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3,403,721

TENSILE STRENGTHS OF CERTAIN SAND CORES
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ABSTRACT OF THE DISCLOSURE

Process for forming foundry cores comprising sand and an organic binder comprising a hydroxyl-containing material, an isocyanate and a silane.

This invention relates to sand cores having increased tensile strengths at high temperatures. In one aspect, this invention relates to a foundry process for making sand cores using organic core binders containing an isocyanate, which process includes the incorporation into said cores of certain silanes.

In the foundry art, cores for use in making metal castings are usually prepared from mixtures of an aggregate (e.g. sand) which has been mixed with a binding amount of a polymerizable or curable binder. Such mixtures are referred to herein as "foundry mixes." The amount of binder used is typically less than 10% by weight based on the weight of the sand, e.g. from 0.5 to 5% on the same basis. Frequently, minor amounts of other materials are also included in foundry mixes, e.g. iron oxide, ground flax fibers, and the like. The binder permits a foundry mix to be molded or shaped into the desired form, usually in a pattern box or mold, and thereafter cured to form a self-supporting structure (e.g. to form a sand core).

In recent years, the foundry art has been provided with core binders containing polyisocyanates and suitable co-reactants. See, for example, U.S. Ser. No. 447,513, filed Apr. 12, 1965, now Patent No. 3,255,500. Certain binders of this general type (i.e. containing an isocyanate) have a number of outstanding advantages. One such advantage is their ability to effectively and rapidly form cured cores at room temperature without the use of gaseous catalysts. Optionally, cores prepared with such binders can be baked to accelerate the cure.

It has now been discovered that the tensile strengths of sand cores containing such isocyanate binder compositions can be substantially increased at elevated temperatures and under high humidity conditions by the simple addition of a silane (e.g. γ -aminopropyl tri-ethoxy silane) to the foundry mix. For example, one popular commercially-available isocyanate binder composition contains both an aromatic polyisocyanate and an oil-modified alkyd resin. When this binder composition was used in the manner recommended by its manufacturer and a small amount of an amino silane was simply added to the foundry mix, sand cores prepared from this foundry mix had tensile strengths at 300° F. which were 40% above the strengths obtained by exactly the same procedure, omitting only the silane.

Thus, in the ordinary practice of this invention, sand cores (or sand molds) for use in making metal castings will be prepared by the following steps:

(1) Forming a foundry mix containing sand as the predominant ingredient and an isocyanate core binder, which binder usually includes a hydroxyl-containing co-reactant and one or more catalysts;

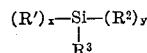
(2) Simultaneously or separately mixing a silane with the sand of step 1;

(3) Introducing the resulting foundry mix of step 2 into a mold or pattern to thereby shape said mix; and

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(4) Thereafter curing the shaped foundry mix to thereby form a sand core (or sand mold).

The silanes used in this invention have the formula:



wherein x and y are integers, x being zero (0) or one (1) and y being two (2) or preferably three (3) with the sum of x and y being three (3). R' is a hydrocarbon radical, usually a C₁-C₄ alkyl radical. R² is an alkoxy radical, usually a C₁-C₅ alkoxy radical; ethoxy and methoxy radicals are preferred. R³ is a radical selected from the group of aminoalkyl, hydroxyalkyl, sulfhydryl-alkyl, carboxyalkyl and N(aminoalkyl)aminoalkyl radicals. The alkyl portion(s) of R³ will usually contain 1-8 carbon atoms, preferably 1-3 carbon atoms, in each uninterrupted carbon chain (ignoring the carbon atom in the carboxyl group).

Suitable silanes include hydroxypropyl tri-methoxy silane, hydroxymethyl di-ethoxy methyl silane, aminobutyl tri-methoxy silane, N(gamma-aminopropyl)-gamma-aminopropyl tri-methoxy silane, aminobutyl dimethoxymethyl silane, carboxypropyl tri-ethoxy silane, mercaptopropyl tri-methoxy silane, gamma-aminopropyl tri-ethoxy silane, and the like. The preferred silanes are the amino and poly-amino tri-alkoxy silanes. N(beta-aminoethyl)-gamma-aminopropyl tri-methoxy silane and gamma-aminopropyl tri-ethoxy silane are the most preferred, with the latter being especially preferred.

The amount of silane included in the foundry mix will be an effective amount of up to 1% based on the weight of sand. Frequently, the amount of silane will be within the range of 0.002 to 0.1% based on the weight of sand, e.g. from 0.005 to 0.05%.

The binder compositions which can be benefited by the practice of this invention are known to the art and are those which contain a polyisocyanate, usually with a hydroxyl-containing material as a co-reactant. Such isocyanate/hydroxyl binder systems are co-reacted at or about the time of use in the presence of sand. Typically, the reactive ingredients of such binder compositions are sold, shipped, and stored in separate packages (i.e. a multiple package core binder) to avoid undesirable deterioration due to premature reaction between the components. Solvents, catalysts, various additives, and other known binders can optionally be used in conjunction with these essential ingredients, i.e. used with the polyisocyanate and its co-reactant.

Typically, cyclic and acyclic polyisocyanates containing from 2-5 isocyanate groups are employed. If desired, mixtures of polyisocyanates can be employed. Less preferably, isocyanate prepolymers formed by reacting excess polyisocyanate with a polyhydric alcohol (e.g. a prepolymer of toluene diisocyanate and ethylene glycol) can be employed. Suitable polyisocyanates include the aliphatic polyisocyanates such as hexamethylene diisocyanate; alicyclic polyisocyanates such as 4,4'-dicyclohexylmethane diisocyanate; and aromatic polyisocyanates such as 2,4- and 2,6-toluene diisocyanate, and diphenyl methane diisocyanate and the dimethyl derivative thereof. Further examples of suitable polyisocyanates are 1,5-naphthalene diisocyanate; triphenyl methane triisocyanate; xylylene diisocyanate and the methyl derivative thereof; polymethylene polyphenyl isocyanate; chlorophenylene-2,4-diisocyanate, and the like. All polyisocyanates do not serve with the same effectiveness. While the aforementioned polyisocyanates are, to a greater or lesser degree, effective in practicing the present invention, there are significant advantages associated with the use of cyclic polyisocyanates, especially the aromatic polyisocyanates, as contrasted to the aliphatic polyisocyanates. In general, aromatic polyisocyanates impart more rigidity to cores

than do the aliphatic polyisocyanates. Polymethylene polyphenyl isocyanate, diphenylmethane diisocyanate, triphenylmethane triisocyanate, and mixtures thereof are preferred because of their high degree of reactivity, desirable core forming properties, and low vapor pressure. The latter minimizes any possible toxicity problems.

The co-reactant for the polyisocyanate can be hydroxyl-containing material, a natural drying oil, an air-hardenable petroleum polymer, a synthetic drying oil such as a dicyclopentadiene copolymer or a butadiene/styrene copolymer, or the like. Mixtures of such co-reactants can be used. Co-reactants containing free or reactive hydroxyl groups are preferred.

The hydroxyl-containing material to be co-reacted with the isocyanate can be a polyhydric alcohol (e.g. pentaerythritol). However, high molecular weight hydroxyl-containing materials are preferred. Preferably, the hydroxyl-containing co-reactant will be an alkyd resin (e.g. an oil-modified alkyd resin), a hydroxyl-terminated polyester (e.g. alcoholysis products of fatty triglycerides), and polymers and copolymers containing reactive hydroxyl groups (e.g. hydroxy-alkyl acrylate copolymers). Hydroxyl-containing materials which can be hardened, at least in part, by air oxidation are particularly preferred. Thus, drying oil-modified alkyd resins, as well as various unsaturated fatty acid esters and unsaturated fatty acid modified polyesters are preferred. Oil-modified alkyd resins are the most preferred hydroxyl-containing reactants.

It is preferred to employ oil-modified alkyd resins which have been prepared by co-reacting the following three classes of ingredients:

(a) Polyhydric alcohols having at least three hydroxyl groups, e.g. glycerol, pentaerythritol, trimethylol propane and the like. Pentaerythritol is preferred. Mixtures of polyhydric alcohols can be used. While glycols can be used, better results are obtained if such glycols are used in conjunction with the polyhydric alcohols (use a mixture of ethylene glycol and pentaerythritol). Ordinarily only the polyhydric alcohols will be used.

(b) Polycarboxylic acids (or their anhydrides) such as maleic acid, fumaric acid, phthalic acid, phthalic anhydride, isophthalic acid, chlorendic acid and the like. The various phthalic acids (particularly isophthalic acid and phthalic anhydride) are preferred. Mixtures of acids can be used.

(c) Oil such as soybean oil, linseed oil, cottonseed oil, castor and dehydrated castor oils, tall oil, tung oil, fish oil and the like. Mixtures of oils can be used. Linseed oil is preferred.

The more preferred oil-modified alkyd resins will contain at least 40 weight percent oil (based on the total weight of the alkyd resin formulation). More desirably, the alkyd resins will contain at least 50 weight percent oil on the same basis (i.e. a "long oil alkyd"). It should be pointed out that oil-modified alkyd resins can also be prepared (as is known in the resin art) from fatty acids rather than the corresponding oils or glycerides. With alkyd resins, especially the oil-modified alkyd resins, the hydroxyl value should be at least 25 and preferably above 50. The upper limit of hydroxyl value is only limited by practical considerations, e.g. viscosity. For most ordinary applications, oil-modified alkyd resins having hydroxyl values of from 50-250, e.g. 60-150, are desirable.

Catalysts are optionally and desirably used in conjunction with isocyanate core binders. The catalysts which are usually employed are those which accelerate the air oxidation or hardening of the oil-modified alkyd resin, those which accelerate the reaction between the polyisocyanate and the oil-modified alkyd resin, and those which do both. The amount of catalyst employed will be a catalytic amount, with the total amount of catalyst(s) usually ranging from 0.01-20%, based on the combined weight of the polyisocyanate and oil-modified alkyd resin. More frequently, from 0.1-15%, e.g. 0.25-10% catalyst will be

used on the same basis. The choice of catalyst and the amount thereof will affect the curing rate of the system. Metal naphthenates (e.g. cobalt naphthenate) are effective catalysts for both the isocyanate/hydroxyl reaction and the air oxidation of the hydroxyl-containing alkyd resin, the latter being their primary function. Sodium perborate can also be used to promote the oxygen cross-linking of the oil-modified alkyd resin. Metal ion catalysts such as tetra(hydro-carbyl) tin catalysts are especially desired. Particularly preferred catalysts are the dibutyl tin di-hydrocarbyl catalysts. Dibutyl tin dilaurate is a very effective catalyst.

The isocyanate binder system of the present invention can optionally be used in combination with other known binder systems. Also, the foundry mixes of this invention can optionally include other ingredients such as iron oxide, ground flax fibers, wood cereal, pitch, etc.

When combining the isocyanate and its co-reactant (e.g. an oil-modified alkyd resin) with sand at or about the time a sand core is to be made, it is common to use from 5-150 parts by weight of polyisocyanate per 100 parts by weight of the coreactant. More frequently, from 5-90 parts, e.g. from 8-50 parts of polyisocyanate will be used on the same basis. With our preferred embodiment it is common to use from 10-40 parts, e.g. 10-30 parts of polyisocyanate on the same basis.

The total amount of isocyanate binder employed (i.e. the total weight of isocyanate plus co-reactant), based on the weight of sand, will be a binding amount of up to 10%. Generally, the amount of binder (on the same basis) will be from 0.5 to weight percent, e.g. 1-3 weight percent.

In mixing the silane, isocyanate, co-reactant, and catalyst with sand, it is advantageous to first mix the co-reactant (e.g. oil-modified alkyd resin or polyester) with the sand (and other optional ingredients), then add the catalyst with mixing, and finally add the polyisocyanate. The silane can be added at any point in this sequence of events. No advantages have been noted by, for example, pre-coating the sand with the silane. The resulting foundry mix will typically remain workable or plastic at room temperature for from 20-100 minutes. Other variations of this procedure are known and, under certain conditions, the catalyst can be omitted. However, catalysts are commonly and generally employed.

This mixture is then molded or shaped into the desired form, usually in a pattern box or mold, and thereafter cured to form a sand core. Depending upon the nature of the polyisocyanate, co-reactant, and catalyst, this curing will be accomplished by simply allowing the binder to react at room temperature or by baking, or a combination of both techniques.

The present invention will be further understood by reference to the following specific examples which include the best mode known to the inventors for practicing their invention. Unless otherwise indicated, all parts and percentages are by weight.

EXAMPLE I

Sand cores were prepared in the conventional dog bone shape used for determining tensile strengths. These specimens were prepared by conventional techniques from a foundry mix containing 100 parts of Lake sand, (1) 1.6 parts of a mixture containing 47% oil-modified alkyd resin, 29% air-hardenable petroleum polymer, and 24% mineral spirits; (2) one part of a solution of cobalt naphthenate and dibutyl tin dilaurate; and (3) 0.24 part diphenylmethane diisocyanate (Mondur MR). The oil-modified alkyd resin had a hydroxyl number of about 105 and was prepared from about 65% linseed oil, 14% pentaerythritol, and 21% isophthalic acid by conventional alkyd techniques. This multiple-package core binder was a commercially-available isocyanate binder (Lino-Cure, a product of Archer Daniels Midland Co.). During the preparation of this foundry mix, 0.01 part of gamma-

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aminopropyl tri-ethoxy silane was added to the foundry mix.

For purposes of comparison, the procedure was repeated exactly, with the sole exception being the omission of the silane.

The specimens prepared from both foundry mixes were cured by heating overnight at 125° F. (about 20 hours).

When the tensile strengths of these specimens were tested at 300° F. using a commercial tensile tester, the silane-containing cores had an average tensile strength of 70 p.s.i. The other specimens, without any silane, had an average tensile strength of only 50 p.s.i. The tensile strengths were determined under identical conditions and the reported values are the actual measured values extrapolated back to zero bench time.

EXAMPLE II

Two foundry mixes were prepared by repeating the procedure of Example I. Tensile specimens were prepared from both foundry mixes. The tensile specimens were cured for one hour at room temperature, then baked for 30 minutes at 300° F., and then cooled to room temperature in a desiccator. Tensile strengths were then obtained using a commercial tensile tester. The silane-containing specimens had an average tensile strength of 550 p.s.i. while the specimens without any silane had an average tensile strength of only 435 p.s.i. Again, the reported values are the actual values extrapolated back to zero bench time.

EXAMPLE III

The procedure of Example II was repeated except that the cooling step was accomplished at 100% relative humidity instead of in a desiccator. The purpose of this was to determine the effect of humidity, known to have an adverse effect on the tensile strengths of conventional isocyanate bonded sand cores.

The average tensile strengths thus obtained were 450 p.s.i. for the silane-containing specimens and 360 p.s.i. for the specimens without the silane (strengths extrapolated to zero bench time).

EXAMPLE IV

Results similar to those obtained in Examples I-III will be obtained when N(β -aminoethyl)-gamma-aminopropyl tri-methoxy silane is substituted for the gamma-aminopropyl tri-ethoxy silane of Examples I-III.

EXAMPLE V

Results similar to those obtained in Examples I-III will be obtained when a mixture of equal parts by weight of mercaptopropyl tri-methoxy silane and aminobutyl tri-methoxy silane is substituted for the gamma-aminopropyl tri-ethoxy silane of Examples I-III.

From the foregoing description and examples, it will be appreciated that a novel procedure has been developed for increasing the tensile strengths of sand cores at elevated temperatures and under conditions of high humidity, which cores have been prepared using isocyanate binder compositions. By simply adding small amounts, e.g. 0.01% of a silane of the type described herein (based on the weight of sand) to a foundry sand mix highly desirable sand cores and molds can be obtained.

A further advantage to the inventive system is that the addition of a silane (or mixture thereof) does not ad-

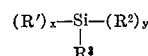
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versely effect the performance of the otherwise effective isocyanate core binders.

Although the present invention has been described with a certain degree of particularity, it will be realized that numerous minor changes and variations, falling within the spirit and scope of this invention, will become obvious to those skilled in the art. It is not intended that this invention be limited to any of the materials which have been specifically mentioned for the sake of illustration, nor by the specific proportions which have been given for the sake of illustration.

What is claimed is:

1. In a process for preparing sand cores wherein an organic binder containing an isocyanate and a suitable co-reactant for said isocyanate is mixed with sand to form a foundry mix, the foundry mix is shaped and thereafter cured to form a sand core by reacting said isocyanate and said co-reactant in the presence of said sand, the improvement which comprises including in said foundry mix a silane of the formula:



wherein x and y are integers, x being zero (0) or one (1) and y being two (2) or three (3) with the sum of x and y being three (3); wherein R' is an alkyl radical having 1 to 4 carbon atoms; wherein R² is an alkoxy radical having 1 to 5 carbon atoms; and wherein R³ is an aminoalkyl, hydroxyalkyl, sulphydrylalkyl, carboxyalkyl, or N(aminoalkyl)aminoalkyl radical having 1 to 8 carbon atoms in each of said alkyl groups.

2. The process of claim 1 wherein the amount of silane is from 0.005 to 0.05% by weight based on the weight of said sand.

3. The process of claim 2 wherein:

- (a) x is zero(0);
- (b) the alkyl portions of R³ each contain 1-3 carbon atoms;
- (c) said co-reactant comprises oil-modified alkyd resin having a hydroxyl value of at least 25; and
- (d) said isocyanate comprises aromatic isocyanate having 2-5 isocyanate groups.

4. The process of claim 3 wherein:

- (a) said isocyanate comprises polymethylene polyphenyl isocyanate, diphenylmethane diisocyanate, or triphenylmethane triisocyanate;
- (b) said alkyd resin is prepared from linseed oil, isophthalic acid and pentaerythritol and contains over 50 weight percent linseed oil based on the total weight of the alkyd resin formulation; and
- (c) said curing is accomplished at room temperature with the aid of catalyst which has been included in said foundry mix.

5. The process of claim 4 wherein said silane comprises N(β -aminoethyl)-gamma-aminopropyl tri-methoxy silane or gamma-aminopropyl tri-ethoxy silane.

References Cited

UNITED STATES PATENTS

3,246,048	4/1966	Haluska.
3,255,500	6/1966	Engel et al.

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U.S. DEPARTMENT OF COMMERCE

PATENT OFFICE

Washington, D.C. 20231

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,403,721

October 1, 1968

Janis Robins et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 25, "10-30" should read -- 15-30 --; line 31, after "0.5" insert -- 5 --. Column 5, line 1, "aminophopyl" should read -- aminopropyl --; line 63, "obatined" should read -- obtained --.

Signed and sealed this 10th day of March 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents