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Sand Binder Systems

Technical Paper

ASK CHEMICALS

Part VII: ACID Catalyzed PNB and Blown No-Bake

Seventh of a 13-part series filled with useful and up-to-date information about sand binder systems.

The Phenolic No-Bake Process

Introduced around 1960. They found some acceptance in large casting applications because of their excellent hot strength and low resin cost, but compared to the more reactive furan binders, they did not capture much market share. A sequence of events occurred in the late 1960s to change that. The shortage of furfuryl alcohol caused foundrymen to seek an alternative to the furan no-bake system just as sulfonic acids were being combined with phenolic resins to suddenly make the phenolics a much improved no-bake binder.

PNB is typically chosen in applications in which a high hot strength, low cost no-bake is needed.

The Resin

Phenolic resin is resole-based, meaning that it has more formaldehyde than phenol on a mole ratio basis. It usually contains 10–25% water. It is relatively viscous, and thickens when stored for prolonged periods of time, especially at elevated temperatures. The resin can be stored for 3–4 months at 60°F, 1 1/2–2 months at 80°F, and storage is not recommended at temperatures greater than 95°F. Table 1 (see Fig. 1) is a typical viscosity/temperature curve for “fresh” phenolic no-bake resin. The phenolic resin requires a strong sulfonic acid to properly cure. Table 2 presents work and strip times with various catalysts, as well as the immediate and ultimate tensile strengths achievable with the PNB system using various catalysts.

The typical properties of the phenolic resin are outlined in Table 3.

Fig. 1:

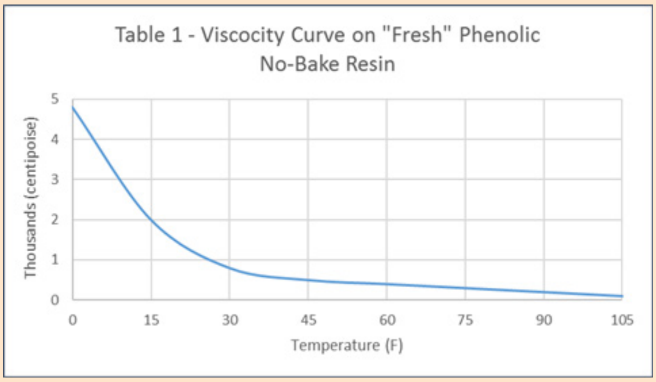

Table 2 - Suggested Sand Mix

Sand:	Wedron 540			
Resin:	1.25% (Based on Sand)			
CHEM-REZ™ Catalyst:	40% Typical BSA	40% BSA/TSA	40% Strong TSA	40% Typical TSA
Work/Strip (min)	19/26	30/40	35/45	46/61
Tensile (psi) @ 1 hr	143	104	109	70
Tensile (psi) @ 3 hr	238	218	277	187
Tensile (psi) @ 24 hr	285	285	322	232

Table 3: Typical Physical Properties

Viscosity, (fresh material), cps	100-150
Pounds per gallon	10
pH	7.0 Typical
Flash Point (°F)	>201
Nitrogen, %	0.4 Typical
Water, %	15 Typical
Color	Clean, Clear Amber to Red

PNBs require special processing considerations for the following reasons:

- The phenolic no-bake resin is relatively low in reactivity relative to the furan no-bake resin. It is therefore slow to strip and difficult to cure, especially at low ambient temperatures.
- The sluggish reactivity requires the use of relatively strong sulfonic acid. The use of milder, less corrosive 75% or 85% phosphoric acid is not recommended.
- Blending other types of acid, such as sulfuric, can lead to the corrosion of storage devices. It will also produce sulfur emissions, and subsequent sulfur pick-up on casting surfaces.
- Sand heaters are a necessity to facilitate coating the sand and mixing binder system components.
- The resin's already high viscosity increases during storage, i.e., the binder has limited storage life, especially in warm conditions.
- The viscosity climbs dramatically when the temperature drops below 70°F.

Operational Considerations

Both batch and continuous mixers may be used with PNB systems.

Because of the high viscosity of the phenolic resin and it's even higher viscosity when stored for extended periods, particular attention should be paid to the resin temperature, size and temperature of resin delivery lines, and pumping capabilities.

As is the case for all acid catalyzed no-bakes, in order to achieve ultimate strength characteristics, the coated sand should always be used as soon as possible after mixing.

Strip times can vary from 5 min. to more than 2 hr., depending on the combination of resin, catalyst, additives and temperature.

A properly acid catalyzed phenolic no-bake will turn reddish pink when curing. If the sand has changed color significantly before it has been worked into place, unsatisfactory properties will result.

Since flowability of the acid catalyzed phenolic no-bake is relatively poor, even under ideal conditions, it should be used with a compaction table and given extra tucking and ramming.

Environmental Considerations

Any binder constituent that affects the disposal and re-use of foundry sand is an important issue. Samples of PNB sand (both cured and shakeout sand) were evaluated under the Toxicity Characteristic and Leachate Procedure (TCLP) as prescribed by U.S. Environmental Protection Agency (USEPA) regulations. Samples were analyzed and the data reported for phenol are listed in Table 4.

Table 4 - TCLP Phenol for PNB

Parameter	Cured Resin on Sand w/TSA	Shakeout Sand w/TSA	Cured Resin on Sand w/BSA	Shakeout Sand w/BSA
Phenol (TCLP), mg/l	< 0.068	< 0.050	< 0.068	< 0.050

The PNB binder system tested was found not to have leachable levels of any material in excess of EPA regulatory limits. It should be noted that phenol is not regulated under federal TCLP regulations, but is generally regulated at the state level. The data indicate that the amount of leachable phenol from the PNB was below detectable limits. But for beneficial re-use of foundry sand the phenol levels must be below the state regulatory level. Therefore, specific state and local regulations on phenol should be consulted. It's a good idea for all foundries to have their waste sand tested to determine leachate values.

Aggregate Considerations

Silica sand in all AFS/GFN ranges is generally used without any problem. Lake and bank sands are useable, but attention must be paid to the acid demand value (ADV). Contaminants that might affect the surface chemistry of the sand, necessitating an appropriate adjustment to the catalyst level, must also be identified. Chromite and zircon sands are utilized for specialized casting purposes without any problems. Olivine sand, because of its alkaline nature, is not recommended.

Reclamation

PNB is acid catalyzed. Thus, mechanical reclamation of PNB coated sand will probably result in sand with a negative ADV. This may necessitate catalyst adjustments and may preclude the use of this system in twin screw and ribbon flow mixers in which there is not complete discharge of the coated sand from the machine when it is turned off. Inorganic components left in the sand after mechanical reclamation, such as sulfur from sulfonic acid, can pose unique mechanical reclamation problems.

Thermal reclamation can also create special problems. Lake and bank sands usually contain a significant amount of carbonates from sea shells and other residues in the sand. These materials are likely to be converted into highly alkaline, water (and acid) soluble lime by the heat from the casting process and through exposure to the thermal reclamation process temperature. Therefore, reclaimed sand must be closely monitored for changes in ADV and adjustments made to the catalyst to compensate as necessary.

The temperature of the sand discharged from both mechanical and thermal reclaimers needs to be monitored and controlled. Remember that temperature is just as important a system operating parameter as the catalyst itself.

Loss on Ignition (LOI)

The LOI test is a measure of the amount of combustible materials and moisture present in the raw, coated, or reclaimed sand. The LOI of raw sand indicates the amount of combustible materials and moisture present. LOI of coated sand indicates the amounts of binder, catalyst, and, sometimes, additives present in the sand. The LOI of reclaimed sand measures the amount of combustible materials remaining on the sand after reclamation. The best value for the LOI of reclaimed sand is zero, but less than 2% is generally acceptable. Higher-than-normal LOI values indicate the presence of excessive gas, producing residual materials in the reclaimed sand. This can lead to a number of operational and casting defect problems.

Temperature Control

Phenolic no-bakes run better at higher temperature than at lower temperatures. The ideal operating temperature is 85–100°F. At temperatures below 70°F the binder's viscosity increases and the already sluggish chemical reaction becomes even slower. The upper, normal operating temperature should not exceed 100°F. Considerable work time is lost and subsequent compaction problems are encountered when the temperature exceeds 110°F.

Pattern temperature control is an especially important consideration in phenolic no-bake core/mold making. Metallic pattern inserts are cause for special concern. Since the catalyst might freeze at a relatively high temperature and the resin viscosity builds-up quickly when stored above 90°F, liquid process materials should be stored in a temperature regulated area in summer and winter. A well-insulated or specially constructed compartment equipped with a room heater/air conditioner can serve this purpose.

PNB vs. FNB

Acid-catalyzed phenolic no-bake systems are not normally considered a good substitute for the quick setting phenolic urethanes, but can be a viable alternative to agriculturally based furan systems. However, when a phenolic no-bake is used instead of a furan no-bake, the process needs to be run with care and all of the process parameters need to be carefully controlled.

The Shortage of Furan Resins

The foundry industry utilizes two types of acid catalyzed no-bake binders to produce castings– furan (FNB) and phenolic (PNB). Phenolic no-bake is a petroleum based product. Furan no-bake is based on furfuryl alcohol, which is derived from agricultural by-products such as corn cobs, oat hulls, cottonseed hulls, bagasse, etc. When no-bake foundrymen select a binder based on material handling, core/mold making, and casting properties, a furan-type will usually be chosen. However, when the choice is driven by something like a material shortage the system that is not in short supply is generally selected. When this article was originally written (1990s), the world's metalcasters were facing a furfuryl alcohol shortfall of 20 to 40%.

The foundry industry is no stranger to shortages of furan-based resins. The first occurred in the late 1960s, resulting in oil-urethane no-bakes gaining significant market share. Another shortage in 1975 gave a boost to the relatively new phenolic urethane cold box and no-bake systems. Many large casting producers switched, at least temporarily, from furan no-bake to phenolic no-bake binders.

Occasionally the worldwide supply of furfuryl alcohol grows tight for all users of furan based products. Where furan no-bake binders are the resin systems of choice, there are typically shortages that can last for a year or two.

This shortfall will prompt many users of furan-based foundry resins to switch to an alternative binder system. Phenolic hot box, or another core making process is an alternative for users of furan hot box and warm box, but the obvious binder system replacement for producers of large ferrous castings will be phenolic no-bake or perhaps more logically a phenolic modified furan system.

The Blown No-Bake (BNB] Core/Mold Process

Where the number of cores needed exceed the capacity of a standard no-bake process, or when a conversion from shell, core oil, or hot box is in order, the BNB process is a viable alternative. It can make cores and molds in simple tooling at production cycles that rival any resin bonded core/mold making process.

BNB, originally introduced in Europe, came into North America at the AFS St. Louis Casting Exposition in 1980. It was one of the big innovations in core making, with machines displayed by various manufactures who all had their own name for the process: Baker Perkins FAS CORE, Shalco BLO-SET, Dependable Fordath. Eventually, Beardsley & Piper introduced a machine that blew 8 pounds of coated sand, along with a 25 pound capacity unit, and became known as The ABC Process. Later on, equipment had been introduced by Redford Carver under the name of The Simple Advantage.

An interesting piece of equipment for blowing no-bake resin coated sand into a foundry pattern was displayed by Loramendi at a GIFA Exposition in Germany. Their equipment consists of a reinforced steel vacuum chamber fitted with doors on the front and back along with a coated sand hopper located on the roof of the chamber. The hopper connects through the top of the chamber by a pipe to a clamping mechanism that attaches against the top of a pattern when it is rolled into the chamber. Once sufficient vacuum has been attained in the cavity, a valve is actuated in the pipe allowing the coated sand to be forced into the tooling by high volume, low pressure compressed air. At the completion of the fill cycle the pattern is removed and a box-like tray is moved under the discharge pipe to receive any residual sand from the magazine. This blown vacuum assisted fill technique enables complex tooling to be uniformly filled and compacted with the coated sand without the need for a blow magazine or a plunger-like device to supplement the blowing operation.

Blowing No-Bake Sand

Since blowing a catalyzed no-bake coated sand does not require a gassing cycle to cure, it eliminates not only that step, but also the necessity to capture, neutralize, and dispose the flammable gas addition. Not having to handle, use, close capture, neutralize, and dispose of a highly flammable, odorous, vaporized amine catalyst has provided new environmental and ecological incentives. In addition, the humidity resistance of the liquid catalyzed PUNB is better than that of its cold box counterpart.

The Trick of Blowing No-Bake Sand

Blowing cores and molds with no-bake binders has been attempted since the binders' inception of the no-bake process. But it was not until a high speed catalyst system was developed for the PUNB that it became practical from the quality and productivity standpoints.

This left the problem of blowing a uniformly dense core. It was discovered that a uniformly dense core could only be made if some excess sand was used. Thus, a necessary and important part of achieving uniform fill with the blown no-bake coated sand consists of having some excess sand sitting over the blow ports in the tooling after the blow has been completed. Of course, this residual sand has to be removed, which is a negative aspect of the process.

Techniques for Blowing No-Bake Sand

Any no-bake sand can be used to produce cores and molds by blowing the coated sand into the tooling, but no-bake binder systems suffer significant degradation of physical properties when they are over catalyzed. Although phenolic urethane systems suffer some loss in strength and humidity resistance when they are hyper-catalyzed, they withstand the effects of hyper-catalyzation better than other no-bake systems.

In producing BNB cores and molds the sand can be split into two equal streams for coating. One part is coated with Part I and the other with Part II of the phenolic urethane binder system. The two streams of hyper-catalyzed coated sand are brought together in a special high speed mixer and, after mixing for a short time, dropped into a blow-type of magazine for introduction into the pattern. The transfer of the sand into the tooling can be aided with a plunger, as it is in the ABC Process, or simply blown into the pattern, as it is in the Simple Advantage Process or aided with a vacuum as in Loramendi's Blown Vacuum Assisted/Atmosphere Process.

It is also possible to use a high speed turbo, zero retention mixer and coat with both binder parts simultaneously. This is the coating technique utilized by the Simple Advantage process.

As previously mentioned, in order to achieve a uniformly dense core or mold an excess of sand must be used in the blowing process. This has to be removed at the completion of the blow cycle.

Comparing No-bake, Cold Box and Other Systems

With respect to tooling wear, BNB core blowing is advantageous because the process fills the pattern cavity utilizing very low sand blow pressure. This is made possible because the sand in the blow magazine of ABC machines is first fluidized. Then it is forced into the pattern cavity by gravity, pressure, and a vented plunger mechanism. Note that not all BNB core blowers utilize plungers. The Simple Advantage machine, for example, employs a plungerless design.

The non-aggressive entry of sand into the tooling permits the use of abrasively vulnerable wooden patterns as well as more durable aluminum tooling. Old, tattered tooling cannot normally be adapted to gas curing in the cold box process without high cost. Since the BNB process does not need a gassing cycle, it obviates the need for a multitude of strategically located vents, along with the necessity to capture the gas and subsequently neutralize and dispose of it.

In addition, the humidity resistance of liquid catalyzed, phenolic urethane no-bake is better than that of its cold box counterpart.

Advantages of BNB

With the BNB process foundrymen can quickly produce cores and molds by blowing coated sand into simple patterns of wood, aluminum, or any other tooling material. Utilizing the liquid amine-type catalyst to hyper-catalyze the phenolic/urethane no-bake reaction offers a unique, versatile alternative to all current high production blown cold box systems.

The BNB process, when first introduced into the foundry industry, was limited to small cores and molds. Then larger machines increased core blowing capacity to 150 lbs. Eventually, innovative foundry engineers increased blow capacity to 250 lbs. and added a multiple blowing sequence to enable cores and molds of any size to be produced. Thus, the only real limit on size was the capacity of the tooling and handling equipment. This multi-blow feature is especially useful when making both small and large cores on the same machine.

In its early stages, the BNB process suffered from a number of equipment related sand coating and mixing problems. This inhibited its immediate industry wide acceptance. Over the years the equipment has been modified and drastically improved. More efficient mixers, better control devices, and improved core and mold handling designs are the most noteworthy improvements

If there is one nagging problem that still accompanies the process, it is that the blow weight must always be more than the actual weight of the sand required to fill the core box to ensure that adequate density is achieved throughout the core. Excess coated sand must then be removed from over the top of the tooling and from the blow system, if any remains there.

No-bake core blowing equipment has been slowly, but continually, emerging as an alternative to producing cold box cores and molds with the phenolic urethane, phenolic/ester and sodium silicate/CO2 cold box processes.

Process Differences

With the exception of its specially formulated catalyst, the BNB system is identical to the standard phenolic urethane no-bake (PUNB) system (discussed previously in Part IV of this series).

In terms of chemical components and resin handling requirements all phenolic urethane systems are quite similar. The casting performance, shakeout and reclamation properties are the same.

The difference between BNB, cold box, and standard no-bake versions is to be found in the catalysts and the process use of the coated sand. The cold box version utilizes vaporized amine catalyst and a buffered resin that enables extended bench life. The no-bake version uses a liquid catalyst that is blended into the resin when the sand is coated and, although it has a unique latent curing reaction, is intended to be used immediately after coating.

Although the cycle speed of BNB can match or exceed that of cold box, it is generally set-up to blow only one or two cores per cycle (compared to ten or even more for cold box), and is rarely fitted with the expensive automated core removal equipment found with phenolic urethane cold box core machines.

Since the cores are usually handled by the machine operator the process is considered labor intensive and, in effect, functions at the speed of the machine operator removing the core from the pattern.

The most noteworthy similarity of the two processes is that they can make uniformly dense cores rapidly using binders that react very quickly and rather predictably based on temperature and exposure to their particular catalyst. The biggest single difference between the cold box processes and the BNB process is found in the tooling and rigging. Coated sand from the newer cold box process is blown into a relatively sophisticated and expensive core box, usually made of iron, and equipped with ejector pins, blow tubes for introducing the sand, and strategically located vents to allow entry, dispersion, and exhaust of the amine curing gas. BNB tooling is usually wood or aluminum and free of vents.

Past, Present and Future

In the past, many foundrymen tried blowing no-bake coated sand. They found that the method did not profitably deliver the quality and productivity needed. However, improved binder technology, along with specialized core machines, drastically improved mixing, and innovative core handling equipment, remedied many of the shortcomings of the early trials. With new equipment, better resin systems, and increased environmental benefits, the process of blowing no-bake coated sand has been found to cleanly, reliably, and profitably produce quality cores and molds.

References

Fig 1 - ASK owned picture

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