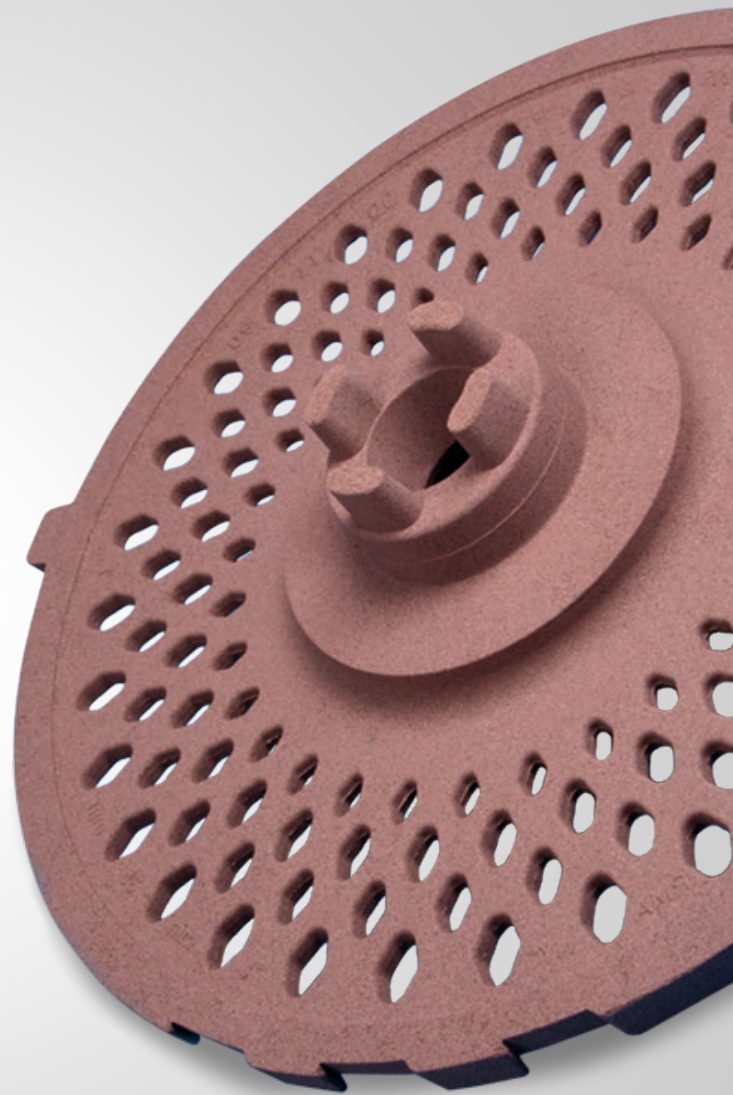


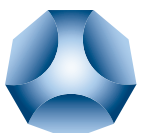
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# Sand Binder Systems



Technical Paper

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# Part VIII: Ester-Cured Alkaline Phenolic Resins

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

The crosslinking of alkaline phenolic resole resins by the addition of organic esters was discovered in the 1960s. However, ester-cured alkaline phenolic binders were not used in the foundry industry until the mid-1980s, when they were introduced in the UK.

Foundrymen there had high hopes for this new binder because its water base was expected to eliminate many handling and casting defect problems associated with solvent based systems. After more than a decade of experience and continuing development there have been a number of successful system applications, especially in the steel foundry industry.

However, there are still several challenges that are being worked on to enable additional conversions to the process. These are related to sand reclamation, low core/mold handling strength, binder storage life, shakeout problems, formaldehyde evolution, and scrubbing or recycling the methyl formate co-reactant used in the cold box version.

## The APNB System

The system yields lower tensile strengths than organic binders, so adequate handling strength for small cores and molds is achieved with a binder level greater than 1.5%. Notable advantages for the system include low odor, virtually no smoke, ease of stripping, good casting finish, low veining, minimal erosion, and very good hot strength.

However, a number of comparative disadvantages have precluded the system's general acceptance. These include a relatively high resin viscosity that gets worse as the binder ages, relatively poor coated sand flowability and compaction, low core/mold strength, limited storage life of the alkaline binder, poor reclamation due to buildup of inorganic materials during repeated reuse, and a unique increase in coated sand strength during the casting process that makes the coated sand stronger and results in shakeout problems.

## The Part I Resin

The no-bake ester-cured alkaline phenolic (APNB) system is a water based, two component resin binder comprised of a modified phenolic resole resin and a liquid ester co-reactant. Typical resin levels are 1.0–1.5%, based on sand weight. Co-reactant levels are generally in the 20–25% range, based on resin weight.

Part I resin is a water-based alkaline (above the neutral point of 7.0 on the pH scale) phenolic resin. This resin differs from a "standard" resole resin because sodium or potassium ions have replaced hydrogen in the phenolic hydroxyl groups.

Part I resin contains up to 45% water as the carrier. Resin viscosity is higher than many other no-bake systems, but it is still comparable to the viscosity of acid-cured phenolic no-bake resin. Like phenolic acid-cured no-bake resin, the storage life is limited.

The resin can be stored for six months at 70°F. Storage at higher temperatures will shorten storage life. When stored above 100°F the storage life is shortened considerably. As the resin ages its viscosity increases, which decreases performance characteristics.

Progress has been made toward improving the flowability of the coated sand by reducing the initial viscosity of the resin. This is achieved by reducing the resin's molecular weight and solids content. This requires a high pH to keep the solution stable, but this combination negatively effects sand reclamation. Resins with both high and low molecular weights are the best solution; low molecular weight resins for foundries that don't reclaim and high molecular weight resins for those that do.

## The Part II Ester Co-reactant

Esters are a combination of organic acid and alcohol. Liquid ester blends are used to control work and strip times when added to the no-bake resin. Because Part II is a co-reactant (not a catalyst) the ester becomes physically and chemically combined during the chemical reaction between the two components.

There are a number of co-reactants to select from when using a given resin. Raising or lowering the amount of ester co-reactant within the recommended range of 20–25%, results in a slight increase or decrease, respectively, in its effect on the chemical reaction and strip speed. However, to compensate for varying temperature conditions it is better to select another type of ester than to operate outside the recommended range.

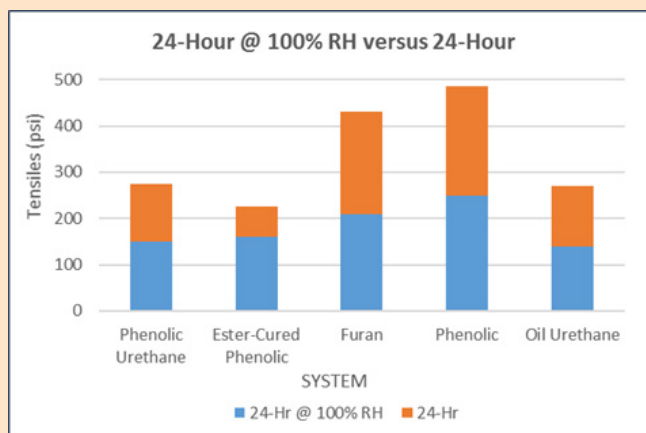
In 1991 new co-reactants were introduced that contained additives to enhance early strength development. Unlike most no-bake binder systems, the ester-cured system does not cure more effectively by slowing it to a reasonable rate. This is due to the chemistry of the “slower” co-reactants.

## Resin System Performance

The APNB system has been especially effective in steel foundries that make large castings. It can be used in very large phenolic ester pit molding applications. Larger phenolic ester no-bake molds are typically done in flasks. The steel flasks facilitate the transportation of large cured sand quantities within the foundry.

Typical tensile strengths and the effects of humidity degradation are shown in Fig. 1. High humidity does not decrease the strength of the estercured system to the extent that it does with other no-bakes. Also, since the resin already contains a high percentage of water, moisture in the sand does not affect tensile development as much as it does in other systems. However, sand moisture should still be controlled to less than 0.2%.

**Fig. 1:** Effect of Humidity on Tensile Strengths.



## Environmental Issues

The ester-cured phenolic system offers environmental advantages such as low odor and smoke, water-based clean-up, and no solvent emissions. However, formaldehyde is formed during curing and during binder decomposition as metal is poured against it. Worker exposure to formaldehyde must be limited to less than 0.75ppm for an 8-hr time weighted average. This is of concern during the pouring and shakeout and should be monitored for each operation.

## The APCB System

Cold box ester-cured alkaline phenolic (APCB) binders have been available since 1984. It is a two-part binder system. The resin is water-soluble. It is cured with a vaporized ester co-reactant: methyl formate. Table 1 lists the properties of the co-reactant.

	Methyl Formate Coreactant
Refractive Index	1.3431
Viscosity (CPS)	0.4
Free Phenol	-
Free Formaldehyde	-
Flash Point	-25°F
Specific Gravity	0.97
Weight/Gallon	8.03
TLV	
8 Hour TWA	100 PPM
15 Min. TWA	150 PPM

**Table 1:** Physical properties of Methyl Formate.

## Making the Core and Mold

The resin is mixed in the sand with any type of batch or continuous mixer and placed in a storage hopper above the sand magazine. APCB has good bench life, but should not be left for long periods in the air exposed hopper. The coated sand is then either blown or hand rammed into the pattern. The methyl formate is vaporized, piped to the pattern, and passed through the compacted binder/sand mixture. A dry air purge generally follows to minimize residual, unreacted methyl formate in the core/mold.

The function of the vaporized methyl formate is identical to that of the liquid ester in Part I, i.e., to chemically react with the alkaline-phenolic resin in order to produce a cross-linked polymer. The difference is that the co-reactant is carried into the sand mixture as a vapor instead of a liquid.

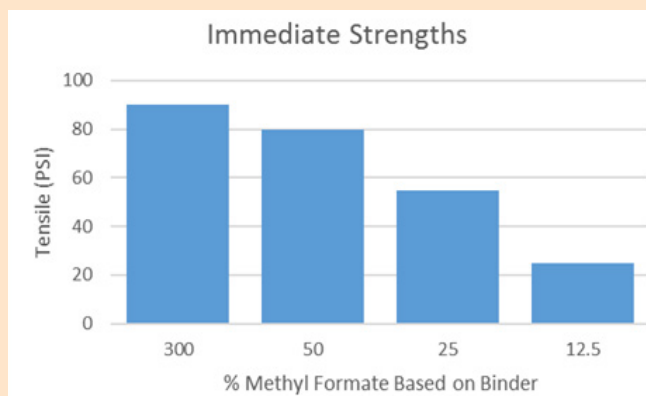
## On-going R&D

Continuous improvements are being made on this system. Research is focused on improving binder storage life and core/mold strength. The ester-cured phenolic resin, whether used for cold-box or no-bake applications, has a usable storage life that is inversely temperature dependent. This shortfall is being addressed along with core/mold strength improvements. The most recent binders available show half the viscosity increase over time as their predecessors. Another new development is a 20–50% increase in up-front and ultimate tensile strengths.

## Methyl Formate Usage

Methyl formate levels are being studied in regard to tensile strength development. Doubling the methyl formate from 12.5% to 25% (based on resin weight) yields an increase in immediate tensiles of over 150%. This is why it is important to rig the pattern so that the proper amount of methyl formate co-reactant is delivered to every part of the tooling (and core/mold). Doubling the level again yields another 55% strength increase. Levels from 35–100%, based on binder weight, are typically used to cure cores. An excess of methyl formate is almost always delivered to the coated sand in the tooling to ensure that all sections receive the minimal amount required for effective cure. As shown in Fig. 2, over-gassing with 200% methyl formate actually has a positive effect on physical properties, but this is not cost effective.

**Fig. 2:** Effect of coreactant level on immediate strengths.



## Proper Rigging

The key to successful gassing with methyl formate is to use a large volume of gas at low pressure. Then try to develop and sustain uniform pressure within the tooling so that the co-reactant will be distributed to all parts of the core/mold. Thus, effective core box rigging is important in the successful application of phenolic-ester cold box.

Judicious location of the input vents, along with ratio of input to exhaust cross sectional open area, will ensure distribution of the co-reactant throughout the core box.

Because you want to maximize the volume of the vaporized methyl formate through the resin coated sand, both input and exhaust cross sectional areas should be maximized. The exhaust cross sectional area should be about half that of the input. This high input to exhaust ratio leads to even co-reactant distribution and shorter gassing cycles. Excessive gassing pressures will produce soft spots below the gas entry vents and should be avoided. Remember, it's gassing with high volume (not high pressure), and the subsequent positive pressure developed in the pattern cavity that produces the greatest number of quality cores/molds in the least time.

## Computer Core Box Rigging

As computer pattern rigging modeling becomes better understood and as it becomes a key part of patternmaking, the modeling of systems utilizing co-reactants will benefit significantly. Current procedures accept overgassing to ensure complete cure in harder-to-gas sections. Computer modeling will be able to identify under gassed sections and suggest optimum vent locations and sizes that will result in uniform gassing.

## Modeling Catalyzed and Chemically Reacted Systems

The amine-gas catalyzed, phenolic/urethane cold box (PUCB), system is the one being examined in most computer core/mold simulations. The system uses an amine catalyst to cure the resin.

It is relatively simple to model a catalyzed system. Not so for one that requires proportioned co-reactants. A catalyst only has to pass through the coated sand to initiate the cure; and easy process.

In a chemically reacted system, such as PUCB, a given amount of co-reactant has to occupy various volumes of the tooling for a finite time in order to react with the resin. That is very difficult to model.

## Excess Methyl Formate Disposal

The phenolic ester cold box process, as with any cold box system, must be utilized with sound cold box gassing, sealing, collection, neutralization, and disposal techniques. The phenolic ester cold box system almost always uses an excess of methyl formate to ensure complete cure. This, unfortunately, means that the process discharges unreacted methyl formate from the tooling and, therefore, generates Volatile Organic Compounds (VOCs) during core/mold manufacturing. If this is not already the case, excess methyl formate eventually will have to be contained, collected, and disposed of in accordance with local, state, and federal regulations.

Thus, ester-cured cold box systems will require scrubbing equipment, just as organic systems do, to comply with present and future regulations. Neutralization of excess methyl formate is best accomplished in a packed tower scrubber using a 5–10% sodium hydroxide in water solution. The scrubbing reaction produces methanol, sodium formate, and formic acid as by-products, which must be disposed of according to legislated guidelines.

## Reclamation of Ester-Cured Alkaline Phenolic Sands

One impediment to greater acceptance of the alkaline phenolic ester-cured process is its inhibition of sand reclamation. Some foundries have achieved 70–80% reclamation by attrition using a mechanical reclaimer and cooler classifier, but with disposal costs and environmental controls on the rise, the need for total reclamation is growing. Total reclamation means the ability to re-use all the available return sand. A reuse rate of 97.5% is the current benchmark.

Thermal reclamation might appear to be an ideal solution. There is, however, a chemical issue that exists with the thermal reclamation of phenolic-ester bonded sand: The presence of residual potassium hydroxide and associated ester salts poses a unique problem for thermal reclamation.

Although many ester salts will decompose during thermal reclamation, little potassium can be removed by exposure to heat alone. Potassium hydroxide melts at 360°C, but does not boil and evaporate until 1,320°C. Since a thermal reclamation unit will run between 700–800°C, the operating temperature range tends to melt the potassium residue on the sand and form agglomerates, or "sinters," which drastically impair sand flow through the reclaimer.

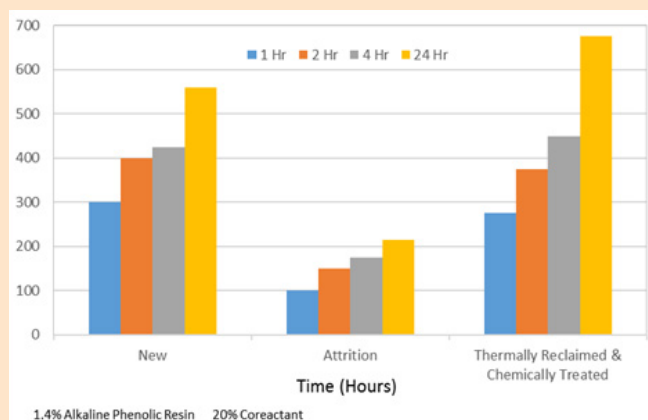
This problem is addressed by using an additive in combination with a new process undergoing development. This converts residual potassium in the reclaimed sand to compounds that have higher melting points. The conversion of residual material to compounds with higher melting points than the reclamation temperature allows organic residues to be removed through a combination of mechanical and thermal reclamation. The treated sand can be processed in a fluidized bed thermal reclaimer. A large portion of the alkaline residue is also removed. The potassium that remains is present in a practically inert form and does not greatly influence the sands' rebonding characteristics.

The additive is mixed with the particulated and attrited sand by a continuous mixer prior to its being charged into the thermal bed. The properties of the new, attrited, and thermally processed sand are given in Table 2 and Fig. 3

	New Sand	Attrited Sand	Thermally Reclaimed
LOI (%)	0.2	1.8	0.1
Potassium (%)	0.01	0.12	0.06
pH	7.2	10.2	9.5

**Table 2:** Mechanically and Thermally Reclaimed Sand Compared to New Sand.

**Fig. 3:** Thermally Reclaimed and Chemically Treated Sand Performance Compared to New Sand and Attrition Reclaimed Sand.



The potassium conversion additive is mixed in at 1.5% for each 0.1% by weight of residual potassium. Excess additions will not impede the process, but they will unnecessarily increase costs.

The reclaimed and chemically treated sand from this process is reportedly so much like new sand that it can be reclaimed at 100% and successfully re-bonded with other binders, such as phenolic urethane cold box.

## Conclusion

From an environmental standpoint, both no-bake and cold box versions of the ester-cured alkaline phenolic resin system demonstrate significant improvements. Successful conversions to ester-cured systems have almost always been driven by their environmental advantages. Processing improvements have been the focus for most of the R&D efforts. Undoubtedly, the ester-cured alkaline phenolic, along with other water based systems and inorganics, will continue to receive much attention from researchers in the future.

Most foundrymen realize that, even with improvements, ester-cured phenolic systems do not possess the physical strength and productivity characteristics that organic solvent systems offer. However, the phenolic ester systems can make acceptable castings when they are carefully applied and the process is carefully monitored.

## Vacuum and Vibrated Production

In Part VII of this series, the subject of Blown No-Bake [BNB] Core/Mold Production was presented. Compared with cold box processes, making cores and molds with a BNB process yields obvious production advantages shown below:

1. Few, if any, blow tubes required.
2. Simple venting.
3. No need to distribute catalyst or co-reactant gas to every part of the tooling.
4. Gassing mechanism and cycle eliminated.
5. No plenum and tooling seals to install and maintain.
6. No need to collect, neutralize, and dispose of catalyst or coreactant gas.
7. Cores and molds almost always have better humidity resistance.

However, there are three troublesome aspects of the BNB process. First is the step of blowing the sand into the tooling. The blowing of coated sand requires complicated and expensive equipment. Second, binder selection is limited to phenolic urethane systems because of their ability to produce acceptable cores and molds using high speed catalysts. Third, the phenolic urethane system tends to lose strength and humidity resistance as strip time is decreased. Strip time in BNB production is very short because productivity is based on manually returning a single pattern to the machine before another cycle can start. Strip time is the factor that, therefore, determines the cycle.

You can eliminate these problems and still retain BNB system advantages with the V&V Process because:

1. The vacuum and vibrated (VV) process does not use a mechanical blow device to introduce the sand into the tooling.
2. The VV process can produce a wide range core and mold shapes with a number of different binders.
3. Both physical strength and humidity resistance worsen as the strip speed of foundry resin binders is accelerated. Strip time can be extended and the catalyst optimized by placing a variety of bar coded tooling on an extended-length, powered, roller conveyor loop line.

### What is the VV Process?

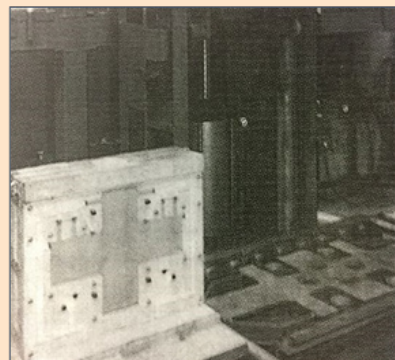
The V & V Process is a core/mold making process that produces uniformly dense units by using a combination of vibrational forces and atmospheric pressure to introduce no-bake coated sand into the pattern. It can utilize a variety of no-bake binder systems in combination with virtually all types of tooling materials.

### VV Process Equipment

The process equipment for the V&V filling process, shown in Fig. 4, consists of the following elements:

- A computer controlled, continuous or batch sand coater for use with temperature controlled sand.
- A small vertically indexed hopper.
- A gate on the discharge opening.
- A vacuum pump and a vacuum accumulator tank.
- A vibration compaction table surrounding a plate that connects the vacuum surge system to the tooling.
- A roller conveyor.

**Fig. 4:** VV process machine with experimental core box.



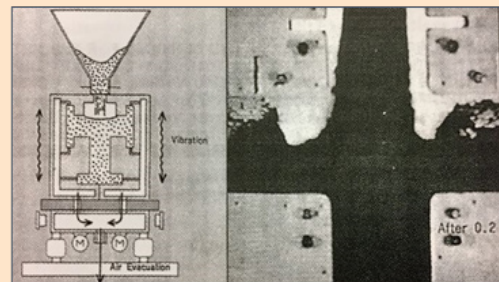


## How VV Process Works

There are four basic steps to the VV Process: 1. Core box positioning under the hopper discharge and over the vacuum holes located on the compaction table; 2. Hopper is lowered into position on the tooling; 3. Vibration actuated vacuum filling (Fig. 5); and 4. Hopper disconnection.

Note the black streaks that can be seen through the clear plastic side of the test pattern. They indicate the paths that the sand followed as it filled the cavity. It is noteworthy that the sand actually moves upward during the filling process as indicated by the streaks. Fig. 6 is a high speed photo taken at 0.2 sec into the core box vacuum and vibrated filling process. Note the upward travel direction of the sand and how it has filled the vertical channel on the left upper section of the core.

**Fig. 5:** VV sand filling (left) and high speed photo taken at 0.2 seconds into the filling process shown in **Fig. 6** (right).



Although the VV process has been utilized to produce cores and molds with phenolic urethane, furan, and phenolic ester no-bakes, for some time in Japan, the process is almost unknown outside that country. VV demonstrates obvious merit because of its manufacturing flexibility and the high quality of cores and molds that it produces. Vacuum assistance, when properly engineered and integrated into the production of no-bake and cold box molds, is simple and has enormous potential for improving manufacturing efficiency and quality.

# References

All ASK owned figures

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