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(54) Novel heat curable organic resin foundry sand binder process.

(57) A heat curable organic foundry sand binder based upon liquid epoxide or epoxide novolac resin and a latent dicyandiamide or imidazole curing agent, with or without an imidazole accelerator, which may be used as a direct replacement for other "Hot Box" and "Warm Box foundry resin binders.

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NOVEL HEAT CURABLE ORGANIC RESIN FOUNDRY SAND BINDER PROCESS

The invention relates to epoxide or epoxide novolac resins mixed with a latent curing agent, with or without an accelerator, cured by heat for the production of foundry sand molds and cores. It is common practice to refer to these heat curable resin binders as "Hot Box" or "Warm Box" binders since the core box or pattern must be heated to affect curing of the sand, resin, curing agent and accelerator mixture.

The "Hot Box" and "Warm Box" processes utilize sand coated with a thermosetting resin in liquid form and a latent curing agent in liquid or dry powder form. This mixing of sand, resin and curing agent is done at ambient temperature. A metal pattern or core box is then heated to a temperature of 200 to 300 degrees C. and the damp mixture of sand, thermosetting resin binder and latent curing agent is applied to it by dropping or by fluidization with air. After a period of a few seconds to several minutes, the pattern or box is inverted or opened. The sand, resin and curing agent mix has now sufficiently hardened so that the mold or core can be handled and stored for later use in the metal casting process. The "Warm Box" process operates at somewhat lower temperatures than the "Hot Box" process.

This type of process is widely used in the foundry industry to make metal castings of high dimensional tolerance. A disadvantage of the "Hot Box" or "Warm Box" process is that the preferred resins are Phenol/Formaldehyde, Urea/Formaldehyde or Furfuryl Alcohol/Formaldehyde or combinations thereof. Formaldehyde is considered to be a toxic material by nearly all industrial nations. There is also a pungent odor generated during the making of the core or mold as well as during metal pouring and shakeout. The problem of toxic materials and/or obnoxious odor exists with most current "Hot Box" and "Warm Box" processes.

It is desireable to have a resin binder system that can be used in a similar manner to the "Hot Box" or "Warm Box" processes without exhibiting obnoxious odors or containing toxic materials such as formal-dehyde. It is further desireable that the said new resin binder process have the same physical strengths and performance benefits as the existing "Hot Box" and "Warm Box" resin binders, thereby allowing for the utilization of the new resin process with existing equipment and tooling.

Epoxide and epoxide novolac resins cured by dicyandiamide with or without an imidazole are used in the aerospace, automotive, electronic, coating and adhesive industries. The cured epoxies are inert, non-toxic polymers. They are not chemically reactive and remain as very stable compounds. There is no presence of formaldehyde or other toxic materials.

It has now been found that a heat curable sand, resin and curing agent mix can be produced utilizing an epoxide or epoxide novolac resin and a latent curing agent with or without an accelerator.

According to the present invention, there is provided a sand, resin, curing agent and accelerator composition comprising a medium to high molecular weight epoxide resin, an epoxide novolac resin, or, a mixture of the two, both having an epoxide equivalent weight of 150 to 250; a latent heat curing agent such as dicyandiamide or an imidizole; and possibly an imidazole accelerator. Certain imidazoles will affect the curing of epoxides without the presence of dicyandiamide. These mixtures will quickly harden when exposed to heat.

Accordingly, to produce a flowable sand, resin, curing agent and accelerator mix, it may be necessary to dilute or dissolve the resin, curing agent or accelerator in a solvent such as propylene carbonate, methylglycol, methoxypropanol, methyl lactate or butyl lactate. The resin/diluent solution is applied to the sand at 0.5 to 5.0 percent by weight of the sand. The heat curable latent curing agent and accelerator may be applied to the sand in liquid (with diluent) or powder form at 2.0 to 25.0 percent by weight of the resin. The resulting damp sand mixture is now ready for use by heating it to temperatures in excess of the curing agent and accelerator activation temperature.

In all cases, various accelerators can be used such as modified or unmodified imidazoles, including, but not limited to 2-methyl imidazole, 2-phenyl imidazole and 1-H-imidazole.

The following examples will serve to illustrate the invention.

EXAMPLE A

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A sand mixture was prepared having the following composition by weight:

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98.2 %	Silica Sand AFS Grain Fineness Number 90	
1.5 %	Liquid Resin -	
	80 % Dow DER 331 Epoxide Resin	
	20 % Propylene Carbonate Diluent	
0.3 %	Powder Curing Agent -	
	100 % Dicyandiamide	

The sand mixture was blown into an AFS Standard Tensile Strength Specimen Core Box which had been heated to 150 degrees C. The test core required 2 minutes of curing time after which it had sufficient strength to be removed from the core box. No odor or smoke were present during the curing cycle. The 24 hour tensile strength of the cured sand core was measured as being over 350 pounds per square inch (over 25 Newtons per square centimeter). The mixed sand was stable for over 1 week at room temperature with no loss of performance.

EXAMPLE B

20 A sand mixture was prepared having the following composition by weight:

98.2 %	Silica Sand AFS Grain Fineness Number 90		
1.5 %	Liquid Resin -		
	40 % Dow DER 331 Epoxide Resin		
	40 % Dow DER 431 Epoxide Novolac Resin		
	20 % Propylene Carbonate Diluent		
0.3 %	Powder Curing Agent -		
	100 % Dicyandiamide		

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The sand mixture was blown into an AFS Standard Tensile Strength Specimen Core Box which has been heated to 150 degrees C. The test core required 1 minute of curing time after which it had sufficient strength to be removed from the core box. No odor or smoke were present during the curing cycle. The 24 hour tensile strength of the cured sand was measured as being over 350 pounds per square inch (over 25 Newtons per square centimeter). The mixed sand was stable for over 1 week at room temperature with no loss of performance.

40 EXAMPLE C

A sand mixture was prepared having the following composition by weight:

45	98.3 % 1.5 %	Silica Sand AFS Grain Fineness Number 90 Liquid Resin - 40 % Dow DER 331 Epoxide Resin
50	0.3 %	40 % Dow DER 431 Epoxide Novolac Resin 20 % Propylene Carbonate Diluent Powder Curing Agent - 80 % Dicyandiamide 20 % 2-Methyl Imidazole

The sand mixture was blown into an AFS Standard Tensile Strength Specimen Core Box which had been heated to 150 degrees C. The test core required only 30 seconds of curing time after which it had sufficient strength to be removed from the core box. No odor or smoke were present during the curing cycle. The 24 hour tensile strength of the cured sand was measured as being over 350 pounds per square

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inch (over 25 Newtons per square centimeter). The mixed sand was stable for over $\frac{8}{2}$ hours at room temperature with no loss of performance.

5 EXAMPLE D

A sand mixture was prepared having the following composition by weight:

10	98.475 %	Silica Sand AFS Grain Fineness Number 90
10	1.5 %	Liquid Resin -
		40 % Dow DER 331 Epoxide Resin
		40 % Dow DER 431 Epoxide Novolac Resin
		20 % Propylene Carbonate Diluent
15	0.075 %	1-H-Imidazole

The sand mixture was blown into an AFS Standard Tensile Strength Specimen Core Box which had been heated to 150 degrees C. The test core required only 15 seconds of curing time after which it had sufficient strength to be removed fromt he core box. No odor or smoke were present during the curing cycle, The 24 hour tensile strength of the cured sand was measured as being over 350 pounds per square inch (over 25 Newtons per square centimeter). The mixed sand was stable for over 8 hours at room temperature with no loss of performance.

Claims

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- 1. A sand mixture composition consisting of 0.5 to 5.0 % by weight of an epoxide resin having an epoxide equivalent weight of about 150 to 500, particuarly to 250; 0.01 to 1.0 % by weight of a latent heat curable curing agent; and the ballance being a clean dry foundry sand.
- 2. A sand mixture composition according to Claim 1 wherein the epoxide resin may be an epoxide novolac resin or a blend of epoxide resin and epoxide novolac resin.
- 3. A sand mixture composition according to Claim 2 wherein the epoxide resin and/or epoxide novolac resin may be diluted with a solvent such as propylene carbonate.
- 4. A sand mixture composition according to Claim 3 wherein the latent heat curable curing agent is Dicyandiamide.
 - 5. A sand mixture composition according to Claim 4 wherein the latent heat curable curing agent may be accelerated by an Imidazole such as 2-Methyl Imidazole, 2-Phenyl Imidazole or 1-H-Imidazole.
 - 6. A sand mixture composition according to claim 3 wherein the latent heat curable curing agent is an Imidazole such as 1-H-Imidazole.
 - 7. A method of making bonded sand foundry cores or molds utilizing the sand mixture compositions according to Claims 1 through 6.

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