superior tensile strengths are obtained with silane solutions in water and in organic solvents.

**EXAMPLE 5****Aqueous Silane Solutions vs. Water Alone**

5 This example shows that pretreatment of mechanically reclaimed sand with aqueous silane solutions provides improved tensile strengths over the addition of water alone, although the addition of water has been found to improve tensile strengths significantly.

Test cores were made from reclaimed sand as treated below.

10 Test-H - The reclaimed sand at 25°C was treated with 0.12 weight percent, based on the weight of sand, of an aqueous silane solution of 40% gamma-aminopropyltriethoxy silane diluted with 0.2 weight percent water, based on the weight of sand.

Control-7 - The reclaimed sand was not treated.

Control-8 - The reclaimed sand was treated with 0.2% weight percent of water, based on the weight of sand.

15 In treating the sand, the silane solution or water was added directly to the sand at 25°C in a Hobart Kitchen Aid Mixer and mixed for 1 minute.

20 The sand used in this example was obtained from foundry molds and cores that had been used in casting iron or steel. The sand was different from that used in Examples 1-4. In forming these molds and cores, the binder solution utilized comprised an ALPHASET 9000® potassium alkali phenol formaldehyde binder solution as described in Example 1. This binder solution had a Brookfield viscosity in the range of 100-150 cps, as determined utilizing a Model RVF Brookfield Viscometer with a No. 1 spindle at 20 r.p.m. at 25°C, at a solids content of 53% to 58%. This binder solution included about 0.4% by weight, based on the weight of said binder solution, of the silane, gamma-aminopropyltriethoxy silane, and it was cured with triacetin curing agent.

25 The foundry molds or cores were dismantled after use in a casting process by the shakeout of any loose sand and breaking up of lumps utilizing a dry attrition unit produced by Redford Carver Foundry Products, Sherwood, Oregon. Sand having an AFS screen distribution of 48.7 Grain Fineness and an LOI of 0.80 was obtained.

30 To prepare the test cores, from 1500-2500 gms of sand were added to a Hobart Kitchen Aid Mixer for each test and control. The sand was brought to a temperature of about 25°C, the silane solution was applied, and about 1.5% by weight of an aqueous solution of a potassium alkali phenol-formaldehyde resin, as used to make the test cores of Example 1 and as described in Example 1, was added and mixed for about 1 minute. The weight percent of resin solution was based on the weight of sand. Then, about 25% by weight triacetin, based on the weight of resin solution, was added and mixed for about 40 seconds.

35 After mixing, the sand was immediately used to form tensile briquettes by the methods described in Example 1. The cores were cured at room temperature and broken at intervals of 1 hr., 2 hr., 4 hr. and 24 hr., after the mix was made. Tensile measurements were made as reported in Example 1.

From 3 to 4 tensile strength measurements were obtained and averaged for each test and control. These average results are reported in Table 5 with the percent improvement in tensile strengths obtained.

TABLE 5

| Total Silane Solution<br>% Based on Sand Wt. |                 |                |                    |          |                     |          |       |               |     |
|----------------------------------------------|-----------------|----------------|--------------------|----------|---------------------|----------|-------|---------------|-----|
| Test                                         | Silane<br>(wt%) | Water<br>(wt%) | Tensiles kpa (psi) |          | In Tensile Strength |          |       | % Improvement |     |
|                                              |                 |                | Hrs:1              | 2        | 4                   | 24       | Hrs:1 | 2             | 4   |
| Control-7                                    | ---             | ---            | 117 (17)           | 138 (20) | 193 (28)            | 220 (32) | --    | --            | --  |
| Control-8                                    | ---             | 0.2            | 207 (30)           | 282 (41) | 379 (55)            | 379 (55) | 76%   | 105%          | 96% |
| Test-H                                       | 0.12            | 0.2            | 276 (40)           | 317 (46) | 379 (55)            | 413 (60) | 135%  | 130%          | 96% |

The data in Table 5 show that an improvement in tensile strength can be obtained even with the simple addition of water. The data in Table 5 also show that the combination of water and silane, i.e., an aqueous solution of silane, provides better results than water alone.

**EXAMPLE 6****The Effectiveness of Different Silane Solutions**

5 This example demonstrates the effectiveness of different silanes in different solvents. More particularly, a ureidosilane, an aminosilane, and a glycidoxy silane were used in methanol and water to compare the improvement in tensile strengths of the test cores obtained.

Test cores were made from reclaimed sand as treated below.

Control-9 - The reclaimed sand was untreated.

10 Test-I - The reclaimed sand at 25 °C was treated with 0.036 weight percent, based on the weight of sand, of a silane solution diluted with 0.084% by weight methanol, based on the weight of sand. The silane solution was a 50% ureidopropyl triethoxy silane solution in methanol.

Test-J - The reclaimed sand was treated at 25 °C with 0.036 weight percent, based on the weight of sand, of a silane solution diluted with 0.084% by weight water, based on the weight of sand. The silane solution was 50% ureidopropyl triethoxysilane in water.

15 Test-K - The reclaimed sand at 25 °C was treated with 0.036 weight percent, based on the weight of sand, of a 40% gamma-aminopropyl triethoxysilane solution in water, diluted with 0.084% by weight water, based on the weight of sand.

20 Test-L - The reclaimed sand at 25 °C was treated with 0.036 weight percent, based on the weight of sand, of gamma-glycidoxypropyl triethoxysilane at 98% concentration, diluted with 0.084% by weight methanol, based on the weight of sand.

Test-M - The reclaimed sand at 25 °C was treated with 0.036 weight percent, based on the weight of sand, of a gamma-glycidoxypropyl triethoxysilane at 98% concentration, diluted with 0.084 weight percent water, based on the weight of sand.

25 The sand used in this example was obtained from the same source and treated in the same way as the sand used in Example 5. The sand had the same particle screen distribution as the sand of Example 5 also.

30 To prepare the test cores, from 1500-2500 gms of reclaimed sand for each test and control were transferred to a Hobart mixer. The sand was brought to 25 °C, the silane solution (if used) was applied as described above, and then the silane-treated sand was mixed with a binder solution and curing agent as described in Example 1. After mixing in the curing agent, 1-inch dogbone tensile briquettes were prepared and analyzed as described in Example 1. The average of 3-4 measured values of tensile strength for Tests I-M and Control-9 are reported below in Table 6.

TABLE 6

| Total Silane Solution<br>% Based on Sand Wt. |                       | Tensiles kPa (psi) |          | % Improvement<br>In Tensile Strength |          |
|----------------------------------------------|-----------------------|--------------------|----------|--------------------------------------|----------|
| Test                                         | Silane Water<br>(wt%) | Hrs:1              | 2        | 4                                    | 24       |
| Control-9                                    | ---                   | 117 (17)           | 138 (20) | 193 (28)                             | 220 (32) |
| Ureidosilane Methanol                        |                       |                    |          |                                      |          |
| Test-I                                       | 0.036% 0.084%         | 158 (23)           | 207 (30) | 310 (45)                             | 345 (50) |
| Ureidosilane Water                           |                       |                    |          |                                      |          |
| Test-J                                       | 0.036% 0.084%         | 172 (25)           | 282 (41) | 345 (50)                             | 379 (55) |
| Amino Silane Water                           |                       |                    |          |                                      |          |
| Test-K                                       | 0.036% 0.084%         | 207 (30)           | 276 (40) | 413 (60)                             | 379 (55) |
| Glycidoxy " Methanol                         |                       |                    |          |                                      |          |
| Test-L                                       | 0.036% 0.084%         | 152 (22)           | 207 (30) | 227 (33)                             | 241 (35) |
| Glycidoxy " Water                            |                       |                    |          |                                      |          |
| Test-M                                       | .036% .084%           | 241 (35)           | 310 (45) | 379 (55)                             | 462 (67) |

The results in Table 6 indicate that improvements in tensile properties can be obtained from different types of silanes including gamma-glycidoxy-propyl triethoxy silane, gamma-aminopropyl triethoxy silane and gamma-ureidopropyl triethoxy silane. In addition, these examples also show that both organic and aqueous solutions of silane provide improved tensile strengths, with aqueous solutions being preferred.

EXAMPLE 7

Comparison of Pre-Treatment, Post-Treatment and Simultaneous Treatment of Reclaimed Sand with Silane Solutions

In this example, the tensile strength of test cores obtained from sand that was treated with an aqueous silane solution prior to the addition of binder, subsequent to the addition of binder, and simultaneously with the addition of binder and curative agent, are compared for the purpose of demonstrating the independence of the timing of the treatment steps.

The reclaimed sand used in this example was as described in Example 5. The binder solutions and curing agents used in this example were as described in Example 1.

Test cores were made from reclaimed sand treated as follows.

Control-10 - The reclaimed sand was untreated.

Tests N, O and P - The reclaimed sand at 25°C was treated with 0.08% by weight, based on the weight of sand, of a 40% silane solution as described in Example 1, diluted with 0.12% by weight water, based on the weight of reclaimed sand.

For Test-M, from 1500-2500 gms of reclaimed sand were added to a Hobart Kitchen Aid Mixer and the sand was brought to a temperature of about 25°C. The silane solution was then added directly to the sand and mixed for about one minute. Then, 1.5% by weight resin binder solution, based on the weight of the sand, was added and mixed for one minute. Then, about 25% by weight of triacetin, based on the weight of binder solution, was added and mixed for another 40 seconds. After mixing, the sand was used immediately to form 25.4 mm (1") dogbone tensile briquettes and tensile strength measurements were made as described in Example 1.

For Test N, from 1500 - 2500 gms of reclaimed sand were added to a Hobart Kitchen Aid Mixer and the sand was brought to a temperature of about 25°C, after which about 1.5 weight percent binder solution, based on the weight of the sand, was added to the sand simultaneously with the silane solution and the contents mixed for one minute. Following this, about 25% by weight of triacetin, based on the weight of resin solution, was added and mixed for 40 seconds. After mixing, the sand was used to prepare the 25.4 mm (1-inch) dogbone tensile briquettes and tensile strength measurements were made as described in Example 1.

For Test O, from 1500 - 2500 gms of reclaimed sand at 25°C were first mixed with a curable binder solution in an amount of about 1.5% by weight, based on the weight of sand. After one minute of agitation, about 25% by weight triacetin, based on the weight of the resin binder solution, was added and mixed for another 40 seconds. Prior to preparing the test cores, a quantity of silane solution was added to this raw batch formulation and mixed for about 1 minute, following which 25.4 mm (1-inch) dogbone tensile briquettes were made and tensile strengths determined as described in Example 1.

The average values of 3 - 4 tensile measurements for the test cores of Tests N, O and P and Control-10 are reported in Table 7.

TABLE 7

| Total Silane Solution<br>% Based on Sand Wt. |       | Tensiles kPa (psi) |          | In Tensile Strength |          | % Improvement |     |
|----------------------------------------------|-------|--------------------|----------|---------------------|----------|---------------|-----|
| Silane                                       | Water | Hrs:1              |          | Hrs:1               |          | Hrs:1         |     |
| (wt%)                                        | (wt%) | 2                  | 4        | 24                  | 24       | 2             | 4   |
| Test                                         |       |                    |          |                     |          |               |     |
| Control-10                                   | ---   | 158 (23)           | 241 (35) | 241 (35)            | 193 (28) | --            | --  |
| Test-N                                       | 0.08% | 220 (32)           | 310 (45) | 379 (55)            | 379 (55) | 39%           | 57% |
| Test-O                                       | 0.08% | 262 (38)           | 379 (55) | 413 (60)            | 413 (60) | 65%           | 71% |
| Test-P                                       | 0.08% | 255 (37)           | 310 (45) | 345 (50)            | 345 (50) | 60%           | 42% |
|                                              |       |                    |          |                     |          | 28%           | 78% |

The data in Table 7 show that the method of treating sand with a silane solution is independent of the timing of such treatment.

**EXAMPLE 8****Silane Solution Treatment with a Continuous Mixer**

5 Example 8 demonstrates the effectiveness of a continuous mixer in improving the tensile strengths of foundry cores and molds obtained from reclaimed sands. The reclaimed sand used herein was as described in Example 5. Before use it was brought to 25 ° C.

10 In Controls 11 through 14 and Tests Q and R, a continuous mixer was used, calibrated to deliver 125 pounds per minute of sand from an overhead bin. The resin utilized was as described in Example 1 and was fed in through a port by a pump close to the inlet chute at a rate of about 1.5% by weight, based on the weight of sand introduced. Ester hardener, gamma-butyrolactone, was introduced at a rate of about 25% by weight, based on the weight of resin solution, by means of a pump through another port.

15 Where there is no silane treatment of the reclaimed sand, the resin and hardener were fed as described above and the sand was recovered from the discharge chute. The dogbone tensile briquettes were made from this sand, then tested as described in Example 1.

20 For Tests Q and R, a silane solution was metered by a third pump into the same port delivering the resin solution, to provide a 40% gamma-aminopropyl triethoxy silane solution in water in the amount indicated under the heading "silane", diluted with the amount of water indicated under the heading "water" in Table 8. In Control 13, water was metered through the third pump and introduced into the resin inlet port, to provide 0.2 wt % water, based on the weight of sand. In Control 14, concentrated gamma-aminopropyl-triethoxy silane was metered through the third pump and introduced into the inlet port, to provide about 0.038% by weight silane, based on the weight of sand.

Upon recovering the sand discharged from the mixer in each test and control, 25.4 mm (1") dogbone tensile briquettes were made and tested as described in Example 5.

25 Average values for the 3 to 4 tensile strength measurements made for each test and control are reported in Table 8.

TABLE 8

| Total Silane Solution<br>% Based on Sand Wt. |        | Tensiles kPa (psi) |          | % Improvement<br>In Tensile Strength |      |
|----------------------------------------------|--------|--------------------|----------|--------------------------------------|------|
| Silane                                       | Water  | Hrs:1              |          | Hrs:1                                |      |
| (wt%)                                        | (wt%)  | 2                  | 4        | 2                                    | 4    |
| Test                                         |        | 24                 |          | 24                                   |      |
| Control-11                                   | ---    | 214 (31)           | 220 (32) | ---                                  | ---  |
| Control-12                                   | ---    | 200 (29)           | 248 (36) | ---                                  | ---  |
| Control-13                                   | ---    | 227 (33)           | 276 (40) | 13%                                  | 11%  |
| Control-14                                   | 0.038* | 510 (74)           | 579 (84) | 155%                                 | 133% |
| Test-Q                                       | 0.066  | 469 (68)           | 531 (77) | ---                                  | ---  |
| Test-R                                       | 0.098  | 551 (80)           | 599 (87) | ---                                  | ---  |

\* 98% concentration

The data in Table 8 show that treatment of reclaimed sand with aqueous silane solutions provides significantly higher tensile strengths in test cores than treatment with water, or no treatment with either water or a silane solution. It is noted that treatment with concentrated silane provides test cores with lower tensile strengths than those treated with an equivalent amount of silane in solution, even where a continuous mixer is utilized.

**EXAMPLE 9****Sand Blends of Mechanically Reclaimed Sand and Pristine Sand**

5 This example demonstrates the usefulness of this invention for blends of pristine sand and reclaimed sand. The new, pristine sand used was a washed and dried silica sand of 0.29 mm (52) Grain Fineness, as determined by the methods described in American Foundrymen's Society "Mold and Core Test Handbook", pp. 4.2-4.5. The sand mix consisted of 80 parts by weight of reclaimed sand as described in Example 5 and 20 parts of by weight of the pristine sand. A control sample was prepared using the same  
10 ratios of pristine sand to reclaimed sand, but was not treated with silane solution.

Test cores were prepared from reclaimed sand/pristine sand mixtures treated as follows:

Control 15 - The sand mix was untreated.

15 Test S - The sand mix at 25°C was pretreated with a 40% silane solution in an amount of about 0.068% by weight diluted with 0.132% by weight water, based on the weight of sand. The silane was gamma-aminopropyl triethoxysilane. This pretreatment comprised adding the sand mix to a Hobart Kitchen Aid Mixer at 25°C, followed by the silane solution and mixing the sand and silane solution for about one minute.

To prepare test cores for Control-15 and Test R, 1500 - 2500 gms of sand was brought to a temperature of about 25°C in a Hobart Kitchen Aid Mixer, then the silane solution was applied (if used).  
20 Following any silane pretreatment, 1.5% by weight resin solution, based on the weight of sand, was added. The resin binder solution used was as described in Example 1. The sand and resin were mixed for about one minute. Then about 25% by weight triacetin, based on the weight of resin solution, was added and mixed for another 40 seconds.

25 After mixing, 25.4 mm (1-inch) dogbone tensile briquettes were made and the tensile strengths tested as reported in Example 1. The average tensile strength values of 3-4 measurements for each control and test are reported below in Table 9.

TABLE 9

| Total Silane Solution |        |        |          |                    |          |          |       |               |     |
|-----------------------|--------|--------|----------|--------------------|----------|----------|-------|---------------|-----|
| % Based on Sand Wt.   |        |        |          |                    |          |          |       |               |     |
| Silane                |        | Water  |          | Tensiles kPa (psi) |          |          |       | % Improvement |     |
| Test                  | (wt%)  | (wt%)  | Hrs:1    | 2                  | 4        | 24       | Hrs:1 | 2             | 4   |
| Control-15            | ---    | ---    | 172 (25) | 262 (38)           | 310 (45) | 407 (59) | ---   | ---           | --- |
| Test-S                | 0.068% | 0.132% | 310 (45) | 393 (57)           | 496 (72) | 606 (88) | 80%   | 50%           | 60% |
|                       |        |        |          |                    |          |          |       |               | 49% |

The data in Table 9 show that foundry molds and cores obtained from mixtures of reclaimed sand and new, pristine sand show improvements in tensile strength when treated by the processes of this invention.

**EXAMPLE 10****Aqueous Silane Treatment with Vapor Cure Methods**

5        Example 10 serves to illustrate that treatment of reclaimed sand with silane solutions, as provided by this invention, is useful when preparing foundry cores and molds by a vapor cure method.

Test cores were made with reclaimed sand pretreated as follows.

Control-16 - The reclaimed sand was untreated.

10        Test-T - The reclaimed sand at 25°C was pretreated with 0.2% of a silane solution diluted with 0.3% by weight water, based on the weight of sand. The silane solution was 40% gamma-aminopropyl triethoxysilane in water. The reclaimed sand at 25°C was pretreated with the silane solution by mixing within a Hobart Kitchen Aid Mixer for about 1 minute.

15        The test cores for Control-16 and Test-T were prepared by providing 1500 - 2500 gms. of reclaimed sand in a Hobart Kitchen Aid Mixer. The reclaimed sand was as used in Example 5. Prior to silane pretreatment, the sand was brought to a temperature of about 25°C, and the silane solution, if used, was applied and then about 1.5% by weight of the resin solution described in Example 1, based on the weight of sand, was added and mixed for two minutes. After mixing, the sand was blown with a Redford Carver Core Blower (a tradename of Dependable Foundry Equipment Company, Sherwood, Oregon), using 550 kPa (80 psig) air pressure for about one-half second, into a three cavity corebox for producing the Standard  
20        American Foundrymen's Society's 25.4 mm (1") dogbone tensile briquettes.

After blowing in the sand, the corebox was gassed for 5 seconds with methyl formate vapors generated in a Cerjet gas generator (a tradename of Dependable Foundry Equipment, Sherwood, Oregon). After gassing, the cores were ejected and then allowed to stand under ambient conditions.

25        The tensile strength measurements were made using a Dietert Universal Sand Strength Machine 400-1, fitted with a Tensile Core Strength Accessory 610-N as described in Example 1. Between 3 to 4 measurements of tensile strength were made for each test and control and the average values were determined. The average tensile strength values of 3-4 measurements for each control and test are given in Table 10 below.

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TABLE 10

| Test       | Total Silane Solution<br>% Based on Sand Wt. |                | Tensiles kPa (psi) |          | % Improvement<br>In Tensile Strength |          |                 |
|------------|----------------------------------------------|----------------|--------------------|----------|--------------------------------------|----------|-----------------|
|            | Silane<br>(wt%)                              | Water<br>(wt%) | Hrs:1              | 2        | 24                                   | Hrs:1    | 2 4 24          |
|            |                                              |                |                    |          |                                      |          |                 |
| Control-16 | ---                                          | ---            | 158 (23)           | 165 (24) | 179 (26)                             | 186 (27) | -- -- --        |
| Test-T     | 0.2%                                         | 0.3%           | 220 (32)           | 227 (32) | 269 (39)                             | 324 (47) | 39% 37% 50% 74% |

The results in Table 10 show that the pretreatment of reclaimed sand with silane solutions results in tensile improvements in test cores made by a vapor cure method. Therefore, this invention can be applied in the processes described in U.S. Patent No. 4,468,359.

**EXAMPLE 11****Binder Solutions Without Silane**

5 This example illustrates the effectiveness of this invention in improving the tensile strength of test cores obtained from resin binder solutions which do not contain silane.

10 The sand used in this example was the same as the reclaimed sand described in Example 5. The resin binder solution was a potassium alkali phenol formaldehyde resin having a Brookfield viscosity of 100 cps, as measured in Example 1, at a 53.4% by weight solids content, as determined by the method described in Example 1. The phenol:formaldehyde molar ratio for the resin was 1:1.7 and the KOH:phenol molar ratio for the resin was 0.83 to 1. The resin binder solution did not contain silane.

Test cores were prepared from reclaimed sand treated as follows.

Control-18 - The reclaimed sand was untreated.

15 Test-U - The reclaimed sand at 25 °C was pretreated with a 40% silane solution in water in an amount of 0.1 weight percent, based on the weight of sand, diluted with 0.2 weight percent water, based on the weight of sand. The silane was gamma-aminopropyl triethoxysilane.

This pretreatment comprised adding the sand mix to a Hobart Kitchen Aid Mixer, bringing it to 25 °C, adding the silane solution and mixing the sand and silane solution for about one minute.

20 The test cores were prepared and tested as in Example 1. The average value for 3-4 measurements of the tensile strength for the cores produced are reported in Table 11.

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TABLE 11

| Test       | Total Silane Solution<br>% Based on Sand Wt. |                | Tensiles kPa (psi) |          | % Improvement<br>In Tensile Strength |                     |
|------------|----------------------------------------------|----------------|--------------------|----------|--------------------------------------|---------------------|
|            | Silane<br>(wt%)                              | Water<br>(wt%) | Hrs:1              | 2        | 24                                   | Hrs:1<br>2 4 24     |
|            |                                              |                |                    |          |                                      |                     |
| Control-17 | ---                                          | ---            | 103 (15)           | 138 (20) | 172 (25)                             | 310 (45)            |
| Test-U     | 0.1%                                         | 0.2%           | 227 (33)           | 345 (50) | 413 (60)                             | 620 (90)            |
|            |                                              |                |                    |          |                                      | 120% 150% 140% 100% |

The data in Table 11 illustrates that improvements are obtained in tensile strength with the process of this invention where the resin binder solution does not contain silane.

It is contemplated the present invention can be used in forming sand aggregates for non-foundry applications either as molds or cores or some other shaped structure.



## Claims

1. A method for forming a resin bonded article from reclaimed sand that has previously been used by forming it into a resin-bonded shape with a binder of an ester cured alkaline phenolic resin comprising:
  - (i) treating the reclaimed sand by placing it in contact with from 0.05% to 1.0% by weight based on the weight of the reclaimed sand of a silane solution having a concentration of silane of from 1% to 100% based on the weight of the silane solution, wherein:
    - (a) the solvent in said solution is selected from polar organic solvents, aqueous liquids and mixtures thereof; and
    - (b) the silane has the formula: (1)  $R'Si(OR)_3$  where  $R'$  is a  $C_2-C_6$  alkylene group bonded to an amino, epoxy, mercapto, glycidoxy, ureido, hydroxy, hydroxy- $C_1-C_6$  alkylamino, amino- $C_1-C_6$  alkylamino,  $C_2-C_6$  alkenyl or  $C_2-C_6$  alkenylcarboxy group and  $R$  may be the same or different and are selected from  $C_1-C_6$  alkyl and  $C_1-C_6$  alkoxy-substituted  $C_1-C_6$  alkyl groups; or
    - (2)  $H_2N(CH_2)_nSi(OR^1)_{3-x}(R^2)_x$  where  $n$  equals a whole number of from 2 to 4,  $R^1$  is a  $C_1-C_4$  alkyl group and  $R^2$  is a  $C_1-C_4$  alkyl or phenyl group and  $x$  is 0 or 1; or
    - (3)  $H_2N-(CH_2)_m-NH-(CH_2)_nSi(OR^1)_{3-x}R^2_x$  where  $n$  is a whole number of from 2 to 4,  $m$  is 2 or 3,  $R^1$  is a  $C_1-C_4$  alkyl group,  $R^2$  is a  $C_1-C_4$  alkyl group and  $x$  is 0 or 1; and
  - (ii) mixing the treated reclaimed sand with a resin.
2. A method according to claim 1, wherein said silane solution has a concentration of silane in the range from 1% to 90% by weight, and the amount of residual silane solution on said silane-treated sand is from 0.0025% to 0.9% by weight of said sand.
3. A method according to claim 1 or claim 2, wherein the surfaces of the granules of reclaimed sand are characterized by the presence of an alkaline silicate.
4. A method according to claims 1 to 3, wherein the granules of reclaimed sand are characterized by residual alkalinity.
5. A method according to claims 1 to 4, wherein the surfaces of the granules of reclaimed sand have thereon residual material from previous bonding with a binder of an alkaline phenolic resin.
6. A method according to claim 5, wherein the surfaces of the granules of reclaimed sand have thereon a water-removable residue from previous bonding with a binder of an ester cured alkaline phenolic resin.
7. A method according to claims 2 to 6, wherein said silane contacting step comprises applying to the reclaimed sand a silane solution having a silane concentration of from 5% to 90% by weight based on said solution.
8. A method according to claims 1 to 7, wherein said silane solution has a silane concentration in the range from 10% to 80% by weight.
9. A method according to claims 1 to 8, wherein curing of the cured binder from which said reclaimed sand is obtained is effected by the use of a curing agent selected from the group consisting of lactones, carboxylic acid esters, organic carbonates and mixtures thereof.
10. A method as claimed in claims 1 to 9, wherein the silane is selected from
  - gamma-aminopropyl trimethoxysilane,
  - 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.



11. A method as claimed in claims 1 to 10, wherein the silane is selected from  
N-(gamma-aminopropyl)-gamma-aminopropyl triethoxysilane,  
N-(gamma-aminopropyl)-gamma-aminopropyl trimethoxysilane,  
N-(beta-aminoethyl)-gamma-aminopropyl dimethoxymethylsilane,  
N-methyl-gamma-aminopropyl triethoxysilane,  
N-ethyl-gamma-aminopropyl trimethoxysilane,  
N-methyl-gamma-aminopropyl dimethoxymethylsilane,  
N-(N-methyl-beta-aminoethyl)-gamma-aminopropyl dimethoxymethylsilane, and  
N-(gamma-aminopropyl)-N-methyl-gamma-aminopropyl dimethoxymethylsilane.
12. A method according to claims 1 to 11, wherein, prior to contact with said silane solution, said reclaimed sand is formed into a mixture with pristine sand, the amount of said pristine sand being within the range from about 1% to about 80% by weight of the total weight of the mixture of pristine sand and said reclaimed sand.
13. A method according to claim 12, wherein the mixture of pristine sand and reclaimed sand comprises from 10 to 50% by weight of pristine sand.
14. A method according to claim 12 or claim 13, wherein said mixture is placed in contact with said silane solution by applying to said mixture a silane solution having a silane concentration of from 10% to 50% by weight based on said solution.
15. A method as claimed in claims 1 to 14, wherein the article formed from the reclaimed sand is a foundry shape formed by mixing the treated reclaimed sand or the mixture of pristine sand and treated reclaimed sand with a binding amount of an alkaline phenolic resin binder and effecting curing of said binder.
16. A method according to claim 15, wherein said resin binder comprises an aqueous solution of a phenolic resin that can cure at room temperature with a curing agent having ester functionality.
17. A method according to claim 16, wherein said curing agent is selected from lactones, carboxylic acid esters, organic carbonates and mixtures thereof.
18. A method according to claims 15 to 17, wherein said phenolic resin comprises the reaction product of a phenol and formaldehyde at a phenol:formaldehyde ratio within the range from 1:1 to 1:3, condensed with an alkali comprising potassium hydroxide, sodium hydroxide, lithium hydroxide and mixtures thereof.
19. A method according to claims 15 to 18, wherein said resin binder comprises an aqueous solution of an alkaline phenol formaldehyde resin wherein  
(i) the solids content is in the range from 40% to 75%,  
(ii) the weight average molecular weight (Mw) is from 500 to 2500,  
(iii) the formaldehyde:phenol molar ratio is from 1:1 to 3:1,  
(iv) the alkali:phenol molar ratio is from 0.2:1 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 C<sub>1</sub>-C<sub>3</sub> alkyl formates, organic esters formed from C<sub>1</sub> to C<sub>10</sub> carboxylic acids and mono- and polyhydric alcohols, and low molecular weight lactones including butyrolactone, propiolactone, caprolactone and mixtures thereof.
20. A method as claimed in claim 19, wherein  
(i) the solids content is in the range from 50% to 75%,  
(ii) the weight average molecular weight (Mw) is from 700 to 2000,  
(iii) the formaldehyde:phenol molar ratio is from 1.2:1 to 2.6:1,  
(iv) the alkali:phenol molar ratio is from 0.6:1 to 1.2:1,



21. A method as claimed in claims 1 to 20, wherein the reclaimed sand is obtained from foundry molds or cores.

22. A composition for mixing with a resin in the process of claims 1 to 21 comprising granular foundry sand that has been formed into a resin-bonded shape with an ester cured alkaline phenolic resin binder, then separated from said shape into free-flowing granules, said granules having applied thereto from 0.05% to 1.0% by weight based on the weight of the reclaimed sand of a silane solution having a concentration of silane of from 1% to 100% based on the weight of the silane solution wherein

(a) the solvent in said solution is selected from polar organic solvents, aqueous liquids and mixtures thereof; and

(b) the silane has the formula: (1)  $R'Si(OR)_3$  where  $R'$  is a  $C_2-C_6$  alkylene group bonded to an amino, epoxy, mercapto, glycidoxy, ureido, hydroxy, hydroxy- $C_1-C_6$  alkylamino, amino- $C_1-C_6$  alkylamino,  $C_2-C_6$  alkenyl or  $C_2-C_6$  alkenylcarboxy group and  $R$  may be the same or different and are selected from  $C_1-C_6$  alkyl and  $C_1-C_6$  alkoxy-substituted  $C_1-C_6$  alkyl groups; or

(2)  $H_2N(CH_2)_nSi(OR^1)_{3-x}(R^2)_x$  where  $n$  equals a whole number of from 2 to 4,  $R^1$  is a  $C_1-C_4$  alkyl group and  $R^2$  is a  $C_1-C_4$  alkyl or phenyl group and  $x$  is 0 or 1; or

(3)  $H_2N-(CH_2)_m-NH-(CH_2)_nSi(OR^1)_{3-x}R^2_x$  where  $n$  is a whole number of from 2 to 4,  $m$  is 2 or 3,  $R^1$  is a  $C_1-C_4$  alkyl group,  $R^2$  is a  $C_1-C_4$  alkyl group and  $x$  is 0 or 1.

23. A composition comprising granular foundry sand in accordance with claim 22, wherein the silane solution has a concentration of from about 5% to about 90% by weight of said silane.

24. A composition as claimed in claim 22 or claim 23, wherein the silane is selected from gamma-aminopropyl trimethoxysilane, 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.

25. A composition as claimed in claim 22 or claim 23, wherein the silane is selected from N-(gamma-aminopropyl)-gamma-aminopropyl triethoxysilane, N-(gamma-aminopropyl)-gamma-aminopropyl trimethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyl dimethoxymethylsilane, N-methyl-gamma-aminopropyl triethoxysilane, N-ethyl-gamma-aminopropyl trimethoxysilane, N-methyl-gamma-aminopropyl dimethoxymethylsilane, N-(N-methyl-beta-aminoethyl)-gamma-aminopropyl dimethoxymethylsilane, and N-(gamma-aminopropyl)-N-methyl-gamma-aminopropyl dimethoxymethylsilane.

26. A composition as claimed in claims 22 to 25 further comprising up to 80% pristine sand.

27. A composition according to claims 22 to 26, wherein said used sand granules are derived from sand that has been formed into a resin-bonded shape with an alkaline phenolic resin binder, then separated for reuse into free-flowing granules having residual alkalinity.

28. A composition according to claims 22 to 27, wherein said silane solution has a concentration of from 10% to 50% by weight of said silane.

29. A raw batch formulation for use in producing foundry molds or cores from sand of which at least 20% by weight is reclaimed from dismantled foundry moulds or cores following use in a metal casting process comprising

(i) the composition of claims 22 to 28 or a mixture of the composition and pristine sand; and

(ii) a solution of a curable binder, comprising an aqueous solution of a phenolic resin which aqueous solution is curable at ambient temperature with a curing agent selected from the group consisting of



lactones, carboxylic acid esters, organic carbonates and mixtures thereof.

### Patentansprüche

- 5 1. Verfahren zur Formung eines harzgebundenen Artikels aus wiedergewonnenem Sand, welcher zuvor verwendet wurde, indem er in eine harzgebundene Form mit einem Bindemittel eines estergehärteten alkalischen Phenolharzes geformt wird, welches folgendes umfaßt:
  - (i) Behandeln des wiedergewonnenen Sandes, indem dieser mit 0,05 bis 1,0 Gew.-%, bezogen auf das Gewicht des wiedergewonnenen Sandes, einer Silanlösung mit einer Silankonzentration von 1 %
    - 10 bis 100 %, bezogen auf das Gewicht der Silanlösung, in Kontakt gebracht wird, worin:
      - (a) das Lösungsmittel in der Lösung aus polaren organischen Lösungsmitteln, wäßrigen Flüssigkeiten und Mischungen hiervon gewählt ist; und
      - (b) das Silan die Formel: (1)  $R'Si(OR)_3$ , worin  $R'$  eine  $C_2$ - $C_6$ -Alkylengruppe ist, die mit einer Amino-, Epoxy-, Mercapto-, Glycidox-, Ureido-, Hydroxy-, Hydroxy- $C_1$ - $C_6$ -alkylamino-, Amino- $C_1$ - $C_6$ -alkylamino-,  $C_2$ - $C_6$ -Alkenyl- oder  $C_2$ - $C_6$ -Alkenylcarboxy-Gruppe verbunden ist, und die  $R$ -Reste gleich oder unterschiedlich sein können und aus  $C_1$ - $C_6$ -Alkyl- und  $C_1$ - $C_6$ -Alkoxy-substituierten  $C_1$ - $C_6$ -Alkylgruppen gewählt sind; oder
      - 15 (2)  $H_2N(CH_2)_nSi(OR')_{3-x}(R^2)_x$ , worin  $n$  eine ganze Zahl von 2 bis 4 ist,  $R'$  eine  $C_1$ - $C_4$ -Alkylgruppe und  $R^2$  eine  $C_1$ - $C_4$ -Alkyl- oder Phenylgruppe bedeuten und  $x$  gleich 0 oder 1 ist; oder
      - 20 (3)  $H_2N-(CH_2)_m-NH-(CH_2)_nSi(OR')_{3-x}R^2_x$  hat, worin  $n$  eine ganze Zahl von 2 bis 4,  $m$  gleich 2 oder 3,  $R'$  eine  $C_1$ - $C_4$ -Alkylgruppe,  $R^2$  eine  $C_1$ - $C_4$ -Alkylgruppe und  $x$  gleich 0 oder 1 sind; und
    - (ii) Mischen des behandelten wiedergewonnenen Sandes mit einem Harz.
  2. Verfahren nach Anspruch 1, wobei die Silanlösung eine Silankonzentration im Bereich von 1 bis 90 Gew.-% hat und die Restmenge der Silanlösung bei dem mit Silan behandelten Sand zwischen 0,0025 und 0,9 Gew.-%, bezogen auf den Sand, liegt.
  3. Verfahren nach Anspruch 1 oder Anspruch 2, wobei die Oberflächen der Körnchen des wiedergewonnenen Sandes durch das Vorhandensein eines alkalischen Silikats gekennzeichnet sind.
  - 30 4. Verfahren nach den Ansprüchen 1 bis 3, wobei die Körnchen des wiedergewonnenen Sandes durch eine End- bzw. Residualalkalität gekennzeichnet sind.
  5. Verfahren nach den Ansprüchen 1 bis 4, wobei die Oberflächen der Körnchen des wiedergewonnenen Sandes Restmaterial aus dem vorhergehenden Binden mit einem Bindemittel eines alkalischen Phenolharzes aufweisen.
  - 35 6. Verfahren nach Anspruch 5, wobei die Oberflächen der Körnchen des wiedergewonnenen Sandes einen mit Wasser entfernbaren Rückstand von dem vorhergehenden Binden mit einem Bindemittel eines estergehärteten alkalischen Phenolharzes aufweisen.
  - 40 7. Verfahren nach den Ansprüchen 2 bis 6, wobei der Kontaktbehandlungsschritt mit Silanlösung das Anwenden einer Silanlösung auf den wiedergewonnenen Sand umfaßt, wobei diese eine Silankonzentration von 5 bis 90 Gew.-%, bezogen auf die Lösung, hat.
  - 45 8. Verfahren nach den Ansprüchen 1 bis 7, wobei die Silanlösung eine Silankonzentration im Bereich von 10 bis 80 Gew.-% hat.
  9. Verfahren nach den Ansprüchen 1 bis 8, wobei das Härten des gehärteten Bindemittels, aus dem man den wiedergewonnenen Sand erhält, durch die Verwendung eines Härtungsmittels bewirkt wird, das aus einer aus Lactonen, Carbonsäureestern, organischen Carbonaten und Mischungen hiervon bestehenden Gruppe gewählt ist.
  - 50 10. Verfahren nach den Ansprüchen 1 bis 9, wobei das Silan gewählt ist aus
    - gamma-Aminopropyltrimethoxysilan,
    - gamma-Aminobutyltriethoxysilan,
    - gamma-Aminopentyltriethoxysilan,
    - gamma-Aminopropyldiethoxymethylsilan,
  - 55



gamma-Aminopropyldiethoxyethylsilan,  
gamma-Aminopropyldiethoxyphenylsilan,  
delta-Aminobutyldiethoxyphenylsilan,  
delta-Aminobutyldiethoxymethylsilan und  
delta-Aminobutyldiethoxyethylsilan.

11. Verfahren nach den Ansprüchen 1 bis 10, wobei das Silan aus

N-(gamma-Aminopropyl)-gamma-aminopropyltriethoxysilan,  
N-(gamma-Aminopropyl)-gamma-aminopropyltrimethoxysilan,  
N-(beta-Aminoethyl)-gamma-aminopropyldimethoxymethylsilan,  
N-Methyl-gamma-aminopropyltriethoxysilan,  
N-Ethyl-gamma-aminopropyltrimethoxysilan,  
N-Methyl-gamma-aminopropyldimethoxymethylsilan,  
N-(N-Methyl-beta-aminoethyl)-gamma-aminopropyldimethoxymethylsilan und  
N-(gamma-Aminopropyl)-N-methyl-gamma-aminopropyldimethoxymethylsilan  
gewählt ist.

12. Verfahren nach den Ansprüchen 1 bis 11, wobei vor dem Kontakt mit der Silanlösung aus dem wiedergewonnenen Sand eine Mischung mit ursprünglichem Sand gebildet wird, wobei die Menge des ursprünglichen Sandes im Bereich zwischen circa 1 Gew.-% bis circa 80 Gew.-%, bezogen auf das Gesamtgewicht der Mischung des ursprünglichen Sandes und des wiedergewonnenen Sandes, liegt.

13. Verfahren nach Anspruch 12, wobei die Mischung des ursprünglichen Sandes und des wiedergewonnenen Sandes 10 bis 50 Gew.-% des ursprünglichen Sandes beinhaltet.

14. Verfahren nach Anspruch 12 oder Anspruch 13, wobei die Mischung mit der Silanlösung in Kontakt gebracht wird, indem man auf die Mischung eine Silanlösung mit einer Silankonzentration von 10 bis 50 Gew.-%, bezogen auf die Lösung, anwendet.

15. Verfahren nach den Ansprüchen 1 bis 14, wobei der aus dem wiedergewonnenen Sand geformte Artikel eine Gießform ist, die durch Mischen des behandelten wiedergewonnenen Sandes oder der Mischung des ursprünglichen Sandes und des behandelten wiedergewonnenen Sandes mit einer Bindemenge eines alkalischen Phenolharz-Bindemittels und durch Härten des Bindemittels gebildet wird.

16. Verfahren nach Anspruch 15, wobei das Harz-Bindemittel eine wäßrige Lösung aus einem Phenolharz enthält, das sich bei Raumtemperatur mit einem Härtungsmittel mit Esterfunktionalität aushärten kann.

17. Verfahren nach Anspruch 16, wobei das Härtungsmittel aus Lactonen, Carbonsäureestern, organischen Carbonaten und Mischungen davon gewählt wird.

18. Verfahren nach den Ansprüchen 15 bis 17, bei dem das Phenolharz das Reaktionsprodukt eines Phenols und Formaldehyds bei einem Phenol : Formaldehyd-Verhältnis von 1 : 1 bis 1 : 3 beinhaltet, kondensiert mit einem Alkali, das Kaliumhydroxid, Natriumhydroxid, Lithiumhydroxid und Mischungen hiervon enthält.

19. Verfahren nach den Ansprüchen 15 bis 18, bei dem das Harzbindemittel eine wäßrige Lösung eines alkalischen Phenol-Formaldehydharzes umfaßt, wobei

- (i) der Feststoffgehalt im Bereich zwischen 40 % und 75 % liegt,
- (ii) das gewichtsmittlere Molekulargewicht (Mw) 500 bis 2500 beträgt,
- (iii) das Formaldehyd : Phenol-Molverhältnis 1 : 1 bis 3 : 1 beträgt,
- (iv) das Alkali : Phenol-Molverhältnis 0,2 : 1 bis 1,2 : 1 beträgt,
- (v) das verwendete Alkali Natriumhydroxid, Kaliumhydroxid und deren Mischungen enthält,
- (vi) die Lösung gegebenenfalls ein Silan in einer Menge von 0,05 bis 3,0 Gew.-%, bezogen auf die wäßrige Harzlösung, enthält, und
- (vii) das Harz bei Raumtemperatur härter ist mit C<sub>1</sub>-C<sub>3</sub>-Alkylformiaten, organischen Estern, die aus C<sub>1</sub>- bis C<sub>10</sub>-Carbonsäuren und ein- und mehrwertigen Alkoholen gebildet werden, und Lactonen mit niedrigerem Molekulargewicht, die Butyrolacton, Propiolacton, Caprolacton und Mischungen hiervon einschließen.



20. Verfahren nach Anspruch 19, wobei
- (i) der Feststoffgehalt im Bereich von 50 % bis 75 % liegt,
  - (ii) das gewichtsmittlere Molekulargewicht (Mw) 700 bis 2000 beträgt,
  - (iii) das Formaldehyd : Phenol-Molverhältnis 1,2 : 1 bis 2,6 : 1 beträgt,
  - (iv) das Alkali : Phenol-Molverhältnis 0,6 : 1 bis 1,2 : 1 beträgt.
21. Verfahren nach den Ansprüchen 1 bis 20, wobei man den wiedergewonnenen Sand aus Gießereiformen oder -kernen erhält.
22. Zusammensetzung zum Vermischen mit einem Harz bei dem Verfahren der Ansprüche 1 bis 21, umfassend granulären Gießereisand, der zu einer harzgebundenen Form mit einem estergehärteten alkalischen Phenol-Harzbindemittel geformt wird, dann von dieser Form zu freifließenden Körnchen abgetrennt wird, wobei auf die Körnchen 0,05 bis 1,0 Gew.-%, bezogen auf das Gewicht des wiedergewonnenen Sandes, einer Silanlösung mit einer Silankonzentration von 1 % bis 100 %, bezogen auf das Gewicht der Silanlösung, angewandt wurden, wobei
- (a) das Lösungsmittel in der Lösung aus polaren organischen Lösungsmitteln, wäßrigen Flüssigkeiten und Mischungen hiervon gewählt ist; und
  - (b) das Silan die Formel: (1)  $R'Si(OR)_3$ , worin  $R'$  eine  $C_2$ - $C_6$ -Alkylengruppe ist, welche mit einer Amino-, Epoxy-, Mercapto-, Glycidoxy-, Ureido-, Hydroxy-, Hydroxy- $C_1$ - $C_6$ -alkylamino-, Amino- $C_1$ - $C_6$ -alkylamino-,  $C_2$ - $C_6$ -Alkenyl- oder  $C_2$ - $C_6$ -Alkenylcarboxygruppe verbunden ist, und die  $R$ -Reste gleich oder unterschiedlich sein können und aus  $C_1$ - $C_6$ -Alkyl- und  $C_1$ - $C_6$ -Alkoxy-substituierten  $C_1$ - $C_6$ -Alkylgruppen gewählt sind; oder
  - (2)  $H_2N(CH_2)_nSi(OR')_{3-x}(R^2)_x$ , worin  $n$  eine ganze Zahl von 2 bis 4,  $R'$  eine  $C_1$ - $C_4$ -Alkylgruppe und  $R^2$  eine  $C_1$ - $C_4$ -Alkyl- oder Phenylgruppe bedeuten und  $x$  gleich 0 oder 1 ist; oder
  - (3)  $H_2N-(CH_2)_m-NH-(CH_2)_nSi(OR')_{3-x}R^2_x$  hat, worin  $n$  eine ganze Zahl von 2 bis 4,  $m$  gleich 2 oder 3,  $R'$  eine  $C_1$ - $C_4$ -Alkylgruppe,  $R^2$  eine  $C_1$ - $C_4$ -Alkylgruppe und  $x$  gleich 0 oder 1 sind.
23. Zusammensetzung, umfassend granulären Gießereisand gemäß Anspruch 22, wobei die Silanlösung eine Konzentration von circa 5 Gew.-% bis circa 90 Gew.-%, bezogen auf das Silan, hat.
24. Zusammensetzung nach Anspruch 22 oder Anspruch 23, wobei das Silan aus
- gamma-Aminopropyltrimethoxysilan,
  - gamma-Aminobutyltriethoxysilan,
  - gamma-Aminopentyltriethoxysilan,
  - gamma-Aminopropyldiethoxymethylsilan,
  - gamma-Aminopropyldiethoxyethylsilan,
  - gamma-Aminopropyldiethoxyphenylsilan,
  - delta-Aminobutyldiethoxyphenylsilan,
  - delta-Aminobutyldiethoxymethylsilan und
  - delta-Aminobutyldiethoxyethylsilan gewählt ist.
25. Zusammensetzung nach Anspruch 22 oder Anspruch 23, wobei das Silan aus
- N-(gamma-Aminopropyl)-gamma-aminopropyltriethoxysilan,
  - N-(gamma-Aminopropyl)-gamma-aminopropyltrimethoxysilan,
  - N-(beta-Aminoethyl)-gamma-aminopropyldimethoxymethylsilan,
  - N-Methyl-gamma-aminopropyltriethoxysilan,
  - N-Ethyl-gamma-aminopropyltriethoxysilan,
  - N-Methyl-gamma-aminopropyldimethoxymethylsilan,
  - N-(N-Methyl-beta-aminoethyl)-gamma-aminopropyldimethoxymethylsilan und
  - N-(gamma-Aminopropyl)-N-methyl-gamma-aminopropyldimethoxymethylsilan gewählt ist.
26. Zusammensetzung nach den Ansprüchen 22 bis 25, welche ferner bis zu 80 % ursprünglichen Sand enthält.
27. Zusammensetzung nach den Ansprüchen 22 bis 26, wobei die verwendeten Sandkörnchen von Sand gewonnen werden, welcher zu einer harzgebundenen Form mit einem alkalischen Phenol-Harzbindemittel geformt wurde und dann zur Wiederverwendung zu freifließenden Körnchen mit einer Endalkalität getrennt wurde.



28. Zusammensetzung nach den Ansprüchen 22 bis 27, wobei die Silanlösung eine Konzentration von 10 bis 50 Gew.-%, bezogen auf das Silan, hat.

29. Rohchargen-Zubereitungsform zur Verwendung bei der Herstellung von Gießereiformen oder -kernen aus Sand, von dem mindestens 20 Gew.-% aus abgebauten Gießereiformen oder -kernen nach der Verwendung in einem Metallgußverfahren rückgewonnen wurde, umfassend:

(i) die Zusammensetzung der Ansprüche 22 bis 28 oder eine Mischung der Zusammensetzung und des ursprünglichen Sandes;

und

(ii) eine Lösung eines härtbaren Bindemittels, umfassend eine wäßrige Lösung eines Phenolharzes, wobei diese wäßrige Lösung bei Raumtemperatur mit einem Härtungsmittel härtbar ist, das aus der aus Lactonen, Carbonsäureestern, organischen Carbonaten und Mischungen hiervon bestehenden Gruppe gewählt wird.

## 15 Revendications

1. Un procédé pour former un article lié à l'aide d'une résine à partir d'un sable de récupération précédemment utilisé en lui donnant une forme liée à l'aide d'une résine au moyen d'un liant de résine phénolique alcaline durcissable en présence d'un ester, consistant à :

(i) traiter le sable de récupération en le mettant en contact avec 0,05 % à 1,0 % en poids, sur la base du sable de récupération, d'une solution de silane ayant une concentration de silane d'1 % à 100 % sur la base du poids de la solution de silane, dans laquelle :

(a) le solvant de cette solution est sélectionné parmi des solvants organiques polaires, des liquides aqueux et des mélanges de ceux-ci ; et

(b) le silane a la formule suivante : (1)  $R'Si(OR)_3$ , où  $R'$  est un groupe alcoylidène  $C_2-C_6$  lié à un groupe amino, époxy, mercapto, glycidoxy, uréido, hydroxy, hydroxy-alkylamino  $C_1-C_6$ , amino-alkylamino  $C_1-C_6$ , alcényle  $C_2-C_6$  ou alcéno-carboxy  $C_2-C_6$  et  $R$  peuvent être les mêmes ou différents et sont sélectionnés parmi les groupes alcoyle  $C_1-C_6$  et alcoyle  $C_1-C_6$  substitué par un alcoolate  $C_1-C_6$  ; ou

(2)  $H_2N(CH_2)_nSi(OR')_{3-x}(R^2)_x$ , où  $n$  est égal à un nombre entier compris entre 2 et 4,  $R'$  est un groupe alcoyle  $C_1-C_4$  et  $R^2$  est un groupe alcoyle ou phényle  $C_1-C_4$  et  $x$  est égal à 0 ou 1 ; ou

(3)  $H_2N-(CH_2)_m-NH-(CH_2)_nSi(OR')_{3-x}R^2_x$ , où  $n$  est un nombre entier compris entre 2 et 4,  $m$  est égal à 2 ou 3,  $R'$  est un groupe alcoyle  $C_1-C_4$ ,  $R^2$  est un groupe alcoyle  $C_1-C_4$  et  $x$  est égal à 0 ou 1 ; et

(ii) mélanger le sable de récupération traité avec une résine.

2. Un procédé selon la revendication 1, dans lequel la solution de silane a une concentration de silane comprise entre 1 % et 90 % en poids, et la quantité de solution de silane résiduelle sur ce sable traité au silane est comprise entre 0,0025 % et 0,98 % en poids du sable.

3. Un procédé selon la revendication 1 ou la revendication 2, dans lequel les surfaces des granules de sable de récupération sont caractérisées par la présence d'un silicate alcalin.

4. Un procédé selon les revendications 1 à 3, dans lequel les granules de sable de récupération sont caractérisées par une alcalinité résiduelle.

5. Un procédé selon les revendications 1 à 4, dans lequel les surfaces des granules de sable de récupération portent une matière résiduelle provenant d'une précédente liaison à l'aide d'un liant à base de résine phénolique alcaline.

6. Un procédé selon la revendication 5, dans lequel les surfaces des granules de sable de récupération portent un résidu qui peut être enlevé à l'eau provenant d'une précédente liaison à l'aide d'un liant à base de résine alcaline durcissable en présence d'un ester.

7. Un procédé selon les revendications 2 à 6, dans lequel cette étape de mise en contact avec un silane consiste à

appliquer au sable de récupération une solution de silane ayant une concentration de silane de 5 % à 90 % en poids sur la base de cette solution.



8. Un procédé selon les revendications 1 à 7, dans lequel la solution de silane a une concentration de silane comprise entre 10 % et 80 % en poids.
- 5 9. Un procédé selon les revendications 1 à 8, dans lequel le durcissement du liant durci à partir duquel est obtenu le sable de récupération est effectué au moyen d'un agent de durcissement sélectionné dans le groupe constitué de lactones, d'esters d'acides carboxyliques, de carbonates organiques et de mélanges de ceux-ci.
- 10 10. Un procédé selon les revendications 1 à 9, dans lequel le silane est sélectionné parmi  
 le triméthoxysilane gamma-aminopropylique,  
 le triéthoxysilane gamma-aminobutylique,  
 le triéthoxysilane gamma-aminopentyle,  
 le diéthoxyméthylsilane gamma-aminopropylique,  
 le diéthoxyéthylsilane gamma-aminopropylique,  
 15 le diéthoxyphénylsilane gamma-aminopropylique,  
 le diéthoxyphénylsilane delta-aminobutylique,  
 le diéthoxyméthylsilane delta-aminobutylique, et  
 le diéthoxyéthylsilane delta-aminobutylique.
- 20 11. Un procédé selon les revendications 1 à 10, dans lequel le silane est sélectionné parmi :  
 le triéthoxysilane N-(gamma-aminopropyl)-gamma-aminopropylique,  
 le triméthoxysilane N-(gamma-aminopropyl)-gamma-aminopropylique,  
 le diméthoxyméthylsilane N-(bêta-aminoéthyl)-gamma-aminopropylique,  
 le triéthoxysilane N-méthyl-gamma-aminopropylique,  
 25 le triméthoxysilane N-éthyl-gamma-aminopropylique,  
 le diméthoxyméthylsilane N-méthyl-gamma-aminopropylique,  
 le diméthoxyméthylsilane N-(N-méthyl-bêta-aminoéthyl)-gamma-aminopropylique, et  
 le diméthoxyméthylsilane N-(gamma-aminopropyl)-N-méthyl-gamma-aminopropylique.
- 30 12. Un procédé selon les revendications 1 à 11, dans lequel, avant d'être mis en contact avec la solution de silane, le sable de récupération est formé en un mélange avec du sable primitif, la quantité de sable primitif étant comprise entre environ 1 % et environ 80 % en poids du poids total du mélange de sable primitif et de sable de récupération.
- 35 13. Un procédé selon la revendication 12, dans lequel le mélange de sable primitif et de sable de récupération comprend 10 % à 50 % en poids de sable primitif.
14. Un procédé selon la revendication 12 ou la revendication 13, dans lequel le mélange est mis en contact avec la solution de silane par l'application à ce mélange d'une solution de silane ayant une  
 40 concentration de silane de 10 % à 50 % en poids sur la base de la solution.
15. Un procédé selon les revendications 1 à 14, dans lequel l'article formé à partir du sable de récupération est une forme de fonderie obtenue en mélangeant le sable de récupération traité ou le mélange de sable primitif et de sable de récupération traité à une quantité de liaison d'un liant de  
 45 résine phénolique alcaline et en procédant au durcissement du liant.
16. Un procédé selon la revendication 15, dans lequel le liant de résine comprend une solution aqueuse d'une résine phénolique qui peut durcir à température ambiante à l'aide d'un agent de durcissement fonctionnel en présence d'un ester.
- 50 17. Un procédé selon la revendication 16, dans lequel l'agent de durcissement est sélectionné parmi les lactones, les esters d'acides carboxyliques, les carbonates organiques et des mélanges de ceux-ci.
18. Un procédé selon les revendications 15 à 17, dans lequel la résine phénolique comprend le produit de  
 55 réaction d'un phénol et d'un formaldéhyde à un rapport phénol/formaldéhyde compris entre 1 à 1 et 1 à 3, condensé avec un alcali comprenant l'hydrate de potassium, l'hydrate de sodium, l'hydrate de lithium et des mélanges de ceux-ci.



19. Un procédé selon les revendications 15 à 16, dans lequel le liant de résine comprend une solution aqueuse d'une résine à base de phénol-formaldéhyde alcaline dans laquelle

- (i) la teneur en solides est comprise entre 40 % et 75 %,
  - (ii) le poids moléculaire moyen en poids (PM) est compris entre 500 et 2 500,
  - (iii) le rapport molaire formaldéhyde/phénol est compris entre 1 à 1 et 3 à 1,
  - (iv) le rapport molaire alcali/phénol est compris entre 0,2 à 1 et 1,2 à 1,
  - (v) l'alcali utilisé comprend l'hydrate de sodium, l'hydrate de potassium et leurs mélanges,
  - (vi) la solution peut contenir optionnellement un silane à raison de 0,05 % à 3,0 % en poids de la solution aqueuse de résine, et
  - (vii) la résine est durcissable à température ambiante à l'aide de formates d'alcoyle  $C_1-C_3$ , d'esters organiques formés à partir d'acides carboxyliques  $C_1$  à  $C_{10}$  et de mono- et polyalcools, et de lactones de faible poids moléculaire comprenant la butyrolactone, la propiolactone, la caprolactone, et des mélanges de ceux-ci.

20. Un procédé selon la revendication 19, dans lequel

- (i) la teneur en solides est comprise entre 50 % et 75 %,
  - (ii) le poids moléculaire moyen en poids (MP) est compris entre 700 et 2000,
  - (iii) le rapport molaire formaldéhyde/phénol est compris entre 1,2 à 1 et 2,6 à 1,
  - (iv) le rapport molaire alcali/phénol est compris entre 0,6 à 1 et 1,2 à 1.

21. Un procédé selon les revendications 1 à 20, dans lequel le sable de récupération provient de moules ou noyaux de fonderie.

22. Une composition à mélanger à une résine dans le procédé des revendications 1 à 21, comprenant du sable de fonderie granulaire qui a été façonné en une forme liée à l'aide d'une résine au moyen d'un liant de résine phénolique alcaline durcissable en présence d'un ester, puis séparé de cette forme en granules à écoulement libre, ces granules étant soumis à l'application de 0,05 % à 1,0 % en poids, sur la base du poids du sable de récupération, d'une solution de silane ayant une concentration de silane d'1 % à 100 % sur la base du poids de la solution de silane dans laquelle :

- (a) le solvant de cette solution est sélectionné parmi des solvants organiques polaires, des liquides aqueux et des mélanges de ceux-ci ; et
- (b) le silane a la formule suivante : (1)  $R'Si(OR)_3$ , où  $R'$  est un groupe alcoylidène  $C_2-C_6$  lié à un groupe amino, époxy, mercapto, glycidoxy, uréido, hydroxy, hydroxy-alkylamino  $C_1-C_6$ , amino-alkylamino  $C_1-C_6$ , alcényle  $C_2-C_6$  ou alcéno-carboxyle  $C_2-C_6$  et  $R$  peuvent être les mêmes ou différents et sont sélectionnés parmi les groupes alcoyle  $C_1-C_6$  et alcoyle  $C_1-C_6$  substitué par un alcoolate  $C_1-C_6$  ; ou
- (2)  $H_2N(CH_2)_nSi(OR')_{3-x}(R^2)_x$ , où  $n$  est un nombre entier de 2 à 4,  $R'$  est un groupe alcoyle  $C_1-C_4$  et  $R^2$  est un groupe alcoyle ou phényle  $C_1-C_4$  et  $x$  est égal à 0 ou 1 ; ou
- (3)  $H_2N-(CH_2)_m-NH-(CH_2)_nSi(OR')_{3-x}R^2_x$ , où  $n$  est un nombre entier de 2 à 4,  $m$  est égal à 2 ou 3,  $R'$  est un groupe alcoyle  $C_1-C_4$ ,  $R^2$  est un groupe alcoyle  $C_1-C_4$  et  $x$  est égal à 0 ou 1.

23. Une composition comprenant un sable granulaire de fonderie selon la revendication 22, dans laquelle la solution de silane a une concentration d'environ 5 % à environ 90 % en poids du silane.

24. Une composition selon la revendication 22 ou la revendication 23, dans laquelle le silane est choisi parmi :

- le triméthoxysilane gamma-aminopropylique,
- le triéthoxysilane gamma-aminobutylique,
- le triéthoxysilane gamma-aminopentylique,
- le diéthoxyméthylsilane gamma-aminopropylique,
- le diéthoxyéthylsilane gamma-aminopropylique,
- le diéthoxyphénylsilane gamma-aminopropylique,
- le diéthoxyphénylsilane delta-aminobutylique,
- le diéthoxyméthylsilane delta-aminobutylique, et
- le diéthoxyéthylsilane delta-aminobutylique.

25. Une composition selon la revendication 22 ou la revendication 23, dans laquelle le silane est sélectionné parmi :



le triéthoxysilane N-(gamma-aminopropyl)-gamma-aminopropylque,  
le triméthoxysilane N-(gamma-aminopropyl)-gamma-aminopropylque,  
le diméthoxyméthylsilane N-bêta-aminoéthyl)-gamma-aminopropylque,  
le triéthoxysilane N-méthyl-gamma-aminopropylque,  
5 le triméthoxysilane N-éthyl-gamma-aminopropylque,  
le diméthoxyméthylsilane N-méthyl-gamma-aminopropylque,  
le diméthoxyméthylsilane N-(N-méthyl-bêta-aminoéthyl)-gamma-aminopropylque, et  
le diméthoxyméthylsilane N-(gamma-aminopropyl)-N-méthyl-gamma-aminopropylque.

10 26. Une composition selon les revendications 22 à 25 comprenant en outre jusqu'à 80 % de sable primitif.

27. Une composition selon les revendications 22 à 26, dans laquelle les granules de sable usé proviennent  
de sable qui a été façonné en une forme liée à l'aide de résine au moyen d'une résine phénolique  
15 alcaline, puis séparé en vue d'être réutilisé en granules à écoulement libre ayant une alcalinité  
résiduelle.

28. Une composition selon les revendications 22 à 27, dans laquelle la solution de silane a une  
concentration de 10 % à 50 % en poids du silane.

20 29. Une formulation de charge brute à utiliser dans la production de moules ou noyaux de fonderie à base  
de sable dont au moins 20 % en poids sont récupérés à partir de moules ou noyaux de fonderie  
démontés après utilisation dans un processus de coulée de métal, comprenant

(i) la composition des revendications 22 à 28 ou un mélange de la composition et de sable primitif ;  
et

25 (ii) une solution d'un liant durcissable, comprenant une solution aqueuse d'une résine phénolique,  
cette solution aqueuse étant durcissable à température ambiante avec un agent de durcissement  
sélectionné dans le groupe constitué de lactones, d'esters d'acides carboxyliques, de carbonates et  
de mélanges de ceux-ci.

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