Authors: P. R. Carey & J. Archibald

Sand Binder Systems

Technical Paper

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Part X: The Phenolic Urethane Amine Cold Box System

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

Section A

The next two articles examine the phenolic urethane amine cold box (PUCB) process. In Part A, we will cover process fundamentals, resin system components, reclamation properties, environmental considerations, and unique production considerations. Part B will cover the equipment used in the process, tooling and rigging and special applications for PUCB.

History

The PUCB process is the oldest of the organic cold box systems. The term "cold box" is a generic term that was originally understood to mean the PUCB process. However, it is now used to describe any core binder process that uses a gas or vaporized catalyst to cure resin-coated sand while it is in contact with a room-temperature pattern. The PUCB Process was introduced formally to the foundry industry at the 1968 AFS Casting Congress and Exposition. Since its introduction the process and its related equipment have been continually refined, making PUCB the foremost binder system used for large volume, high speed production of cores and molds.

In addition to offering other production and environmental advantages, the cold box processes revolutionized foundry core and mold making because they eliminated the need for expensive, inconvenient heat curing. Cold box binders provide a flowable sand mix that is easily blown into intricate shapes utilizing tooling made of wood, metal, or plastic. The size of the cores and molds produced in the cold box processes is only limited by machine handling capacity. Cores in excess of 5,000 pounds have been successfully blown and gassed on a production basis. Smaller cores with complex configurations are well suited to this type of process since the system has excellent blowability and good stripability. Because of the ambient cure, small, thin sections are not over-cured and burned during the time thicker sections take to cure. It offers foundrymen advantages in terms of dimensional accuracy, productivity, and potentially higher quality than other core/mold systems. All of the cold box processes, except those using CO_2 gas, have the typical blow, gas, purge, and strip coremaking sequence.

The PUCB Process

The process utilizes a three-part binder system consisting of: Part I, a phenolic resin; Part II, a polymeric isocyanate; and a tertiary vaporized amine catalyst.

Sand is coated with the Part I and II resin components. Then the sand is blown with dry air, into a room-temperature pattern. Once in the pattern's cavity, a tertiary amine catalyst is vaporized and introduced through openings in the pattern to harden the coated sand. After quickly hardening the resin the amine catalyst gas cycle is flushed from the sand mass by a dry air purge that forces the amine vapor through the coated sand mass and out of the hardened core. After exiting the tooling the amine is piped through exhaust piping to a scrubber where it is converted into an acid salt. The acid salt can then either be disposed of, or chemically processed back into recycled amine.

Key factors for optimum utilization for the amine used in the PUCB process are:

- Concentration of the curing gas (typically 6–12% in the carrier gas).
- Volume of catalyst gas and purge air.
- Size of gas and purge lines.
- Temperature of catalyst and purge air.
- Tooling venting and sealing.
- Exhaust area.
- Direct exhaust from the exhaust plenum to the scrubber.

The concentration of curing gas produced by the particular generator design can be calculated by the generator supplier and is furnished with the equipment. The specific concentration will vary depending on the catalyst type used and its operating pressure and temperature ranges. Too little catalyst causes under-curing and scrap cores. Excessive catalyst results in waste and added cost, in addition to making cores with an objectionable residual amine odor.

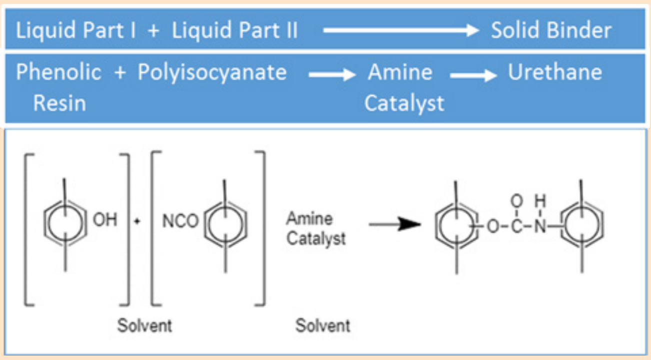
Although there have been other catalysts used in the PUCB process, such as trimethylamine (TMA) and dimethylisopropylamine (DMIA), they are now rarely used.

Liquid amine can be supplied in 5 gallon pails or 55 gallon drums, but the safest and most convenient way to handle the material is in 110 gallon pressurizable cylinders. The cylinders can be returned for refilling after use.

Chemistry and Curing Mechanism

The reactive component of the PUCB Part I is phenolic resin. It is dissolved in solvents to yield a low viscosity resin solution to facilitate coating the sand and blending it with the second component. Part II is a polymeric MDI-type isocyanate that is also blended with solvents to form a low-viscosity resin solution. The hydroxyl groups provided by the Part I phenolic resin react with the isocyanate groups in Part II in the presence of the amine catalyst to form the solid urethane resin shown in Fig. 1. It is the urethane

Fig. 1: Hydroxl groups provided by the phenolic resin in the Part I react with the isocyanate groups of the Part II in the presence of an amine catalyst to form a solid urethane resin.



The Part I resin contains less than 1% water, while the Part II component and the amine catalyst are water free. The urethane reaction does not produce water or any other by-product. The system contains 3–4% nitrogen, which is introduced from the Part II polymeric isocyanate. The organic resins and solvents in the PUCB system make it high in carbon content and result in a reducing atmosphere in the mold cavity during the pouring. This high carbon content contributes to good casting "peel." Unfortunately, excess carbon could result in lustrous carbon defects and carbon pick-up in the surface of the casting if proper process controls are not exercised. New PUCB binders have been introduced to control lustrous carbon casting defects.

Besides modifications in the basic phenolic and isocyanate chemistries, a variety of additives is used to modify casting properties, enhance release properties, improve moisture resistance, and extend bench life. In addition, significant strides have been made in custom designed shakeout equipment and castings designed with improved sand removal as a basic consideration.

Ortho-cresol modified resins are used for light metal applications. This also enhances bench life, sand flowability, and humidity resistance. Shakeout properties in aluminum castings are significantly improved through the use of the ortho-cresol chemistry.

The Amine Catalyst Component

The tertiary amines commonly used to cure PUCB binders are triethylamine (TEA) or dimethylethylamine (DMEA). Various designs of generators vaporize and blend those amines with a carrier gas and deliver them to the core machine. The best generators provide a consistent, high concentration of amine to facilitate fast, predictable cure cycles. Table I compares TEA and DMEA. Although the DMEA can be more effective due to its greater vapor pressure and higher solubility in the carrier gas, it is more expensive and far more pungent than TEA. At the time this article was originally written, most North American, large volume users of amine utilized TEA. However, in the rest of the world, DMEA is widely used in conjunction with shrouded core/mold machines. Today, dimethyliso-propylamine (DMIPA) and dimethylpropylamine (DMPA) are gaining popularity. The properties of each fall in between those of DMEA and TEA, making them attractive alternatives that offer a balance of reactivity and odor.

The amine's most important handling consideration is its low flash point. In terms of flammability, it should be handled and treated with the same care that is given to handling gasoline.

	DMEA	DMIPA	DMPA	TEA
Vapor Pressure (liquid @ 20°C)	435 mm	142 mm	129 mm	54 mm
% Amine by Weight	51.1	24.0	22.1	11.7
Ft^3 N_2 / lb. Amine	13.2	43.7	48.5	103.5
Ft^3 N_2 / 10 cc Amine	0.20	0.69	0.76	1.67

Table 1: Comparing ISOCURE Amines
Calculated at Saturation with Generator Operation @ 70°F & 15 psig

TEA requires 7.8 times as much inert gas or air to deliver the same amount of amine to the core box and through the sand to cure as does DMEA.

Amine usage and cure rate depend largely on how efficiently the tooling is vented and on core/mold geometry. In controlled laboratory experiments, as little as 0.1 lbs. of amine can cure a ton of sand. In practice, however, 0.8–2.0 lbs. of amine per ton of cured PUCB sand is the goal. Heated catalyst gas, heat-traced and insulated amine delivery lines, along with heated purge air can reduce cycle times, cure the core/mold more effectively, and minimize amine usage. When heating the amine delivery line there should be a 25°F step-up in line temperature between the generator and the input plenum of core/mold machine to prevent amine vapor from condensing back into liquid form.

The Amine Catalyst Component

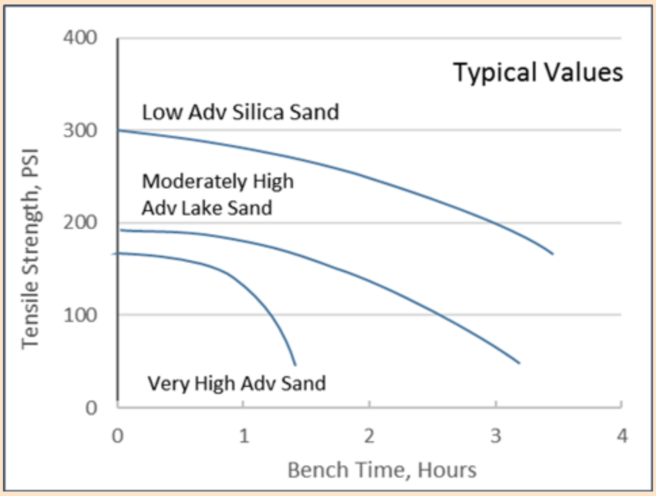
The PUCB Process works with all sands commonly used for core making. Very basic silica sands, with a very high Acid Demand Value (ADV), and olivine sands result in reduced bench life.

The limited bench life of coated sand is the most negative aspect of the process. Therefore, consideration must be given to the effects of high sand temperature, ADV, and moisture content, as well as blow air and relative humidity, since they all have an effect on bench life and performance.

Particular consideration should be given to sand temperature. All sand binder reactions are significantly influenced by temperature, and an 18°F change in temperature will double or halve the reactivity of PUCB binders. The ideal sand temperature is 70–85°F. Lower temperature can reduce mixing efficiency and increase cure times, but improve bench life. Higher sand temperatures reduce gassing cycles but shorten the blowable life of the coated sand mix.

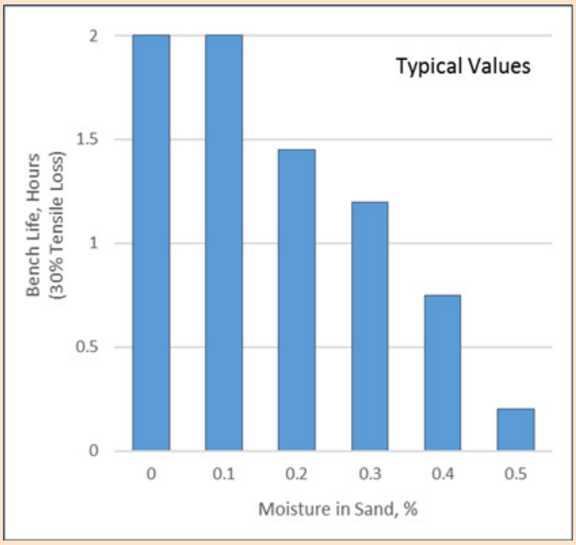
Similarly, the presence of high levels of alkaline impurities or sands with basic (high ADV) chemistry shorten bench life, while acid impurities can contribute to improving bench life, as shown in Fig. 2.

Fig. 2: High levels of alkaline impurities in the sand, as measured by ADV and pH, can shorten bench life.



Moisture in the sand reduces tensile strength and shortens bench life. Fig. 3 shows this effect. A maximum sand moisture content of 0.2% is acceptable for the PUCB process at room temperature (70°F), but it should be pointed out that when the sand temperature goes above 90°F, moisture content of the sand must be kept at less than 0.1% for the process to function properly.

Fig. 3: Moisture in the sand reduces tensile strengths and shortens bench life.



Part I and Part II binders are applied to the sand individually or at the same time through separate delivery systems. Binder percent is usually based on the strength required to strip the core or mold from the tooling and stay intact throughout the subsequent steps in core handling and setting. Typically, 1.5% total binder is used on a washed and dried sand for ferrous casting production with small, rangy cores. Binder levels as low as 0.8% are achievable in the production of large cores for aluminum castings. Although the resin components are formulated to react fully when mixed at a 50/50 ratio many users choose to offset the ratio for the specific purposes.

Equipment suppliers have designed sand heaters, intelligent binder metering systems, and weight controlled, mixed sand delivery systems that not only deliver the proper amounts of materials, but are totally automated. These reduce labor and control bench life by making adjustments to the resin and catalyst additions based on climatic operating conditions.

Although computer controlled resin delivery based on parameter monitoring is normally associated with no-bake binder systems, the same cost and quality advantages are realized when this technology is applied to any cold box process. And since the coated sand throughput is so large, the payback period is generally brief when computer controlled monitoring and delivery is applied to large volume cold box applications.

The Blow Cycle

This is the short time interval in the core making process where the dry blow air conveys the sand from the blow magazine into the tooling. The interval should be the minimum time necessary to fill the core box cavity completely. Increasing blow time will not produce a denser core, but will, in fact, have the opposite effect. Increasing blow time results in additional resin wipe off, parting blowout, and sticking.

The blow pressures required with PUCB can be significantly lower than those commonly used in heated pattern processes. Minimum blow pressure reduces sticking, retards resin wipe off, reduces blowout at the parting lines and prolongs tooling life. Blow pressure, like blow time, should be held as low as possible (in the 35 to 45 psi range).

Gas and Purge Cycle

The initial catalyst gassing pressure should be as high as possible, but must not blow a hole in the surface of the core/mold directly below the gas inlet. To accomplish this, the initial introduction of amine gas into the tooling should be done at relatively low pressure, then rapidly increased. The dry air purge should be introduced at the maximum pressure that will not cause the box to separate at the parting line and the seals not to leak. It is a great benefit to heat the purge air so that the temperature at the input plenum is between 154–175°F.

Heated purge air, which can be produced in a unit like that pictured in Fig. 4, should be introduced into the tooling cavity prior to start-up in order to preheat the pattern surface and minimize resin build-up during startup. Cold start-up is a significant contributor to sticking. The heated purge air start-up can be easily automated by the installation of a timer that will start this part of the operation before anyone arrives in the plant.

Fig. 4: Purge air heater.

Lustrous Carbon

Because of the PUCB's high carbon content, lustrous carbon (soot) can be produced in excess amounts during metal pouring. Lustrous carbon can enhance the casting surface when it lays between the sand and the metal, but if it over accumulates it can cause surface wrinkles or other flaws known as "lustrous carbon defects." Lustrous carbon produces a reducing atmosphere in the mold cavity that induces penetration defects and leads to coating problems in the green sand system.

Some PUCB resins are specially formulated to reduce the amount of lustrous carbon generated during casting. Lustrous carbon quantities can also be controlled by lowering resin content, increasing pouring temperature, reducing pouring time, improving core and mold venting, and using iron oxide at 1–3% based on sand weight (BOS), to generate a richer oxidizing atmosphere in the cavity. Black and red iron oxide additions of 2–3% BOS, are recommended for steel casting production. Unfortunately iron oxide additions can have an adverse effect on strength properties of the core / mold. A relatively new form of black iron oxide which is supplied in the form of hollow spheres, minimize strength loss and has found some success in steel foundry applications.

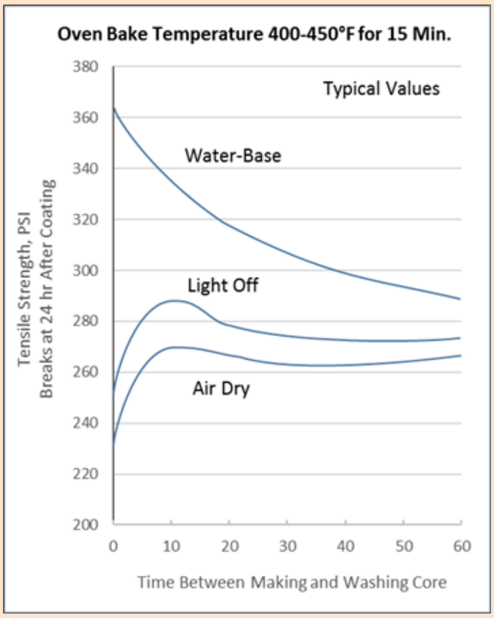
Sand Additives

Certain sand additives can be used with the PUCB system to minimize specific casting defects. A proprietary gypsum-type additive has proven effective in the control of penetration and expansion defects when used in the order of 5–10%. Veining in ferrous and brass castings can be reduced substantially with the addition of 1–2% BOS of proprietary clay/sugar bends, or by adding 1–2% of iron oxide. As little as 0.25% of coarse red iron oxide has been shown to eliminate gas pinhole defects. From 1–3% of red or black iron oxide minimizes lustrous carbon, as well as penetration.

Refractory Coatings

Cores and molds made using the PUCB process can be coated with virtually any type of refractory. Water-based coating systems should be applied as soon as possible after the core/mold is removed from the tooling, then dried immediately in a well exhausted oven. Alcohol-based coatings should be applied after the core has cured for a minimum of 10 minutes. Note in Fig. 5, that the application of the light off refractory coating minimizes strength deterioration, whereas the water-based coating application causes a loss in strength. Modern binder formulations offer significant improvements in water-based coating strength degradation.

Fig. 5: Effects of washes on tensile strengths.



Sand Reclamation

Sand from PUCB cores and molds is easily reclaimed either mechanically or thermally. The brittle nature of the coating results in its easy removal from the sand surface in mechanical reclamation. In thermal reclamation, the organic nature of the binder adds to the combustion process that burns the resin off the sand.

Environmental Issues and Regulations

The Clean Air Act and regulations controlling the use of ozone depleting chemicals have driven the development of PUCB binders and cold box release agents. Regarding VOC control and Title V permitting new PUCB binders have been developed that are not photochemically reactive. These binders reduce the aromatic solvents used in PUCB resins and can reduce the need for control technology for VOC's. In addition, they have the high performance characteristics needed to reduce the need for external release agents, improve moisture resistance /compatibility with the aqueous coating process and reduce carbon content in the binder systems.

In the PUCB process the environmental concerns include: control of VOC's during sand mixing; control of amine in the workplace; elimination of ozone depleting external release agents; scrubbing of amines; and disposal or recycling of spent scrubber solutions.

These issues can be addressed by using non-photochemically reactive PUCB binders, wet packed tower scrubbers, binders with internal release properties, external release agents that do not contain ozone depleting carriers or VOC's, and recycling amine catalysts from spent scrubber solutions. All of these issues can be addressed without sacrificing productivity or casting quality if the PUCB binder is developed for the specific metal casting process.

Conclusion

The chemical and physical elements in the PUCB Process are constantly undergoing changes to better conform to environmental requirements without losing their productivity advantages.

Section B will examine the operational aspects of PUCB so that the subtle operating parameters can be better understood and adjustments can be made to run it faster and cleaner. Better process understanding invariably leads to improved productivity and fewer problems.

References

Fig. 1-5: ASK owend figures

Please do not hesitate to contact us for further information:
Customer Service
Phone: +1 800 848 7485
Email: info.usa@ask-chemicals.com