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INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

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(54) Title: BINDER SYSTEM FOR PRODUCING POLYURETHANE-BASED CORES AND MELTING MOULDS

(54) Bezeichnung: BINDEMITTELSYSTEM ZUR HERSTELLUNG VON KERNEN UND GIESSFORMEN AUF POLYURETHANBASIS

(57) Abstract

The present invention relates to a binder system that comprises a phenolic-resin component and a polyisocyanate component. This system is characterised in that the phenolic-resin component includes an alkoxy-modified phenolic resin, wherein less than 25 mole % of the phenolic hydroxy groups are etherified with a primary or secondary aliphatic alcohol comprising between 1 and 10 carbon atoms.

(57) Zusammenfassung

Die Erfindung betrifft ein Bindemittelsystem, umfassend eine Phenolharzkomponente und eine Polyisocyanatkomponente, gekennzeichnet dadurch, daß die Phenolharzkomponente ein alkoxy-modifiziertes Phenolharz umfaßt, wobei weniger als 25 mol-% der phenolischen Hydroxygruppen durch einen primären oder sekundären aliphatischen Alkohol mit 1 bis 10 Kohlenstoffatomen verethert sind.

ABSTRACT

This invention relates to a binder system comprising a phenolic resin component and an isocyanate component where the phenolic resin component comprises an alkoxy-modified phenolic resole resin such that less than 25 mole percent of the phenolic hydroxyl groups of the phenolic resole resin are etherified by a primary or secondary aliphatic monoalcohol.

AUSTRALIAN PATENT OFFICE

POLYURETHANE BASED BINDER SYSTEM FOR THE MANUFACTURE OF FOUNDRY CORES AND MOLDS

Field of the Invention

This invention deals with a polyurethane based binder system for the manufacture of foundry cores and molds.

Background of the Invention

The method which has come into existence for the manufacture of cores, known as the "Cold-Box-Process" or the "Ashland-Process", has achieved a top position in the foundry industry. With this method, two-component polyurethane systems are used for the bonding of sand. The first component consists of a solution of some polyols which contain at least two OH groups per molecule. The second component is a solution of some isocyanates with at least two NCO groups per molecule. The curing of the binder system follows with the help of basic catalysts. Liquid bases can be added to the binder system before the molding stage, in order to bring the two components to reaction (US-A-3,676,392). Another possibility, according to US-A-3,409,579, is to pass gaseous tertiary amines through the molding material/binder system-mixture after the shaping.

In both the above-named patents, phenolic resins are used as polyols, which are prepared through condensation of phenol with aldehydes, preferably formaldehyde, in the liquid phase, at temperatures of up to around 130 °C in the presence of divalent metal catalysts. The manufacture of such phenolic resins is described in detail in US-A-3,485,797. In addition to unsubstituted phenol, substituted phenols, especially o-cresol and p-nonyl phenol, can be used (for example, EP-A-183 782). As additional reaction components, according to EP-B-0 177 871, aliphatic monoalcohols with one to eight carbon atoms can be used in the manufacture of phenolic resins. Through lkoxylation, the binder systems should have a higher thermal stability. As solvents for the phenolic components, mixtures of high-boiling point polar solvents (for example, esters and ketones) and high boiling point aromatic hydrocarbons should mainly be used. The polyisocyanates, on the other hand, are preferably dissolved in high boiling point aromatic hydrocarbons. In European Patent application EP-A-0 177 599, formulations are described, which can do without aromatic solvents entirely, or, to a great extent, as a result of the use of fatty acid methylesters. The fatty acid methylesters are used either as stand-alone solvents or with the addition of polarity-raising solvents (phenolic-components), or, as the case may be, aromatic solvents (isocyanate components). Cores manufactured with this binder system are particularly easy to remove from the mold tooling.

In practice, however, binder systems formulated according to EP-A-0 771 599, display a serious disadvantage: So much smoke develops during the casting process, that in many foundries, they would not make it past the experimental stage.

In order to comply with the increasingly higher environmental standards and health and safety requirements, there has for many years been a growing interest in binder systems which contain no, or very few, aromatic hydrocarbon solvents.

For these reasons, the task of the present invention was to develop a low odor or odor-free binder system. In addition, the invention has the task of making available a binder system which exhibits a low incidence of smoke buildup. To these ends, the cores/molds manufactured with this binder system should exhibit a good flexural strength, and above all, a good immediate strength.

Summary of the Invention

The present invention relates to a cold-box process for preparing a foundry shape which comprises:

(a) forming a foundry mix comprising a major amount of aggregate and an effectively binding amount of a binder system comprising:

(i) a phenolic resole resin component, and

(ii) an isocyanate component,

wherein the phenolic resin component comprises (a) an alkoxy-modified phenolic resole resin such that the mole ratio of alcohol to phenol used to prepare said alkoxy-modified phenolic resole resin is less than 0.25:1.0, and (b) an oxygen-rich, polar organic solvent, wherein the solvent portion of the phenolic resin component of the binder system amounts to no more than 40 % by weight based upon the weight of the phenolic resin component and the amount of oxygen-rich polar organic solvent is at least 50 weight percent based on the total weight of the solvent in the phenolic resin component;

(b) forming a foundry shape by introducing the foundry mix obtained from step (a) into a pattern;

(c) contacting foundry shape mix with a volatile tertiary amine catalyst; and

(d) removing the foundry shape of step (c) from the pattern.

In a second aspect, the invention relates to a process for preparing a foundry shape by the no-bake process which comprises:

(a) forming a foundry mix comprising a major amount of aggregate and an effectively binding amount of a binder system comprising:

(i) a phenolic resole resin component,
(ii) an isocyanate component, and
(iii) a catalytically effective amount of a liquid tertiary amine catalyst,

wherein the phenolic resin component comprises (a) an alkoxy-modified phenolic resole resin such that the mole ratio of alcohol to phenol used to prepare said alkoxy-modified phenolic resole resin is less than 0.25:1.0, and (b) an oxygen-rich, polar organic solvent, wherein the solvent portion of the phenolic resin component of the binder system amounts to no more than 40 % by weight based upon the weight of the phenolic resin component and the amount of oxygen-rich polar organic solvent is at least 50 weight percent based on the total weight of the solvent in the phenolic resin component;

(b) forming a foundry shape by introducing the foundry mix obtained from step (a) into a pattern;

(c) removing the foundry shape of step (c) from the pattern.

In a third aspect the present invention relates to a process of casting a metal which comprises:

(a) preparing a foundry shape in accordance with the first aspect;

(b) pouring said metal while in the liquid state into and a round said shape;

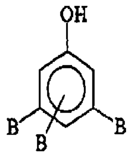
(c) allowing said metal to cool and solidify; and

(d) then separating the molded article.

Selecting an alkoxy-modified phenolic resin that exhibits low viscosity and favourable polarity is fundamental to the invention. According to the invention, the alkoxy-modified phenolic resin makes it possible to reduce the quantities of solvents needed, both in the phenolic resin component and also in the isocyanate component. Furthermore, the use of aromatic hydrocarbons in one or both of the binder components can be dispensed with. Through the combination of the alkoxy-modified phenolic resin with oxygen-rich, polar, organic solvents, improved immediate strengths are achieved with reduced build up of smoke. The addition of fatty acid ester has a positive effect on the separation effect and on moisture resistance.

Phenolic resins are manufactured by condensation of phenols and aldehydes (Ullmann's Encyclopedia of Industrial Chemistry, Bd. A19, page 371 ff, 5th, edition, VCH Publishing House, Weinheim). In the framework of this invention, substituted phenols and mixtures thereof can also be used. All conventionally used substituted phenols are suitable. The phenolic binders are not substituted, either in both ortho-positions or in one ortho- and in the para-position, in order to enable the polymerization. The remaining ring sites can be substituted. There is no particular limitation on the choice of substituent, as long as the substituent does not negatively influence the polymerization of the phenol and the aldehyde. Examples of substituted phenols are alkyl-substituted phenols, aryl-substituted phenols, cycloalkyl-substituted phenols, alkenyl-substituted phenols, alkoxy-substituted phenols, aryloxy-substituted phenols and halogen-substituted phenols.

The above named substituents have 1 to 26, and preferably 1 to 12, carbon atoms. Examples of suitable phenols, in addition to the especially preferred un-substituted phenols, are o-cresol, m-cresol, p-cresol, 3,5-xylol, 3,4-xylol, 3,4,5-trimethyl phenol, 3-ethylphenol, 3,5-diethylphenol, p-butylphenol, 3,5-dibutylphenol, p-amylphenol, cyclohexylphenol, p-octylphenol, 3,5-dicyclohexylphenol, p-crotylphenol, p-phenylphenol, 3,5-dimethoxyphenol, 3,4,5-trimethoxyphenol, p-ethoxyphenol, p-butoxyphenol, 3-methyl-4-methoxyphenol, and p-phenoxyphenol. Especially preferred is phenol itself. The phenols can likewise be described with the general formula:



where A, B and C can be hydrogen, alkyl radicals, alkoxy radicals or halogens.

All aldehydes which are traditionally used for the manufacture of phenolic resins, can be used within the scope of the invention. Examples of this are formaldehyde, acetaldehyde, propionaldehyde, furfuraldehyde, and benzaldehyde. Preferably, the aldehydes commonly used should have the general formula R'CHO, where R' is hydrogen or a hydrocarbon radical with 1-8 carbon atoms. Particularly preferred is formaldehyde, either in its diluted acqueous form or as paraformaldehyde.

In order to obtain the phenolic resins on which this invention is based, a molar number of the aldehyde should be used which is at least equivalent to the molar number of the phenolic component. A molar ratio of aldehyde to phenol is preferred of at least 1:1.0, with at least 1:0.58 being the most preferable.

In order to obtain alkoxy-modified phenolic resins, primary and secondary aliphatic alcohols should be used with an OH-group containing from 1 to 10 carbon atoms. Suitable primary or secondary alcohols include, for example, methanol, ethanol, n-propanol, isopropanol, n-butanol, and hexanol. Alcohols with 1 to 8 carbon atoms are preferred, in particular, methanol and butanol.

The manufacture of alkoxy-modified phenolic resins is described in EP-B-0 177 871. They can be manufactured using either a one-step or a two-step process.

With the one-step-process, the phenolic components, the aldehyde and the alcohol are brought to a reaction in the presence of suitable catalysts . With the two-step-process an unmodified resin is first manufactured, which is subsequently treated with alcohol.

The ratio of alcohol to phenol influences the properties of the resin as well as the speed of the reaction. The molar ratio of alcohol to phenol amounts to less than 0.25. A molar ratio of from 0.18 – 0.25 is preferred. If the molar ratio of alcohol to phenol amounts to more than 0.25, the moisture resistance decreases.

Suitable catalysts are divalent salts of Mn, Zn, Cd, Mg, Co, Ni, Fe, Pb, Ca and Ba. Zinc acetate is preferred.

Alkoxylation leads to resins with a low viscosity. The resins predominantly exhibit ortho-ortho benzyl ether bridges and furthermore, in ortho- and para-position to the phenolic OH-groups, they exhibit alkoxymethylene groups with the general formula $-(CH_2O)_nR$. In this case R is the alkyl group of the alcohol, and $_n$ is a small whole number in the range of 1 to 5.

All solvents, which are conventionally used in binder systems in the field of foundry technology, can be used in the systems which are the subject of the invention. It is even possible to use aromatic hydrocarbons in large quantities as essential elements in the solution, except that those solvents mentioned at the beginning, which might endanger health, safety, and the environment, should be avoided. For that reason, the use of oxygen-rich, polar, organic solvents are preferred as solvents for the phenolic resin components. The most suitable are dicarboxylic acid ester, glycol etherester, glycol diester, glycol diether, cyclic ketone, cyclic ester (lactone) or cyclic carbonate. Cyclic ketone and cyclic carbonate are preferred. Dicarboxylic acid ester exhibits the formula $R_1OOC\text{-}R_2\text{-}COOR_1$, where R_1, represents an independent alkyl group with 1-12, and preferably 1-6 carbon atoms, and R_2 is an alkylene group with 1-4 carbon atoms. Examples are dimethylester from carboxylic acids with 4 to 6 carbon atoms, which can, for example, be obtained under the name dibasic ester from DuPont. Glycol etheresters are binders with the formula $R_3\text{-}O\text{-}R_4\text{-}OOCR_5$, where R_3 represents an alkyl group with 1-4 carbon atoms, R_4 is an alkylene group with 2-4 carbon atoms, and R_5 is an alkyl group with 1-3 carbon atoms (for example butyl glycolacetate), with glycol etheracetate being preferred. Glycol diesters exhibit the general formula $R_5COO\text{-}R_4\text{-}$

$OOCR_5$ where R_4 and R_5 are as defined above and the remaining R_5, are selected, independent of each other (for example, propyleneglycol diacetate), with glycol diacetate being preferred. Glycol diether is characterized by the formula R_3-O-R_4-O-R_3, where R_3 and R_4 are as defined above and the remaining R_3 are selected independent of each other (for example, dipropyleneglycol dimethylether). Cyclic ketone, cyclic ester and cyclic carbonate with 4-5 carbon atoms are likewise suitable (for example, propylene carbonate). The alkyl- and alkylene groups can be branched or unbranched. These organic polar solvents can preferably be used either as stand-alone solvents for the phenolic resin or in combination with fatty acid esters, where the content of oxygen-rich solvents in a solvent mixture should predominate. The content of oxygen-rich solvents should come to more than 50% by weight, preferably more than 55% by weight.

Reducing the content of solvents in binder systems can have a positive effect on the development of smoke. Whereas conventional phenolic resins generally contain around 45% by weight and, sometimes, up to 55% by weight of solvents, in order to achieve an acceptable process viscosity (of up to 400 mPa-s), the amount of solvent in the phenolic-component can be restricted to at most 40% by weight, and preferably even 35% by weight, through the use of a low viscosity phenolic resin called for in this invention. The dynamic viscosity is determined according to the Brookfield Head Spindle Process.

If conventional non alkoxy-modified phenolic resins are used, the viscosity with reduced quantities of solvent lies well outside the range which is favorable for technical applications of up to around 400 mPa-s. In some parts, the solubility is also so bad that at room temperature phase separation can be observed. At the same time the immediate strength of the cores manufactured with this binder system is very low. Suitable binder systems exhibit an immediate strength of at least 150 N/cm_2 when 0.8 parts by weight each of the phenolic resin and isocyanate component are used for 100 parts by weight of an aggregate, like, for example, Quarzsand H32 (s. EP-A-0 771 599 or DE-A-4 327 292).

The addition of fatty acid ester to the solvent of the phenolic component leads to especially good release properties. Fatty acids are suitable, such as, for example, those with 8 to 22 carbons, which are esterified with an aliphatic alcohol. Usually fatty acids with a natural origin are used, like, for example, those from tall oil, rapeseed oil, sunflower oil, germ oil, and coconut oil. Instead of the natural oils, which are found in most mixtures of various fatty acids, single fatty acids, like palmitic fatty acid or myristic fatty acid can, of course, be used.

Aliphatic mono alcohols with 1 to 12 carbons are suitable for the esterification of fatty acids. Alcohols with 1 to 10 carbon atoms are preferred, with alcohols with 4 to 10 carton atoms being especially preferred. Based on the low polarity of fatty acid esters, whose alcohol components exhibit 4 to 10 carbon atoms, it is possible to reduce the quantity of fatty acid esters, and to reduce the buildup of smoke. A line of fatty acid esters is commercially obtainable.

Surprisingly, it has been shown that fatty acid esters, whose alcohol components contain from 4 to 10 carbon atoms, are especially advantageous., since they also give binder systems excellent release properties, when their content in the solvent of the phenolic component amounts to less than 50% by weight. As examples of fatty acid esters with longer alcohol components, are the butyl esters of oleic acids and tall oil fatty acid, as well as the mixed octyl-decylester of tall oil fatty acids.

Through the use of the invention-based alkoxy-modified phenolic resins, aromatic hydrocarbons can be avoided as solvents for the phenolic component. This is because of the excellent polarity of the binders. Oxygen-rich organic, polar solvents, can now be used as stand-alone solvents. Through the use of the invention-based alkoxy-modified phenolic resins, the quantity of solvents required can be restricted to less than 35% by weight of the phenolic component. This is made possible by the low viscosity of the resins. The use of aromatic hydrocarbons can, moreover, be avoided. The use of invention based binder systems with at least 50% by weight of the above named oxygen-rich, polar, organic solvents as components in the solvents of the phenolic components leads, moreover, to a doubtlessly lower development of smoke, in comparison with conventional systems with a high proportion of fatty acid esters in the solvent.

The two components of the binder system include an aliphatic, cycloaliphatic or aromatic polyisocyanate, preferably with 2 to 5 isocyanate groups. Based on the desired properties, each can also include mixtures of organic isocyanates. Suitable polyisocyanates include aliphatic polyisocyanates, like, for example, hexamethylenediisocyanate, alicyclic polyisocyanates like, for example, 4,4'-dicyclohexylmethanediisocyanate, and dimethyl derivates thereof. Examples of suitable aromatic polyisocyanates are toluol-2,4-diisocyanate, toluol-2,6-diisocyanate, 1,5-napththalenediisocyanate, triphenylmethanetriisocyanate, xylylenediisocyanate and its methyl derivatives, polymethylenepolyphenyl isocyanate and chlorophenylene-2,4-diisocyanate. Preferred polyisocyanates are aromatic polyisocyanates, in particular, polymethylenepolyphenyl polyisocyanates such as diphenylmethane diisocyanate.

In general 10 – 500 % by weight of the polyisocyanates compared to the weight of the phenolic resins are used. 20 – 300 % by weight of the polyisocyanates is preferred. Liquid polyisocyanates can be used in undiluted form, whereas solid or viscous polyisocyanates can be dissolved in organic solvents. The solvent can consist of up to 80% by weight of the isocyanate components. As solvents for the polyisocyanate, either the above-named fatty acid esters or a mixture of fatty acid esters and up to 50% by weight of aromatic solvents can be used. Suitable aromatic solvents are naphthalene, alkyl-substituted naphthalenes, alkyl-substituted benzenes, and mixtures thereof. Especially preferred are aromatic solvents, which consist of mixtures of the above named aromatic solvents and which have a boiling point range of between 140° C and 230° C. However, preferably no aromatic solvents are used. Preferably, the amount of polyisocyanate used results in the number of the isocyanate group being from 80 to 120% with respect to the number of the free hydroxyl group of the resin.

In addition to the already mentioned components, the binder systems can include conventional additives, like, for example, silane (US 4,540,724), drying oils (US 4,268,425) or "Komplexbildner" (WO 95/03903). The binder systems are offered, preferably, as two-component-systems, whereby the solution of the phenolic resin represents one component and the polyisocyanate, also in solution, if appropriate, is the other component. Both components are combined and subsequently mixed with sand or a similar aggregate, in order to produce the molding compound. The molding compound contains an effective binding quantity of up to 15% by weight of the invention-based binder system with respect to the weight of the aggregate. It is also possible to subsequently mix the components with quantities of sand or aggregates and then to join these two mixtures. Processes for obtaining a uniform mixture of components and aggregates are known to the expert. In addition, if appropriate, the mixture can contain other conventional ingredients, like iron oxide, ground flax fiber, xylem, pitch and refractory meal (powder).

In order to manufacture foundry molded pieces from sand, the aggregate should exhibit a sufficiently large particle size. In this way the founded piece has sufficient porosity, and fugitive gasses can escape during the casting process. In general at least 80% by weight and preferably 90% by weight of the aggregate should have an average particle size of less than or equal to 290 µm. The average particle size of the aggregate should have between 100 and 300 µm.

For standard-founded pieces, sand is preferred as the aggregate material to be used, where at least 70% by weight, and preferably more than 80% by weight of the sand is silicon dioxide. Zircon, olivine, aluminosilicate sands and chromite sands are likewise suitable as aggregate materials.

The aggregate material is the main component in founded pieces. In founded pieces from sand for standard applications, the proportion of binder in general amounts to up to 10% by weight, and often between 0.5 and 7% by weight, with respect to the weight of the aggregate. Especially preferred is 0.6 to 5% by weight of binder compared to the weight of the aggregate.

Although the aggregate is primarily added dry, up to 0.1% by weight of moisture can be tolerated, with respect to the weight of the aggregate. The founded piece is cured so that it retains its exterior shape after being removed from the mold. Conventional liquid or gaseous curing systems can be used for hardening in the invention-based binder system. A slightly volatile tertiary amine, like, for example, triethylamine or dimethylethylamine, as described in US-A-3,409,579, can also be passed through the founded piece.

It is further possible, to add a liquid amine to the molding compound in order to cure it. After removing the piece from the mold, further hardening takes place in the well-known way, finally resulting in the finished piece.

In a preferred implementation, silane with the general formula $(R'O)_3Si$ is added to the molding compound before the curing begins. Here, R' is a hydrocarbon radical, preferably an alkyl radical with 1 – 6 carbon atoms, and R is an alkyl radical, an alkoxy-substituted alkyl radical or an alkyl amine-substituted amine radical with alkyl groups, which have 1-6 carbon atoms. The addition of from 0.1 to 2% by weight with respect to the weight of the binder system and catalysts, reduces the moisture sensitivity of the system. Examples of commercially obtainable silanes are Dow Corning Z6040 and Union Carbide A-187 (γglycidoxypropyltrimethoxysilane), Union Carbide A-1100 (γ-aminopropyl triethoxysilane), Union Carbide A-1120 (N-ß-(aminoethyl)-γ-amino-propyltrimethoxysilane) and Union Carbide A1160 (ureidosilane).

If applicable, other additives can be used, including wetting agents and sand mixture extending additives (English Benchlife-additives), such as those in US 4,683,252 or US 4,540,724. In addition, mold release agents like fatty acids, fatty alcohols and their derivatives can be used, but as a rule, they are not necessary.

The invention is further clarified by the following examples.

Examples

If not otherwise specified, all percentages are by weight.

1. Manufacture of phenolic resins

The raw materials in Table I are placed in a reaction vessel fitted with reflux condenser, thermometer and agitator. The temperature is raised uniformly, under agitation, to 105 – 115 °C, and held there until a refractive index of 1.5590 is reached. Next the condenser is switched over to distillation and the temperature is brought up to 124 – 126 °C over the course of an hour. At this temperature, further distillation should occur until obtaining a refractive index of 1.5940. Next a vacuum is applied, and distillation is continued under reduced pressure, until reaching a refractive index of 1.600. The yields amount to around 83% in Example 1 and around 78% in Example 2.

Table I

Example	1	2
	not according to the invention	according to the invention
phenol	2130.7 g	1770.6 g
paraformaldehyde 91%	865.3 g	984.3 g
n-butanol	-	279.6 g
zinc acetate-dihydrate	1.0 g	1.5 g

2. Manufacture of phenolic resin solutions

With the phenolic resin manufactured according to the above instructions, the solutions shown in Table II are manufactured. Trade names are shown with an (H).

Table II

Example	1A	1B	1C	1D
Not according to the invention				
Phenolic resin 1	67.5%	67.5%	67.5%	67.5%
DBE (H) [a)]	19.0%	24.5%	27.0%	32%
Forbiol 102 (H)[b)]	13.0%	7.5%	5.0%	
Silane	0.5%	0.5%	0.5%	0.5%
Viscosity (mPa-s)	2 phases	659	617	561

Table III (Continuation)

Example	2A	2B	2C	2D	2E	2F	2G	2H
according to the invention								
Phenolic resin 2	67.5%	67.5%	67.5%	67.5%	67.5%	67.5%	67.5%	67.5%
DBE (H)[a]	19.0%	24.5%	27.0%	32.0%				
Butyl glycol acetate					32.0%			
ethylene glycol-diacetate						32.0%		
dipropylene glycol- dimethyl ether							32.0%	
propylenecarbonate								32.0%
Forbiol 102 (H)[b]	13.0%	7.5%	5.0%					
silane	0.5%	0.5%	0.5%	0.5%	0.5%	0.5%	0.5%	0.5%
viscosity (mPa-s)	289	280	264	241	217	297	271	338

a) DBE, dibasic ester, dimethylester mixture of dicarbonic acids with 4 to 6 carbon atoms (Dupont)

b) Forbiol 102, butyl ester of tall oil fatty acids (Arizona Chemical)

The phenolic resin solution, 1A, separates into two phases after cooling down to room temperature, and, for that reason, will not be examined further. The viscosity of the phenolic resin solutions 1B-1D lies way outside the favorable range for technical applications (i.e., up to around 400 mPa.s).

3. Manufacture of polyisocyanate solutions

As component II of the polyurethane-binder system, the solutions shown in Table III are manufactured.

Table III

Example	3A	3B	3C
According to the invention			
diphenyl methane di-isocyanate (techn. MDI)	80%	80%	80%
Forbiol 102 (H)	19.8%		10%
Forbiol 152 (H)[c]		19.8%	
Solvesso 100 (H)[d]			9.8%
Acid chloride	0.2%	0.2%	0.2%

c) Forbiol 152, mixture of octyl-decylester of tall oil fatty acids (Arizona Chemical)

d) Solvesso 100, mixture of aromatic hydrocarbons (Exxon)

4. Manufacture and testing of the molding material-/binder system-mixture. The following information applies to the manufacture of the molding material-/binder system-mixture:

0.8 parts by weight of the phenolic resin solution from Table II, and 0.8 parts by weight of the polyisocyanate solution from Table III are added to 100 parts by weight of Quarzsand H 32 (Quarzwerke GmbH, Frechen), in the order given, and mixed intensively in a laboratory mixer. With this mixture, test bodies are manufactured according to DIN 52401, which are cured by gassing with triethylamine (10 seconds at 4 bar pressure, followed by 10 seconds purging with air).

The flexural strength of the test bodies can be determined by GF-methods. In this way the flexural strength of the test bodies is tested immediately after they are manufactured (immediate strength) as well as after 1, 2, and 24 hours.

The results are shown in Table IV

Table IV

Attempt	1	2	3	4	5	6	7	8	9	10	11	12	13
Component 1	1B	1C	1D	2A	2B	2C	2D	2E	2F	2G	2H	2D	2D
Component 2	3A	3A	3A	3A	3A	3A	3A	3A	3A	3A	3A	3B	3C
	not according to the invention			according to the invention									
Strength (N/cm2)													
Immediate	105	120	140	205	235	225	205	225	200	230	180	190	210
1h	380	355	390	555	575	565	580	560	555	530	430	580	500
2h	400	405	400	555	575	565	580	560	570	590	440	585	530
24h	555	540	530	590	630	610	590	570	570	600	550	590	570

From Table IV one can recognize

Binder systems which are formulated with conventional phenolic resins (Attempt 1-3) have fundamentally lower initial strengths than those binder systems which are based on the invention (Attempts 4-13). Also the increase in strength over time is undoubtedly slower.

- The strengths, above all, the immediate strength, of all invention-based binder systems (Attempt 4-13), are the same within the precision of the test method. There is no identifiable dependency on the content of fatty acid ester/polar solvents.
- Both the fatty acid butyl ester and the fatty acid octyl-/decyl ester are equally suitable for the invention-based binder systems (Attempts 7 and 12).
- Combination with aromatic solvents is just as possible (Attempts 7 and 13).

5. Observation of smoke development

GF-test bars are kept in the oven 1 minute at 650 °C. After removing them, the development of smoke is observed against a dark background and assessed with a rating of 10 (very strong) – 1 (scarcely perceptible).

The results are shown in Table V.

Table V

Cores from Attempt in Table IV	4	5	6	7	8	9	10	11	12
Component 1	2A	2B	2C	2D	2E	2F	2G	2H	2D
Component 2	3A	3A	3A	3A	3A	3A	3A	3A	3B
Value	10	8	8	5	5	5	5	5	5

From Table V it follows that the development of smoke eases up when one reduces the fatty acids in favor of oxygen-rich solvents.

Casting research with cores which correspond to the composition of Attempts 4 and 7, confirmed the above results.

Where the terms "comprise", "comprises", "comprised" or "comprising" are used in this specification, they are to be interpreted as specifying the presence of the stated features, integers, steps or components referred to, but not to preclude the presence or addition of one or more other feature, integer, step, component or group thereof.

The claims defining the invention are as follows:

1. A cold-box process for preparing a foundry shape which comprises:

   (a) forming a foundry mix comprising a major amount of aggregate and an effectively binding amount of a binder system comprising:

      (i) a phenolic resole resin component, and
      (ii) an isocyanate component,

      wherein the phenolic resin component comprises (a) an alkoxy-modified phenolic resole resin such that the mole ratio of alcohol to phenol used to prepare said alkoxy-modified phenolic resole resin is less than 0.25:1.0, and (b) an oxygen-rich, polar organic solvent, wherein the solvent portion of the phenolic resin component of the binder system amounts to no more than 40 % by weight based upon the weight of the phenolic resin component and the amount of oxygen-rich polar organic solvent is at least 50 weight percent based on the total weight of the solvent in the phenolic resin component;

   (b) forming a foundry shape by introducing the foundry mix obtained from step (a) into a pattern;

   (c) contacting foundry shape mix with a volatile tertiary amine catalyst; and

   (d) removing the foundry shape of step (c) from the pattern.

2. The process of claim 1, wherein the oxygen-rich polar, organic solvent is selected from the group consisting of glycol ether esters, glycol diesters, glycol diethers, cyclic ketones, cyclic esters, cyclic carbonate, and mixtures thereof.

3. The process of claim 1 or claim 2, wherein the binder further includes a fatty acid ester.

4. The process of claim 3, wherein the amount of said binder in said foundry mix is about 0.6 percent to about 5.0 percent based upon the weight of the aggregate.

5. A process for preparing a foundry shape by the no-bake process which comprises:

(a) forming a foundry mix comprising a major amount of aggregate and an effectively binding amount of a binder system comprising:

(i) a phenolic resole resin component,
(ii) an isocyanate component, and
(iii) a catalytically effective amount of a liquid tertiary amine catalyst,

wherein the phenolic resin component comprises (a) an alkoxy-modified phenolic resole resin such that the mole ratio of alcohol to phenol used to prepare said alkoxy-modified phenolic resole resin is less than 0.25:1.0, and (b) an oxygen-rich, polar organic solvent, wherein the solvent portion of the phenolic resin component of the binder system amounts to no more than 40 % by weight based upon the weight of the phenolic resin component and the amount of oxygen-rich polar organic solvent is at least 50 weight percent based on the total weight of the solvent in the phenolic resin component;

(b) forming a foundry shape by introducing the foundry mix obtained from step (a) into a pattern;

(c) removing the foundry shape of step (c) from the pattern.

6. The process of claim 5, wherein the oxygen-rich polar, organic solvent is selected from the group consisting of glycol ether esters, glycol diesters, glycol diethers, cyclic ketones, cyclic esters, cyclic carbonate, and mixtures thereof.

7. The process of claim 5 or claim 6, wherein the binder further includes a fatty acid ester.

8. The process of claim 7, wherein the amount of said binder in said foundry mix is about 0.6 percent to about 5.0 percent based upon the weight of the aggregate.

9. A process of casting a metal which comprises:

(a) preparing a foundry shape in accordance with any one of claims 1 to 8;

(b) pouring said metal while in the liquid state into and a round said shape;

(c) allowing said metal to cool and solidify; and

(d) then separating the molded article.

10. A cold-box process of any one of claims 1 to 4 for preparing a foundry shape which process is substantially as herein described with reference to any one of the Examples.

11. A process of any one of claims 5 to 8 for preparing a foundry shape by the no-bake process, which process is substantially as herein described with reference to any one of the Examples.

12. A process of claim 9 of casting metal which process is substantially as herein described with reference to any one of the Examples.

13. A foundry shape whenever produced by the process of any one of claims 1 to 8, 10 or 11.

14. Metal whenever casted by the process of claim 9 or claim 12.

Dated this 3rd day of December 2002
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