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(54) Title: LOW SOLIDS POLYURETHANE-FORMING FOUNDRY BINDERS FOR COLD-BOX PROCESS

(57) Abstract

This invention relates to a low solids polyurethane-forming binder for the cold-box process. The binders utilize specific organic polyisocyanates in conjunction with polymerized linseed oil.

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LOW SOLIDS POLYURETHANE - FORMING FOUNDRY BINDERS FOR COLD-BOX PROCESS

Technical Field

This invention relates to low solids polyurethane-forming foundry binders. The binders are used for forming foundry mixes which are used in a cold-box process for preparing foundry shapes. The polyurethane-forming binders utilize specific organic polyisocyanates in conjunction with polymerized linseed oil.

Background of the Invention

In the foundry industry, one of the procedures used for making metal parts is by sand casting. In sand casting, disposable molds and cores are fabricated with a mixture of sand and an organic or inorganic binder. The binder is usually used to strengthen the cores, which are the most fragile part of the mold assembly.

One of the fabrication processes used in sand casting is the cold-box process. In this process, a gaseous curing agent is passed through a mixture of the sand and binder to cure the mixture.

A binder commonly used in the cold-box fabrication process is a polyurethane binder derived from curing a polyurethane-forming binder composition with a gaseous tertiary amine catalyst. The polyurethane-forming binder composition usually consists of a phenolic resin component and polyisocyanate hardener component which may react prior to curing with the gaseous catalyst. If this reaction occurs, it will reduce the flowability of the mixture when it is used for casting, and the resulting molds and cores will have reduced strength.

The bench life of the mixture of the sand and polyurethane-forming binder composition is the time period between forming the mixture of the sand and polyurethane-forming binder and the time when the mixture is no longer useful for making acceptable molds and cores. A measure of mold and core acceptability is tensile strength. If a mixture of sand and polyurethane-forming binder composition is used after the bench life has expired, the resulting molds and cores will have insufficient tensile strength.

Because it is not always possible to use the mixture of sand and polyurethane-forming binder composition immediately after mixing, it is desirable to prepare mixtures with an extended bench life.

Summary of the Invention

This invention relates to polyurethane-forming foundry binders comprising

(a) a phenolic resin component comprising
  (1) a phenolic resin;
  (2) an aromatic hydrocarbon solvent;
  (3) an ester solvent; and
(b) an isocyanate component comprising
  (1) from 68 weight percent to 75 weight percent of a liquid organic polyisocyanate having a functionality 2.0 to 2.4;
  (2) from 1 weight percent to 5 weight percent of polymerized linseed oil; and
  (3) from 20 weight percent to 31 weight percent of an aromatic hydrocarbon solvent;
  said weight percent being based upon the total weight of the isocyanate component, and such that the ratio of isocyanate groups in the isocyanate component to hydroxyl groups of the phenolic resin component is from 0.9:1.1 to 1.0:0.9, preferably from 0.94:1 to 1.0:0.94.

The polyurethane-forming binders are used to form foundry mixes which are cured by the cold-box process with a gaseous or vaporized tertiary amine, used alone or mixed with an inert carrier gas such as carbon dioxide, to form foundry shapes which are used to prepare metal castings.

Several advantages result when using the subject binders. The major advantage is that foundry mixes prepared with the binders have an extended benchlife. Furthermore, the use of lower solids in the isocyanate component enables the formulator to use a phenolic resin component with lower solids which will result in lower amounts of free formaldehyde. This is advantageous from an environmental standpoint. The use of lower solids formulations also results in a reduction of lustrous carbon when castings are prepared. Lustrous carbon causes casting defects.

Description of Best Mode and Other Modes for Practicing the Invention

The phenolic resin component comprises a phenolic resin and a solvent.

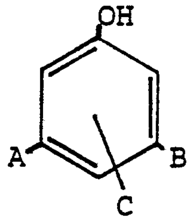
The phenolic resins used in the phenolic resin compositions are well known in the foundry art. Suitable phenolic resins are those which are soluble in the solvents employed, such as phenolic resole or phenolic novolak resins formed by reacting phenolic compounds with aldehydes. Resole or A-stage resins, as well as resitol or B-stage resins, may be made by reacting a molar excess of aldehyde, such as formaldehyde, with a phenolic material in the presence divalent metal ion catalysts. The novolak resins may be formed by reacting a molar excess of phenolic material with an aldehyde in the presence of an acid catalyst.

The preferred phenolic resins used to form the subject binder compositions are well known in the art. Such resins are specifically described in U.S. Patent 3,485,797 which is hereby incorporated by reference.

These resins are the reaction products of an aldehyde with a phenol. They contain a preponderance of bridges joining the phenolic nuclei of the polymer which are ortho-ortho benzylic ether bridges. They are prepared by reacting an aldehyde and a phenol in a mole ratio of aldehyde to phenol of at least

1.0:1.0, preferably from 1.1:1.0 to 2.0:1.0 in the presence of a divalent metal ion catalyst, preferably a divalent metal ion such as zinc, lead, manganese, copper, tin, magnesium, cobalt, calcium, and barium.

The phenols may be represented by the following structural formula:



wherein A, B, and C are hydrogen atoms, or hydroxyl radicals, or hydrocarbon radicals or oxyhydrocarbon radicals, or halogen atoms, or combinations of these. The phenol may be a multiple ring phenol such as bisphenol A.

The phenolic resin is preferably non-aqueous. By "non-aqueous" is meant a phenolic resin which contains water in amounts of no more than about 10%, preferably no more than about 1% based on the weight of the resin. The phenolic resin component preferably includes benzylic ether resins.

The aldehyde has the formula R'CHO wherein R' is a hydrogen or hydrocarbon radical of 1 to 8 carbon atoms.

By "phenolic resin" is meant the reaction product of a phenol with an aldehyde in which the final mixture of molecules in the reaction products is dependent upon the specific reactants selected, the starting ratio of these reactants, and the conditions of the reaction (for example, the type of catalyst, the time and temperature of the reaction, the solvents, and/or other ingredients present, and so forth). The reaction products, that is the phenolic resin, will be a mixture of different molecules and may contain in widely varying ratios addition products, condensation products, and unreacted reactants such as unreacted phenol and/or unreacted aldehyde.

By "addition product" is meant reaction products in which an organic group has been substituted for at least one hydrogen of a previously unreacted phenol or of a condensation product.

By "condensation product" is meant reaction products that link two or more aromatic rings.

The phenolic resins are preferably substantially free of water and are organic solvent soluble. The phenolic component includes any one or more of the phenols which have heretofore been employed in the formation of phenolic resins and which are not substituted at both ortho-positions or at one ortho-position and the para-position. It has been found that substitution in these positions interfere with the polymerization reaction. Any one, all, or none of the remaining carbon atoms of the phenol ring can be substituted. The nature of the substituent can vary widely and it is only necessary that the substituent not interfere in the polymerization of the aldehyde with the phenol at the ortho-position and/or para-position. Substituted phenols employed in the formation of the phenolic resins include alkyl-substituted phenols, aryl-substituted phenols, cyclo-alkyl-substituted phenols, aryloxy-substituted phenols, and halogen-substituted phenols, the foregoing substituents containing from 1 to 26 carbon atoms and preferably from 1 to 12 carbon atoms.

Specific examples of suitable phenols include phenol, 2,6-xylenol, o-cresol, p-cresol, 3,5-xylenol, 3,4-xylenol, 2,3,4-trimethyl phenol, 3-ethyl phenol, 3,5-diethyl phenol, p-butyl phenol, 3,5-dibutyl phenol, p-amyl phenol, p-cyclohexyl phenol, p-octyl phenol, 3,5-dicyclohexyl phenol, p-phenyl phenol, p-crotyl phenol, 3,5-dimethoxy phenol, 3,4,5-trimethoxy phenol, p-ethoxy phenol, p-butoxy phenol, 3-methyl-4-methoxy phenol, and p-phenoxy phenol. Multiple ring phenols such as bisphenol A are also suitable.

The phenol reactant is preferably reacted with an aldehyde to form phenolic resins and more preferably benzylic ether resins. The aldehydes reacted with the phenol can include any of the aldehydes heretofore employed in the formation of phenolic resins such as formaldehyde, acetaldehyde, propionaldehyde, furfuraldehyde, and benzaldehyde. In general, the aldehydes employed have the formula R'CHO wherein R' is a hydrogen or a hydrocarbon radical of 1 to 8 carbon atoms. The most preferred aldehyde is formaldehyde.

The phenolic resin used must be liquid or organic solvent-suitable. Solubility in an organic solvent is desirable to achieve uniform distribution of the binder on the aggregate.

The substantial absence of water in the phenolic resin is desirable in view of the reactivity of the binder composition of the present invention with isocyanates. Mixtures of phenolic resins can be used.

It is also possible to use phenolic resins as described herein which are modified with lower alkyl alcohols having from 1 to 8 carbon atoms such as methanol, n-butanol, ethanol, and the like. By methods well known in the art it is possible to modify the phenolic resin by adding the alcohol to the phenol and formaldehyde during the reaction, or reacting the alcohol with the phenolic resin after the resin has formed.

The liquid organic polyisocyanate used in the isocyanate component has a functionality of 2.0 to 2.4, preferably 2.2 to 2.4 and is used in conjunction with from 1 weight percent to 5 weight percent of polymerized linseed oil, preferably from 2 weight to 4 weight percent, based upon the total weight of the isocyanate component.

Polymerized linseed oil is a type of blown oil prepared by oxidizing linseed according to well known methods. The polymerized linseed oils particularly useful are known as heat bodied medium acid oils, preferably having a viscosity of Z to Z1. In general, such oils meet Federal Specifications TT-L-201.

The manner in which the polymerized linseed oil is added to the organic polyisocyanate is not of particular significance. Usually, it is added as a final ingredient to the polyisocyanate component.

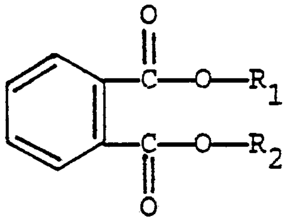
The polyisocyanates are used in sufficient concentrations to cause the curing of the phenolic resin when reacted with the curing catalyst. Preferably, the ratio of the isocyanate groups of the polyisocyanate to the hydroxyl of the phenolic resin is from 0.9:1.1 to 1.1:0.9, most preferably about 0.94:1.0 to 1.0:0.94.

Those skilled in the art will know how to select specific solvents for the phenolic resin and isocyanate components. The resin component contains at least one aromatic hydrocarbon solvent and one ester solvent, while the isocyanate component contains at least one aromatic hydrocarbon solvent.

When selecting the solvents one must realize that the difference in the polarity between the polyisocyanate and the phenolic resins restricts the choice of solvents in which both components are compatible. Such compatibility is necessary to achieve complete reaction and curing of the binder compositions of the present invention. Polar solvents of either the protic or aprotic type are good solvents for the phenolic resin, but have limited compatibility with the polyisocyanate. Aromatic solvents, although compatible with the polyisocyanate, are less compatible with the phenolic results. It is, therefore, preferred to employ combinations of solvents and particularly combinations of aromatic and polar solvents in the polyisocyanate component. Suitable aromatic solvents are benzene, toluene, xylene, ethylbenzene, and mixtures thereof. Preferred aromatic solvents are mixed solvents that have an aromatic content of at least 90% and a boiling point range of 138°C to 232°C.

The polar solvents should not be extremely polar such as to become incompatible with the aromatic solvent. Suitable polar solvents are generally those which have been classified in the art as coupling solvents and include furfural, furfuryl alcohol, Cellosolve acetate, butyl Cellosolve, butyl Carbitol, diacetone alcohol, and Texanol.

Esters which are used in the phenolic resin component are liquid dialkyl esters such as dialkyl phthalate of the type disclosed in U.S. Patent No. 3,905,934, the entire contents of which are incorporated herein by reference. Such esters preferably have the structure:



where R_1 and R_2 are alkyl radicals of 1 to 12 carbon atoms and the total number of carbon atoms in the R groups does not exceed 16. Preferably R_1 and R_2 are alkyl radicals of 3 to 6 carbon atoms and the total number of carbon atoms in R_1 and R_2 is between 6 and 12. Thus in the above structural formula, either R group can be methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, isopentyl, hexyl, isohexyl, heptyl, isoheptyl, octyl, isooctyl, and other isomers of the foregoing.

Other dialkyl esters include dimethyl glutarate such as available from DuPont under the trade designation DBE-5; dimethyl adipate available from DuPont under the trade designation DBE-6, dimethyl succinate; and mixtures of such esters which are available from DuPont under the trade designation DBE, and dialkyl adipates and succinates with alcohols up to 12 carbon atoms.

Generally, the solids level of the isocyanate component is from 68 weight percent to 75 weight percent, based upon the weight of the isocyanate component, preferably from 70 weight percent to 74 weight percent. Furthermore, since an isocyanate to hydroxyl ratio of 0.9:1.1 to 1.1:0.9, preferably from 0.94:1.0 to 1.0:0.94 is used, the phenolic resin will have a solids level 45 weight percent to 55 weight percent based upon the total weight of the resin component, preferably from 49 weight percent to 54 weight percent.

The amount of aromatic hydrocarbon solvent used in the phenolic resin component is from 10 to 30 weight percent, preferably 15 to 25 weight percent, said weight percent based upon the total weight percent of the phenolic resin component. The amount of ester solvent used in the phenolic resin component is generally from 10 weight percent to 20 weight percent based upon the weight percent of the phenolic resin component. The weight ratio of aromatic hydrocarbon solvent to ester solvent in the phenolic resin component is generally from 1:2 to 2:1.

The binder compositions are preferably made available as a two-package system with the phenolic resin in one package and the isocyanate component in the other package. Usually, the binder components are combined and then admixed with sand or a similar aggregate to form a foundry mix or the mix can also be formed by sequentially admixing the components with the aggregate. Methods of distributing the binder on the aggregate particles are well-known to those skilled in the art. The mix can, optionally, contain other ingredients such as iron oxide, ground flax fibers, wood cereals, pitch, refractory flours, and the like.

In many formulations it is preferred to use a benchlife extender. The benchlife extender is added to the isocyanate component in an effective amount to extend the benchlife of the foundry mix. The amount used varies depending upon the benchlife desired but generally is from 0.1 weight percent to 2.0 weight percent based upon the weight of the isocyanate component.

Typically used benchlife extenders are such as those disclosed in U.S. Patent 4,540,724 and 4,683,252 which are hereby incorporated by reference.

When preparing an ordinary sand-type foundry shape, the aggregate employed has a particle size large enough to provide sufficient porosity in the foundry shape to permit escape of volatiles from the shape during the casting operation. The term "ordinary sand-type foundry shapes", as used herein, refers to foundry shapes which have sufficient porosity to permit escape of volatiles from it during the casting operation.

Generally, at least about 80% and preferably about 90% by weight of aggregate employed for foundry shapes has an average particle size no smaller than about 0.1mm. The aggregate for foundry shapes preferably has an average particle size between about 0.1mm and about 0.25mm. The preferred aggregate employed for ordinary foundry shapes is sand wherein at least about 70 weight percent and preferably at least about 85 weight percent of the sand is silica. Other suitable aggregate materials include zircon, olivine, aluminosilicate, chromite, and the like.

When preparing a shape for precision casting, the predominant portion and generally at least about 80% of the aggregate has an average particle size no larger than 0.1mm and preferably between about 0.04mm and 0.075mm. Preferably at least about 90% by weight of the aggregate for precision casting applications has a particle size no larger than 0.1mm and preferably between 0.04mm and 0.075mm. The preferred aggregates employed for precision casting applications are fused quartz, zircon, magnesium silicate, olivine, and aluminosilicate.

When preparing a refactory such as a ceramic the predominant portion and at least 80 weight percent of the aggregate employed has an average particle size under 0.075mm and preferably no smaller than 0.04mm. Preferably at least about 90% by weight of the aggregate for a refractory has an average particle size under 0.075mm and preferably no smaller than 0.04mm. The aggregate employed in the preparation of refractories must be capable of withstanding the curing temperatures such as above about 815°C which are needed to cause sintering for utilization. Examples of some suitable aggregate employed for preparing refractories include the ceramics such as refractory oxides, carbides, nitrides, and silicides such as aluminum oxide, lead oxide, chromic oxide, zirconium oxide, silica, silicon carbide, titanium nitride, boron nitride, molybdenum disilicide, and carbonaceous material such as graphite. Mixtures of the aggregate can also be used, when desired, including mixtures of metals and ceramic.

Examples of some abrasive grains for preparing abrasive articles include aluminum oxide, silicon carbide, boron carbide, corundum, garnet, emery, and mixtures thereof. These abrasive materials and their uses for particular jobs are understood by persons skilled in the art and are not altered in the abrasive articles contemplated by the present invention. In addition, inorganic filler can be employed along with the abrasive grit in preparing abrasive articles. It is preferred that at least about 85% of the inorganic fillers has an average particle size no greater than 0.075mm. It is most preferred that at least about 95% of the inorganic filler has an average particle size no greater than 0.075mm. Some inorganic fillers include cryolite, fluorospar, silica, and the like. When an inorganic filler is employed along with the abrasive grit, it is generally present in amounts from about 1% to about 30% by weight based upon the combined weight of the abrasive grit and inorganic filler.

Although the aggregate employed is preferably dry, it can contain small amounts of moisture, such as up to about 0.3% by weight or even higher based on the weight of the aggregate.

The aggregate constitutes the major constituent and the binder constitutes a relatively minor amount of the foundry mix. In ordinary sand-type foundry applications, the amount of binder is generally no greater than about 10% by weight and frequently within the range of about 0.5% to about 7% by weight based upon the weight of the aggregate. Most often, the binder content ranges from about 0.6% to about 5% by weight based upon the weight of the aggregate in ordinary sand-type foundry shapes.

In molds and cores for precision casting applications the amount of binder is generally no greater than about 40% by weight and frequently within the range of about 5% to about 20% by weight based upon the weight of the aggregate.

In refractories, the amount of binder is generally no greater than about 40% by weight and frequently within the range of about 5% to about 20% by weight based upon the weight of the aggregate.

In abrasive articles, the amount of binder is generally no greater than about 25% by weight and frequently within the range of about 5% to about 15% by weight based upon the weight of the abrasive material or grit.

Although the aggregate employed is preferably dry, moisture of up to about 1 weight percent based on the weight of the sand can be tolerated. This is particularly true if the solvent employed is non-water-miscible or if an excess of the polyisocyanate necessary for curing is employed since such excess polyisocyanate will react with the water.

It will be apparent to those skilled in the art that other additives such as silanes, silicones, benchlife extenders, release agents, solvents, etc. can be added to the phenolic resin composition, polyisocyanate composition, binder composition, aggregate, or foundry mix. The particular additives chosen will depend upon the specific purposes of the formulator.

The molding mix is molded into the desired shape, whereupon it is cured by the so called cold box process at ambient temperature. Curing can be affected by passing a gaseous or vaporized tertiary amine, used alone or mixed with an inert carrier gas such as carbon dioxide, through the molded mix such as described in U.S. Patent 3,409,579 which is hereby incorporated by reference.

EXAMPLES

The examples which follow will illustrate specific embodiments of the invention. These examples along with the written description will enable one skilled in the art to practice the invention. It is contemplated that many equivalent embodiments of the invention will be operable besides these specifically disclosed.

The phenolic resin (abbreviated as PR) used in all of the examples was a resin containing a polymeric material having a preponderance of bridges joining its phenolic nuclei which are ortho-ortho benzylic ether bridges. The resins were prepared by reacting a molar excess of paraformaldehyde with phenol at elevated temperatures in the presence of a divalent metal catalyst. The procedures for preparing such resins are set forth in U.S. Patent 3,485,797.

Unless otherwise indicated the organic polyisocyanate used had a functionality of 2.2 and is sold under the tradename MONDUR MRS-5 by Mobay Chemical Company.

The IC used contained a medium acid polymerized linseed oil (PLO) having a viscosity of Z-Z1 and meets Federal Specifications TT-L-201. The amount of PLO used is specified in the examples and tables that follow.

The general procedure used in the examples was to mix the phenolic resin component with 4,000 parts by weight of Manley

IL5W sand. Then the polyisocyanate component was added to the sand and resin mixture, and was uniformly distributed therein.

The resulting foundry mix was formed into standard AFS tensile test samples (dogbones) according to standard procedures by blowing it into a corebox and contacting it with dimethylethylamine according to the cold-box process. Measuring the tensile strength of the dog bone samples enables one to predict how the mixture of sand and polyurethane-forming binder will work in actual foundry operations.

In the examples which follow, dog bone samples were formed from the foundry mix immediately after mixing, (zero bench) 3 hours after mixing, and 5 hours after mixing. Then tensile strengths of the various cured samples were measured immediately (IMM), 1 hour, and 24 hours after curing. Some of the dog bone samples that were formed from freshly prepared (zerobench) foundry mixes were stored for 24 hours at a relative humidity (RH) of 100% and a temperature of 25°C. Tensile strengths of the dog bone samples are given in the tables.

The specific solvents used in the resin component and isocyanate component are set forth in the examples and tables. The following abbreviations are used:

AHS = an aromatic hydrocarbon solvent such as HI-SOL 15, HI-SOL 10, Getty 400, etc. or mixtures thereof.
DBE = a dibasic ester solvent blend.
DOA = dioctyl adipate.
KER = kerosene.
PMA = propylene glycol mono methyl ether acetate.

Other abbreviations that will be used in the examples and tables are as follows:

A-187 = a silane sold by Union Carbide
MPCP = a benchlife extender known as monphenylchlorophosphate.

The weights in the examples are parts by weight unless otherwise specified.

EXAMPLES 1 - 3

Examples 1 - 3 illustrate the effect of using varying solids levels in the isocyanate component (IC) and phenolic resin component (PRC) when MRS-5 and PLO are used in the isocyanate component. The amount of PLO used in these examples was four weight percent based upon the total weight of the IC.

Table I discloses solids level (SL) of the IC and formulations used in the IC and PRC. The calculated isocyanate to hydroxyl ratio in these examples is 0.94.

TABLE I

Formulation	Examples			
PRC (pbw)	1	2	3	A
PR	48.8	50.2	51.0	59.0
DOA	12.6	12.2	12.0	8.5
PMA	15.6	15.2	15.0	13.0
AHC	22.4	21.8	21.4	18.9
A-187	0.6	0.6	0.6	0.6
IC (pbw)				
MRS-5	68.0	70.0	71.0	83.0
AHC	24.0	22.0	20.0	9.0
KER	4.0	4.0	4.0	4.0
PLO	4.0	4.0	4.0	4.0

The tensile strengths of the dogbone samples made are shown in Table II.

TABLE II

(Tensile Measurement in psi)

		ZERO BENCH				3 HR BENCH		5 HR BENCH	
EXAMPLE	SL	IMM	1 HR	24 HR	24 HR (100% RH)	IMM	24 HR	IMM	24 HR
1	68.0	103	178	216	81	149	257	116	191
2	70.0	125	197	219	56	118	200	82	147
3	71.0	133	216	231	52	125	202	76	135
A	83.0	193	243	251	52	85	133	48	78

Table II shows an interesting and unexpected result. Although Example A had high tensile strengths at zero bench and after 24 hours benchlife, the tensile strength after 5 hours benchlife was unacceptable. On the other hand, Example 1-3, which used a low solids formulation, had had acceptable tensile strengths at zero bench and after 5 hours benchlife.

In some formulations, effective performance can be achieved without the addition of a benchlife extender.

Extended benchlife also occurs if a benchlife extender is added to the formulation as Examples 4 - 5 show. Moreover, because the tensile measurement are better after extended benchlife with the low solids formulation, less benchlife extender can be used.

EXAMPLE 4 - 5

The formulations used in these examples were substantially the same as those in Examples 1-3 except 0.99 pbw of MPCP benchlife extender was added to IC (the AHS was adjusted appropriately for the elimination of the silane and addition of MPCP). The solids levels are given in Table III that follows. Example B is a comparative example. The isocyanate to hydroxyl ratio in these examples was 0.94.

The tensile strengths are also given in the table. The data confirms that formulations using the particular isocyanate component with lower solids provide better tensile strengths when the foundry mix has an extended benchlife, ie. 5 hours.

TABLE III

(Tensile Measurement in psi)

		ZERO BENCH				3 HR BENCH		5 HR BENCH	
EXAMPLE	SL	IMM	1 HR	24 HR	24 HR (100% RH)	IMM	24 HR	IMM	24 HR
4	71.0	168	253	274	50	162	254	153	231
5	74.0	190	270	270	44	154	233	140	222
B	83.0	195	259	259	51	147	195	124	177

EXAMPLE 6

Example 6 and Comparative Example C illustrate the significance of using the organic polyisocyanate with PLO. Both formulations were similar to those used in Examples 4-5 except Comparison Example C did not contain PLO. The results are shown in Table IV which follows. The data indicate that the PLO is needed to obtain acceptable tensile strengths.

TABLE IV

(Tensile Measurement in psi)

		ZERO BENCH				3 HR BENCH		5 HR BENCH	
EXAMPLE	SL	IMM	1 HR	24 HR	24 HR (100% RH)	IMM	24 HR	IMM	24 HR
6	74.0	165	230	261	55	145	225	130	224
C	74.0	106	171	269	59	94	227	94	209

CLAIMS

I claim:

1. A polyurethane-forming foundry binder comprising:
   a. a phenolic resin component comprising;
      (1) a phenolic resin;
      (2) an aromatic hydrocarbon solvent; and
      (3) an ester solvent; and
   b. an isocyanate component comprising:
      (1) from 68 weight percent to 75 weight percent of a liquid organic polyisocyanate having a functionality 2.0 to 2.4;
      (2) from 1 weight percent to 5 weight percent of polymerized linseed oil; and
      (3) from 20 weight percent to 31 weight percent of an aromatic hydrocarbon solvent;

      said weight percent being based upon the total weight of isocyanate component, and

   such that the ratio of isocyante groups in the isocyanate component to hydroxyl groups of the phenolic resin component is from 0.9:1.1 to 1.1:0.9.

2. The polyurethane-forming binder of Claim 1 wherein the weight percent of the liquid organic polyisocyanate is from 70 to 74 weight percent.

3. The polyurethane-forming binder of Claim 2 wherein the isocyanate to hydroxyl ratio is from 0.94:1.0 to 1.0:0.94.

4. The foundry binder of Claim 3 wherein the phenolic resin is a benzylic ether resin having preponderance of bridges joining the phenolic nuclei of the polymer which are ortho-ortho benzylic ether bridges.

5. The foundry binder of Claim 4 wherein the functionality of the organic polyisocyanate is from 2.2 to 2.4.

6. The foundry binder of Claim 5 wherein the phenolic resin of the resin component is from 49 weight percent to 54 weight percent based upon the weight of the resin component.

7. The foundry binder of Claim 6 wherein the isocyanate component contains an effective amount of a benchlife extender.

8. A foundry mix comprising:
   a. a major amount of foundry aggregate
   b. an effective bonding amount of the foundry binder of Claim 2.

9. A foundry mix comprising:
   a. a major amount of foundry aggregate
   b. an effective bonding amount of the foundry binder of Claim 3.

10. A foundry mix comprising:
    a. a major amount of foundry aggregate
    b. an effective bonding amount of the foundry binder of Claim 4.

11. A foundry mix comprising:
    a. a major amount of foundry aggregate
    b. an effective bonding amount of the foundry binder of Claim 5.

12. A foundry mix comprising:
    a. a major amount of foundry aggregate
    b. an effective bonding amount of the foundry binder of Claim 6.

13. A foundry mix comprising:
    a. a major amount of foundry aggregate
    b. an effective bonding amount of the foundry binder of Claim 7.

14. A cold-box process for preparing a foundry shape comprising:
    a. mixing a foundry aggregate with a bonding amount of up to about 10% by weight, based upon the weight of the aggregate, of the polyurethane-forming binder composition of Claim 2;
    b. introducing the foundry mix obtained from step (a) into a pattern;
    c. hardening the foundry mix in the pattern to become self-supporting; and

d. thereafter removing the shaped foundry mix of step (c) from the pattern and allowing it to further cure, thereby obtaining a hard, solid, cured foundry shape.

15. A cold-box process for preparing a foundry shape comprising:
    a. mixing a foundry aggregate with a bonding amount of up to about 10% by weight, based upon the weight of the aggregate, of the polyurethane-forming binder composition of Claim 3;
    b. introducing the foundry mix obtained from step (a) into a pattern;
    c. hardening the foundry mix in the pattern to become self-supporting; and
    d. thereafter removing the shaped foundry mix of step (c) from the pattern and allowing it to further cure, thereby obtaining a hard, solid, cured foundry shape.
16. A cold-box process for preparing a foundry shape comprising:
    a. mixing a foundry aggregate with a bonding amount of up to about 10% by weight, based upon the weight of the aggregate, of the polyurethane-forming binder composition of Claim 4;
    b. introducing the foundry mix obtained from step (a) into a pattern;
    c. hardening the foundry mix in the pattern to become self-supporting; and
    d. thereafter removing the shaped foundry mix of step (c) from the pattern and allowing it to further cure, thereby obtaining a hard, solid, cured foundry shape.
17. A cold-box process for preparing a foundry shape comprising:
    a. mixing a foundry aggregate with a bonding amount of up to about 10% by weight, based upon the weight of

the aggregate, of the polyurethane-forming binder composition of Claim 5;

b. introducing the foundry mix obtained from step (a) into a pattern;

c. hardening the foundry mix in the pattern to become self-supporting; and

d. thereafter removing the shaped foundry mix of step (c) from the pattern and allowing it to further cure, thereby obtaining a hard, solid, cured foundry shape.

18. A cold-box process for preparing a foundry shape comprising:

a. mixing a foundry aggregate with a bonding amount of up to about 10% by weight, based upon the weight of the aggregate, of the polyurethane-forming binder composition of Claim 6;

b. introducing the foundry mix obtained from step (a) into a pattern;

c. hardening the foundry mix in the pattern to become self-supporting; and

d. thereafter removing the shaped foundry mix of step (c) from the pattern and allowing it to further cure, thereby obtaining a hard, solid, cured foundry shape.

19. A cold-box process for preparing a foundry shape comprising:

a. mixing a foundry aggregate with a bonding amount of up to about 10% by weight, based upon the weight of the aggregate, of the polyurethane-forming binder composition of Claim 7;

b. introducing the foundry mix obtained from step (a) into a pattern;

c. hardening the foundry mix in the pattern to become self-supporting; and

d. thereafter removing the shaped foundry mix of step (c) from the pattern and allowing it to further cure, thereby obtaining a hard, solid, cured foundry shape.

20. A foundry shape prepared in accordance with Claim 14.
21. A foundry shape prepared in accordance with Claim 15.
22. A foundry shape prepared in accordance with Claim 16.
23. A foundry shape prepared in accordance with Claim 17.
24. A foundry shape prepared in accordance with Claim 18.
25. A foundry shape prepared in accordance with Claim 19.
26. A process of casting a metal article comprising:
    a. fabricating a shape in accordance with Claim 14;
    b. pouring said metal while in the liquid state into said shape;
    c. allowing said metal to cool and solidify; and
    d. then separating the molded article.
27. A process of casting a metal article comprising:
    a. fabricating a shape in accordance with Claim 15;
    b. pouring said metal while in the liquid state into said shape;
    c. allowing said metal to cool and solidify; and
    d. then separating the molded article.
28. A process of casting a metal article comprising:
    a. fabricating a shape in accordance with Claim 16.
    b. pouring said metal while in the liquid state into said shape;
    c. allowing said metal to cool and solidify; and
    d. then separating the molded article.
29. A process of casting a metal article comprising:
    a. fabricating a shape in accordance with Claim 17.
    b. pouring said metal while in the liquid state into said shape;
    c. allowing said metal to cool and solidify; and
    d. then separating the molded article.
30. A process of casting a metal article comprising:
    a. fabricating a shape in accordance with Claim 18.
    b. pouring said metal while in the liquid state into said shape;
    c. allowing said metal to cool and solidify; and

d. then separating the molded article.

31. A process of casting a metal article comprising:
    a. fabricating a shape in accordance with Claim 19.
    b. pouring said metal while in the liquid state into said shape;
    c. allowing said metal to cool and solidify; and
    d. then separating the molded article.

32. The metal article prepared in accordance with Claim 26.

33. The metal article prepared in accordance with Claim 27.

34. The metal article prepared in accordance with Claim 28.

35. The metal article prepared in accordance with Claim 29.

36. The metal article prepared in accordance with Claim 30.

37. The metal article prepared in accordance with Claim 31.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/00448

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4 C08L 61/10 B22C 1/24,71/22;

U.S CL: 523/143; 164/16, 526

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S. CL.	523/143; 164/16, 526

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 4,268,425 (GARDIKES)19 MAY 1981 (NOTE THE PARAGRAPH OVERLAPPING COLS. 2 AND 3, COL. 3, LINES 49-56 AND THE PARAGRAPH OVERLAPPING COLS. 4 AND 5).	1-37
A	US, A, 3,409,579 (ROBINS) 05 NOVEMBER 1968 (NOTE THE ABSTRACT AND COL. 5, LINES 27-45).	1-37
A	US, A, 3,485,797 (ROBINS) 23 DECEMBER 1969 (NOTE THE ABSTRACT).	1-37
A	US, A, 3,676,392 (ROBINS) 11 JULY 1972 (NOTE THE ABSTRACT).	1-37
A	US, A, 4,698,377 (LAITAR) 06 OCTOBER 1987 (NOTE THE ABSTRACT).	1-37
X,E	US, A, 4,760,101 (FECHTER) 26 JULY 1988 (NOTE ABSTRACT AND COL. 5, LINES 10-19).	1-37

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 21 APRIL 1989	Date of Mailing of this International Search Report 19 MAY 1989
International Searching Authority ISA/US	Signature of Authorized Officer C. WARREN IVY