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Sand Binder Systems

Technical Paper

Part IV: Urethane Binders (Continued)

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

This article continues the discussion about urethane no-bake. Environmentally related improvements to the polyether-polyol-urethane system and the phenolic urethane no-bake are covered in detail.

Solvent-Free Polyether-Polyol-Urethane No-Bake

In Part III of this series we began the discussion about urethane-type no-bakes. Oil-urethane and phenol-free, polyether-polyol-urethane systems were covered. The previous section also made reference to a "special version" of the polyether-polyol-urethane system that has been formulated to be virtually free of volatile organic compounds (VOCs). It is appropriate to elaborate on this system for two reasons. The first is the outstanding potential that this new, relatively unrecognized system has in aluminum casting applications. The second is the high ecological merit of the system based on the absence of phenol and formaldehyde in the binder. It also uses reactive diluent solvents that polymerize along with the binder, resulting in very low to zero reportable VOC emissions during core and mold production.

The polyether-polyol-urethane no-bake is a three-part system composed of a polyol resin (Part I), a coreactant MDI-type isocyanate (Part II), and an amine-type catalyst (Part III). Unlike the other amine-catalyzed polyols discussed last month, which can be used for any non-ferrous application, or the phenolic urethane no-bake system discussed below, which can be used to cast virtually any metal, this binder system is designed specifically for aluminum alloy applications.

A Plastic Tooling Advantage: Plastic tooling is a viable alternative to wood and metal, and its use is becoming more prevalent. However, one of plastic's limitations is its less-than-perfect solvent resistance to the strong organic solvents present in urethane binder systems. Utilizing a solvent-free system can increase both the life expectancy and dimensional accuracy of plastic tooling.

Special Handling Considerations: The unreacted Part I liquid polyol material, unlike other urethane no-bake systems, and the Part II isocyanate material just like other urethane no-bake systems, are both very hydrophilic. They must, therefore, be protected from exposure to moisture during storage and use.

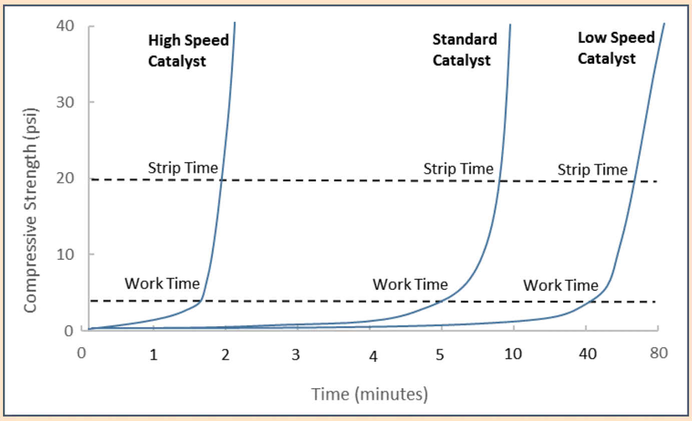
Because this system uses a minimum of the reactive diluent solvent it has a higher viscosity relative to standard PUNB systems. Therefore, any physical property that relates to resin viscosity, such as pumping, sand coating, and coated sand flowability is affected.

The Phenolic Urethane No-Bake System

Phenolic urethane no-bake binders (PUNB) were introduced at the 1970 AFS Casting Congress and Exposition in Cleveland. Since then, they have grown to be among the bestselling binder systems in North America, and are becoming a more significant factor in the production of precision metal castings globally.

The standard PUNB binder system has three components: Part I is a phenolic polyol dissolved in organic solvent; Part II is a polymeric MDI-type isocyanate dissolved in solvent; and Part III is an amine-type catalyst, which regulates the speed of the reaction between Parts I and II, as shown in Fig. 1.

Fig. 1 - Effect of catalyst type on compressive strength buildup for phenolic urethane binders.



Part I, when reacted with Part II, results in the formation of phenolic urethane polymer. It is the phenolic structure that gives this system enough hot strength for use in all types of metal casting applications. When the term "urethane no-bake binder" is mentioned, the PUNB system is the one foundrymen are almost always referring to.

The chemical reaction of PUNB is so controllable, quick, and complete that the liquids actually can be mixed in a cup and "frozen" in the air as it is poured from the mixing container (see Fig. 2). When mixed on sand, the sudden and complete hardening of the coated sand is almost as dramatic.

Fig. 2 - Quick setting PUNB frozen in mid-air.

PUNB systems are noted for their unique, delayed curing mechanism. This enables the catalyzed, resin-coated sand to be free flowing up until the time that its chemical reaction starts, and almost until the time that it's ready to be stripped from the pattern. In other words, the catalyzed sand mix remains flowable and workable until just before the desired strip time. The inherent strength of the polymer and the delayed curing mechanism combine to enable the total PUNB binder level to typically run between 0.8% and 1.75%, based on sand weight.

The chemical reaction between Parts I and II forms a urethane bond and no other by-products. Consequently, strength develops uniformly throughout all section thicknesses, with the thin sections curing at the same rate as the thick ones. The fact that air is not required for curing (the way it is needed to oxidize the oil/urethane alkyd-type resin), makes the PUNB system well suited to rapid no-bake core and mold production cycles.

The PUNB system offers so much speed and application flexibility that it may be the only system that a no-bake foundry, ferrous or nonferrous, would need to satisfy all of its core and mold making requirements. Mixer throughput is the usual deciding factor that determines minimum and maximum core sizes for a given operation.

A swivel mixer running a PUNB system could have the capability to handle a medium-sized flaskless mold line right next to a flasked floor mold requiring tons of PUNB sand. Both molds would use the same resin system and reclaimed PUNB sand, with only adjusting the catalyst level to meet the work time needs of each pattern.

Offsetting the Ratio of Parts I and II

PUNB no-bakes are formulated to operate with one weight unit of Part I reacting with an equal amount of Part II. However, it is common procedure to favor Part I to Part II so that more Part I is used. Ratios are commonly offset from 52.5:47.5 up to a ratio imbalance of 60:40.

This is done because Part II contains virtually all the nitrogen in the system. Part II is also a significant contributor to lustrous carbon defects, as it contains considerably more carbon than Part I. Thus, to reduce both nitrogen and lustrous carbon defects, Part I is favored in the system. The use of excess Part I does not occur without paying some penalty in terms of system performance. As more Part I than Part II is used, the ultimate tensile strength decreases.

PUNB Catalyst

The use of a liquid amine-type catalyst as a third component results in a system with outstanding versatility and flexibility. Using different catalyst types, concentrations, and amounts, strip times from less than a minute to over an hour can be achieved. This wide range of work and strip times enables both very large and very small molds and cores to be made from the same mixer.

The catalyst level is based on the weight of Part I. Depending on the catalyst type and strip time required, normally 2–9% catalyst is blended into the resin. When process conditions require that the catalyst addition falls outside of this range, a catalyst with different reactivity should be substituted.

Because the amount of catalyst is relatively small and needs to be accurately metered on a real time basis, it is recommended that a metering, pump accurate to ±1% be used to control its addition.

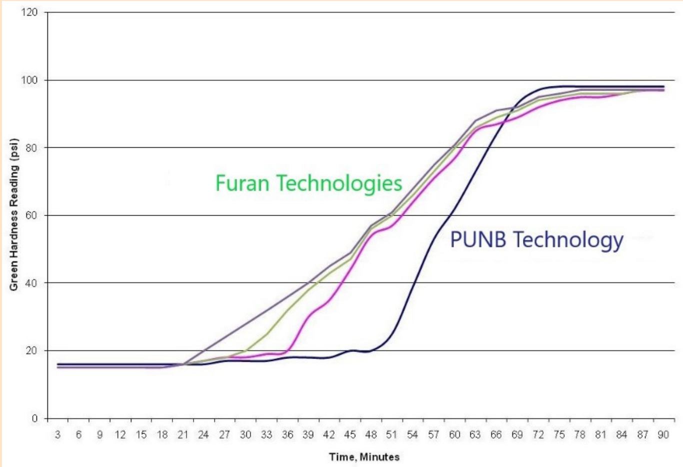
The most effective way to insure even catalyst distribution is to introduce it into the Part I resin feed line close to the discharge into the mixer. This preblending dilutes the small amount of catalyst and avoids hot spots and soft areas in the mixed sand.

"Latent" Curing

When the system's three parts are mixed and combined with the sand, there is a short delay followed by a controlled rapid cure. This unique delayed curing mechanism, known as "latent" curing, or delayed polymerization, enables the sand mix to be free flowing until just before the core/mold is ready to be removed from the pattern.

A high worktime/striptime ratio produces greater productivity and faster pattern turnaround. The time that the PUNB system can be worked and compacted in the pattern can be as much as 75% of the time before it is ready to be stripped from the pattern. Fig. 3 shows the strength development comparing PUNB to the acid-catalyzed furan no-bake binder systems, the difference between the almost instant reaction of the acid-catalyzed furan and the PUNB's delayed polymerization demonstrates the unique and advantageous aspect of the PUNB system.

Fig. 3 – Comparison of strength development of no-bake systems.



Solvent Carriers

Standard PUNB contains about 35% organic solvents. Solvents are necessary to minimize the viscosity of Part I and to facilitate its blending with Part II– especially when the Part I temperature is less than 70°F. Solvents influence physical properties other than those related to mixing, such as odor, smoke evolution, and flash point. Solvent type and amount also contribute significantly to the system's VOC emission.

High Strength/Low Carbon and Nitrogen PUNB

Resin manufacturers have developed a special PUNB system that has higher strength, better flowability, and better shakeout; contains less free formaldehyde and nitrogen; generates lower smoke; and has less odor than standard PUNB. The system has three components, like the standard version, but utilizes a ratio of 70:30. The binder is similar to the standard system in virtually all coating and material handling characteristics.

Process Considerations

Sand Effects: PUNB systems can be used with almost any foundry core sand. Like all coated sands used in the foundry, the physical characteristics of the sand, such as screen distribution, grain fineness number, and grain surface characteristics are important determinants of flowability, compacted density, and strength. Since the system is an alkaline catalyzed and cured system, very high and very low ADV sands are a consideration in long work and strip type applications. Cure and strip times are speeded up with alkaline sand conditions and slowed down with acidic conditions. However, any type of sand, even very basic sand (such as olivine), can be utilized if appropriate adjustments are made to additives or binder formulation.

Normally, a curing rate change that results from switching sand types is easily corrected by a change in the amount or type of catalyst. In extreme situations, when mechanically reclaimed sands with a highly acidic or alkaline residue are to be recoated with a PUNB system, catalyst changes will normally take care of the situation. However, as is the case for very basic olivine sand, resin system chemistry can be altered by means of additives or a formulation change.

Sand Temperature: This has a drastic effect on PUNB work/strip and curing times, as it would with any other no-bake binder. Fortunately, the PUNB reaction is easily and effectively adjusted by catalyst addition. However, for dealing with temperature extremes and for consistency, a sand heater/cooler provides an effective alternative to constant and sometimes drastic catalyst adjustments. Recommended sand temperature for the PUNB is 80 to 90°F and should be controlled to ±5°F. Temperatures above 105°F and below 50°F should be avoided.

Sand Moisture: This is a very important consideration. Since water reacts with Part II, it slows down cure speed, strength development, and lowers the worktime/striptime ratio. The effects of moisture were thoroughly discussed in Part 2 of this series, but it still bears repeating, "the lower the sand moisture the better." When sand moisture is greater than 0.2% in the winter, and 0.1% in the summer, serious core/mold problems can result.

High Compacted Density: This is easily achieved with PUNB because of its good flowability characteristics. Nevertheless, because high core/mold sand density is the key to good quality, compaction of the mixed sand by various methods and, in the case of core/mold blowers, special no-bake blowing with the proper minimum blow pressure is very important.

Pattern Stripping

Since PUNB cures very rapidly, the time required for the compacted pattern to enter the stripping operation must coincide with the setup or cure time of the coated sand. The rapid curing of the binder results in a suddenly very hard core/mold surface, and if the sand remains in contact with the pattern surfaces after it has thoroughly cured, it sticks. In other words, the sand core/mold must come out of the tooling while it is still curing and somewhat plastic, or you won't get it out– at least, not in one piece!

A clean pattern surface is essential and the proper application of pattern release agents is very important. With the advent of new environmental regulations, the release agent trend is toward high solids organic and water based chemistries that need to be applied and renewed carefully.

Hand application of release to specific problem areas utilizing a paint mitten with a rubber glove inserted into it, to prevent direct contact of the operator with the liquid, is preferred to routine application over the entire surface. The mitten, beyond placing the release in the right place also wipes away the initial sand build-up, which can lead to real sticking.

How to Treat a New Wooden No-Bake Pattern

The biggest mistake that foundrymen unwittingly make when purchasing new no-bake wooden patterns is to not specify the way that the wooden surfaces are coated and sealed.

Wooden pattern surfaces are historically painted by the pattern maker with various lacquers to seal them and to color code rigging elements like the runners, gates, section to be cast, etc. Different colored paint applied by the pattern maker can provide useful information and can make the pattern look nice! However, from a productivity standpoint it is not a good idea. Nearly every component in a resin system can attack these pattern paints. Thus, from the very first time that sand comes into contact with these coatings it begins to soften and strip them away, resulting in sticking problems and changing the pattern dimensions.

It is better to apply the pattern release system used in production to impregnate, seal, and establish a base for subsequent application of the release on tooling surfaces. Since wood is a porous material, release agents applied to the clean raw wood surface can seep into the wood's grain and provide an excellent anchor for subsequent releases applications. After application, machine buffing or hand rubbing with a paint mitten can further enhance release effectiveness.

Besides applying release agent to the wood surfaces that contact coated sand, it is also a good idea to paint the rest of the pattern, even underneath, with a urethane varnish to dimensionally stabilize the wood and impart wear resistance.

Refractory Coatings

Water-based and light-off refractory coating can be used with PUNB cores and molds. Aqueous coatings can be applied immediately after strip, provided that they are oven-dried immediately.

Light-off coatings are best applied after the core/mold has aged for at least 10 minutes after strip. Exceptions to this are torched and/or oven-dried sand surfaces, along with cores and molds that are "warm" due to a relatively high sand heater temperature.

Refractory coating should never be applied to a cold core/mold surface.

Mixer Types

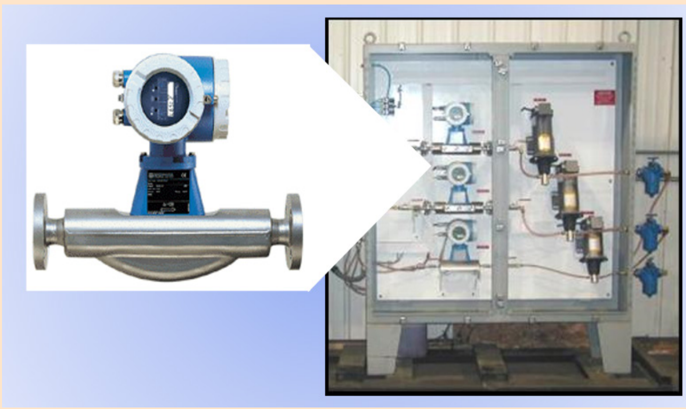
Almost any type of mixer can be used with PUNB. High-speed batch mixers, zero-retention, high-speed continuous mixers, and those with intensifier heads are the most widely used because the catalyzed sand is quickly mixed and discharged with no precatalyzed coated sand being retained in the coating device.

Since the mixing of the sand and catalyzed resin components should take place rapidly, zero-retention mixer designs and the fast strip time of the PUNB are an excellent combination. Further, these mixers are ideal for any type of core/mold production.

Real Time Computer Control of Resin Pumping and Metering

Experience has proven that the best way to optimize resin level, improve core/mold making, and reduce cost is to use a computer to control pumping and metering with batch and continuous mixers (see Fig. 4). Almost every installation of real time computer control has resulted in a payback period of less than one year in resin savings alone!

Fig. 4 – Batch and continuous mixers for pumping and metering control



Humidity Resistance

When any type of resin-coated sand is exposed to high relative humidity, particularly when the relative humidity is greater than 90% in hot weather, resin systems lose significant bonding strength. Cold box phenolic urethane is noted for this apparent loss in strength. Although the no-bake version also suffers from humidity degradation it is not typically cited as a significant problem.

One of the things that leads to humidity degradation is the type of the polymer chain. The longer and more cross-linked the polymer, the better its resistance to humidity degradation. Conversely, the shorter and less cross-linked, the poorer the humidity resistance. Rapid catalyzation rates produce shorter chains with less cross linking. Thus, it is reasonable to expect that an instantaneously polymerized coating, like urethane cold box, would suffer humidity degradation. Further, as long as there is enough catalyst to achieve polymerization, the slower the rate of catalysis, the more humidity resistant and stronger the core/mold becomes.

Additives for Defect Prevention

PUNB binders are used for both ferrous and nonferrous applications. For certain ferrous applications (most commonly steel), the addition of 0.25–3% of red iron oxide or 1–6% of black iron oxide is often added to the sand mix to improve casting surface finish, provide chill, minimize gas-related defects, and control sand expansion defects.

The PUNB resin systems contain about 3.0–3.8% nitrogen, which is about 0.04% based on the sand, and about the same nitrogen content as a high quality, low nitrogen furan no-bake. It has been shown that as little as 0.25% red iron oxide is effective in suppressing ferrous casting subsurface porosity associated with nitrogen in the melt and/or evolved from the PUNB binder.

Iron oxide is also beneficial in reducing lustrous carbon defects associated with the PUNB system. As iron oxide is heated by the molten metal it decomposes and liberates oxygen into the mold cavity. The oxygen combines with carbon released as the binder decomposes to form gaseous CO-type products rather than the sooty carbon, which causes the lustrous carbon defect.

The red iron oxide, hematite, releases proportionally more oxygen than the magnetic, black magnetite. Since hematite liberates oxygen at a faster rate than the magnetite, it tends to be more effective than the black for lustrous carbon control. However, it does not chill as well as magnetite and it requires more resin for equivalent strength.

Proprietary mixtures of carbohydrates, kaolinite clay, and iron oxides are also used with PUNB systems, but the organic carbohydrates can contribute to gas defects.

PUNB Reclamation

The mechanical reclamation properties of PUNB are excellent. Because the coating is relatively brittle, it is easily removed from the surface of the sand by pneumatic or other attrition mechanical reclamation systems.

Thermal reclamation is an excellent way to recycle PUNB no-bake coated sand for producing resin bonded cores and molds in the foundry. Thermal reclamation requires about one million BTUs/ton of sand to effectively remove the resin coating and residues from the sand surface. Organic coatings contribute heat energy to the thermal reclamation based on things like binder level, amount of binder not burned out in the casting process, residual solvent, etc. The latent fuel value of the PUNB can supply up to 75% of the energy required to thermally reclaim the sand.

Most people mistakenly believe that thermal reclamation depends solely on the energy supplied by the heat source of the reclaimer. In thermal reclamation the most important aspect of the reclaimer is for “it to light the fire and then keep it burning efficiently.” Thus, once the binder coating begins to burn the reclaimer adds just enough additional thermal energy and sufficient air to sustain combustion and keep it burning effectively.

For reasons not fully understood at this time, foundrymen report that thermally reclaimed sand can produce phenolic/urethane cores and molds with significantly better humidity resistance than new sand.

Core and Mold Production

Although one of a kind cores and molds can be quickly made with PUNB, the system is used most advantageously when high production of small to medium-sized no-bake cores/molds is accomplished with pattern handling systems.

Turn tables or conveyor loop lines, which maximize quick recycling of the tooling, will be discussed in the next article.

Conclusion

Since their introduction to the foundry industry over 50 years ago, PUNB binder consumption has grown steadily. It offers high strength, predictable stripping, and fast pattern turnaround.

With the constantly improving environmental properties of standard PUNB, the system's ease of reclamation, the introduction of specialized nonferrous urethane versions, and the dimensional predictability of resin-bonded sand cores and molds, PUNB binders will expand and might be considered one of the key elements in the new era of precision sand casting.

References

Fig. 1-3: ASK owned graphics
Fig. 4: Palmer Mfg.

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