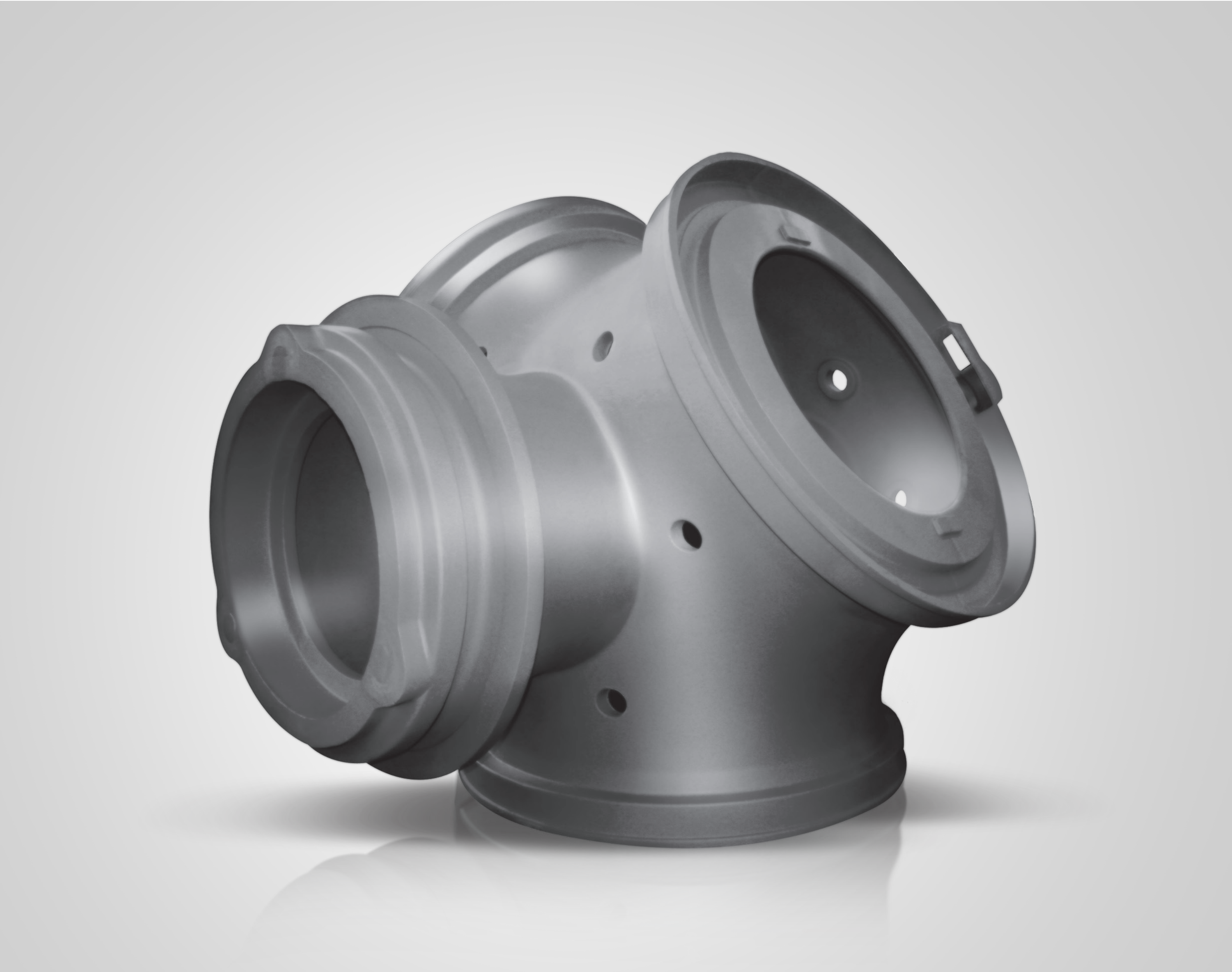
Authors: P. R. Carey & M. Lott

Sand Binder Systems



Technical Paper

ASK CHEMICALS
We advance your casting

Part V: Furan No-Bake

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

Furan-type resin binders were originally introduced in 1958 as an acid-catalyzed no-bake furan binder system. Two years later, the automotive industry modified the resin to operate with an acid salt catalyst for use as a hot box core system. Then, in the early 1980s, furan resin became the largest resin binder consumed, and today it remains as the largest selling no-bake system.

What Is the FNB Resin System?

FNB is the system that foundrymen mean when they say “Acid no-bake.” It is a simple two-part binder system made up of an acid catalyst and a reactive furan-type resin. FNB has high hot strength and excellent shake-out characteristics. It can be utilized to make all types of metal castings in all sizes. However, because the acid can impart a greenish “stain” to the surface of aluminum castings, it is seldom used in their production. The system is easily reclaimable by thermal or mechanical techniques, although attention must be paid to certain residues left on the sand from the catalyst. The amount of furan no-bake binder used is usually 0.9–2.0%, based on sand weight. Catalyst levels generally are from 20-50% based on the weight of the binder. The acid catalyzed FNB does not work well with high acid demand value silica-type sands, and very basic (alkaline) aggregates, such as olivine. As with all no-bake systems, temperature is a primary consideration because the catalyst component must work in combination with temperature to initiate and sustain the chemical curing reaction. A unique characteristic of furan resin is that, when it is polymerized with a strong acid, it undergoes a unique color transformation, first turning green and then black. The color shift results from the formation of chromophoric compounds (chemical reactions that produce color as they occur) during the curing stages. Ultraviolet light breaks down the chromophoric conjugation so that the color eventually will return to that of the naturally coated brownish appearance. The color change has no apparent physical effect on coated sand properties.

The Furan Resin, Part I

Furfuryl alcohol is the basic raw material for the furan family of acid-catalyzed no-bakes. It is produced from waste vegetable materials such as corn husks, rice hulls, etc.

Furan resins are commercially classified according to their nitrogen and water contents. Nitrogen content varies from 0–11%, i.e., zero, low, medium, and high nitrogen furan-types. Water content can range from 0–30%. The lower the nitrogen and water content, the higher is the grade of furan binder. The greater the furfuryl alcohol content, the better the environmental, core/mold making, and casting performance of the system, and, unfortunately, the higher the price.

The FNB base resin is often modified with urea, formaldehyde, phenol and a variety of “extenders.” Other materials, known as “modifiers,” can be used to “scavenge,” or neutralize, free formaldehyde, stabilize the resin, enhance coating properties and strength, and control reactivity. Unfortunately, modifiers invariably accomplish their job at the cost of some other desirable resin property.

The Acid Demand Value (ADV) test is used to quantify the amount of acid soluble material in sand. It has a special significance when FNB systems are involved because these acid soluble materials (usually soluble in the FNB acid catalyst) may not be evident in a simple water based pH determination.

Since water is the suspension medium for the pH test, a pH reading will only show the presence and amount of water soluble materials.

A negative ADV shows the presence of acidic elements in the sand which, in effect, add additional catalyst to the system. The result of residual catalyst materials is to over-catalyze the resin. Mechanically reclaimed sand that contains residual acidic material is a classic example of this effect.

The Acid Catalyst, Part II

The function of the FNB acid catalyst is to neutralize the alkaline contaminants (materials having a pH value greater than 7) in the sand. Then it initiates and sustains the FNB's condensation-type curing and cross linking reaction.

The FNB's condensation reaction produces water, which tends to slow the cure rate. This causes the core/mold sand to cure from "the outside in," meaning that the coated sand that is exposed to the air cures before the subsurface sand. The outside-in type of cure is the reason "deep set" is of concern to the foundryman working with FNB. It is also the reason that a large nail is often used to penetrate the surface of the core/mold as it cures to determine how far back from the air exposed surface the core/mold has cured.

Because of the dilution effect that the reaction's water by-product has on the cure rate, it is advantageous to use concentrated acid catalysts to optimize cure rate and deep-set properties.

Types of FNB Acid Catalysts

The more common FNB acid catalysts are in order of increasing reactivity, 75% phosphoric, 85% phosphoric, toluene sulfonic, xylene sulfonic, and benzene sulfonic. All of the acid catalysts are carried in water, and the sulfonic-types usually contain various percentages of alcohol as well.

Phosphoric acids work well with many furan binders, but because phosphoric is a relatively weak acid, phosphoric-types may not be suitable for the low reactivity, zero nitrogen FNBs.

Catalyst choice is important because it significantly affects binder performance.

The speed of the curing reaction can be adjusted by changing the catalyst type and/or percentage. Faster strip times require an increased amount of catalyst or conversion to a stronger type of catalyst. Curing and strip characteristics depend on such factors as sand ADV, binder reactivity, amount of resin coating the sand, temperature of the components, sand moisture content, humidity, and water content in the resin and catalyst. Note that moisture from any source slows the curing reaction.

Sulfuric acid is sometimes added as a "kicker" to all these acids, but results in strong sulfur-type odor in the pouring areas. It also increases the possibility of sulfur pick-up on the casting surface, which can be a significant problem in steel and ductile iron.

The acid-catalyzed furan systems generally have worked well on foundry sands, with the exceptions of high-acid-demand silica and olivine. It is recommended that for optimum strength properties, a round grain silica sand be used. Lake or bank sand usually develops lower tensile strength and requires a higher amount of catalyst for satisfactory performance.

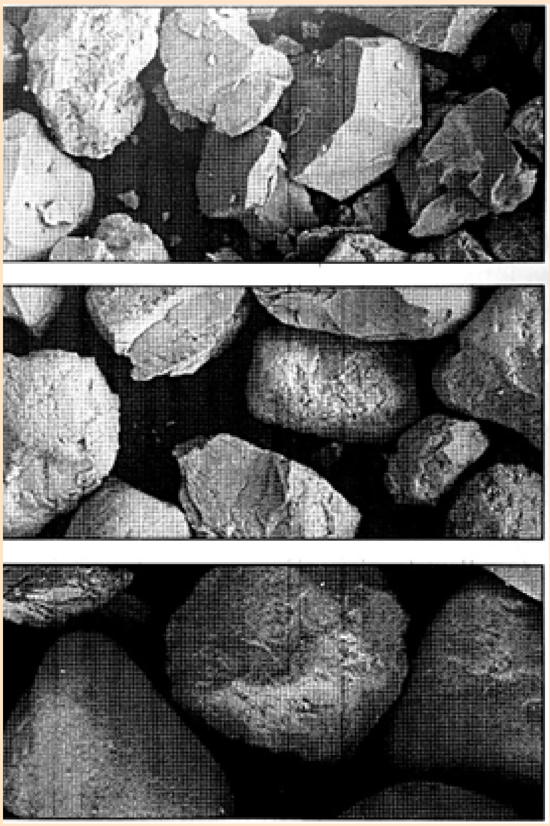
Catalyst Addition Sequence

The catalyst should always be added to the sand first and thoroughly mixed before the addition of the resin. If the resin coats the sand first, the concentration of the catalyst will be too high at the point where it is introduced onto the resin-coated sand. The consequence of this is over-catalyzation of that volume of the resin and a significant loss in strength.

The FNB system forms a brittle, weaker bond when over-catalyzed. An over-catalyzed furan resin tends to go through a rapid color change to black and/or appears speckled like grains of salt and pepper. This effect is the result of uneven distribution of the catalyst over the sand grains. It frequently occurs when the catalyst and resin are applied to an unexpectedly hot sand that is being coated with a muller, or a low intensity mixer, or when the mixer is not working properly.

As shown in Fig. 1, sand is not perfectly smooth. Consequently, when the acid is added to the dry, new sand it tends to fill the "holes" of the sand grains. This results in some grains having more acid on them than others. This is a probable explanation for the "salt and pepper" effect described above. Because the resin will encounter grains containing variable amounts of acid, resin covering acid-rich grains will be over-catalyzed and turn black. If the "salt and pepper" effect is observed, the acid addition procedure should be modified so that the catalyst is atomized when added to the continuous mixer, and mullers should have the acid slowly added in a fine stream as the sand is mixed, instead of being dumped into a hole dug into the sand when the muller is off.

Fig. 1 – The surprisingly rough surfaces of rounded (bottom), sub angular (middle), and angular (top) silica sand grains. Acid catalyst accumulates in these holes and over-catalyzes the resin coating the individual grains.



The catalyst should always be added to the sand first and thoroughly mixed into the sand before the addition of resin. Eventually, even if the "salt and pepper" effect occurs, the entire coated sand surface will usually turn black and the salt and pepper will fade from sight.

The catalyst and resin should never be added simultaneously or under any circumstances mixed together. An explosion can, and probably will, result from the uncontrolled exothermic chemical reaction that follows the mixing of the liquids together.

It is significant to note that a given furan resin catalyzed with phosphoric acid develops higher tensile strength than one catalyzed with a stronger sulfonic acid. In general, the milder the acid and/or the slower the catalyst, the higher the resin bonded sand's tensile strength will be.

How Much Catalyst Is Needed To Cure Acid Catalyzed No-Bake?

The proper amount of acid catalyst required to properly cure a no-bake resin depends on many factors:

- The reactivity of the binder itself – Some are far more reactive than others.
- The amount of water in the system – This includes sand, resin, catalyst, air, release agents, etc.
- Relative humidity – Because acid catalyzed resins produce water as a by-product of the curing reaction, the water needs to evaporate before a completed cure is attained. Therefore, the higher the relative humidity, the slower the evaporation of the water in the system and the slower the apparent cure.
- Temperature of the sand, along with everything else that has some thermal energy, affects the catalyzed resin components – Higher temperature means less catalyst, and lower temperature means more catalyst.
- Sand ADV – The acid must first satisfy the acid demand of the sand before it can begin to cure the resin, so the higher the ADV the more catalyst is needed.
- Reclaimed sand – This is primarily a function of ADV; mechanically reclaimed FNB sand probably has a negative ADV, and thermally reclaimed sand can be neutral or very high in ADV.
- How Fast? – The quicker the strip and cure times, the more catalyst. Slower strip and cure times mean not only less catalyst but, because slower strip and cure times mean stronger cores and molds, it could ultimately mean less binder because of the stronger coated sand.
- Acid type? – Weaker means more needed and stronger means less acid is needed for the same strip time.
- Much Do You Need? – It depends on all of the above!

Process Variables Affecting System Performance

The amount of furan no-bake binder used with silica sand is generally 0.9%–2.0% based on sand weight. Catalyst levels are normally 20%–50% based on the weight of the binder.

The work time of low ADV sand coated with furan no-bake resin is normally 25% of the strip time. Typical strip times range from 15 minutes to one hour. Cure time is one of the more complicated aspects of FNB.

Refractory Coating– Both water and alcohol-based coatings, in combination with just about any refractory, are used successfully with FNB. Under normal conditions, the furan no-bake systems develop 70%–90% of their ultimate properties within three hours after stripping. Therefore, the coating should not be applied until one to three hours have elapsed after stripping, unless the cores and molds have been thoroughly heated before the coating application. Another reason to delay application of a relatively non-permeable coating (especially if it is a water based coating) is that the chemical curing reaction produces water as it cures, and this water needs to come out from inside the core/mold before the curing can be considered complete.

Sand Temperature– Temperature is just as important to the FNB process as the catalyst itself. Temperature must be monitored, controlled and, if possible, kept constant. A sand heater/cooler is the best way to control the most important operating element in the FNB system, which is, of course, the sand. Ideally, sand temperatures should remain between 70–90°F. The rate of cure increases as the temperature rises and slows as the temperature decreases. The change in the rate is based on the Ten Degree Centigrade Rule, which states that for each 10°C increase in temperature the speed of the binder's chemical reaction is doubled, and it is halved for each 10°C decrease in temperature. Catalyst adjustments can be made for temperature fluctuation, but it is better to control the sand temperature than to continually adjust the amount of catalyst.

Types of Sand– Acid-cured furan systems work well with most foundry silica-type sands, including chromite and zircon. The notable exceptions are high-acid demand silica and the very basic olivine. These exceptions exist because "basic" sands with a high ADV, contain contaminants that utilize some portion of the acid catalyst to neutralize them before the acid catalyst can begin to cure the resin. Olivine sand, on the other hand, is an alkaline mineral aggregate, which cannot be acid catalyzed.

Clean, round grain silica sand develops maximum handling strength properties, but it develops such a high compacted density that veining defects can occur. Angular-type silica sands develop lower handling strength, but lessen veining defects. Lake and bank sands require a higher amount of catalyst for satisfactory performance, but contain a significant amount of non-silica materials that reduce veining and other defects.

Compacted Density– Increasing sand density through compaction is important and must take place while the sand is freshly coated and flowable. FNBs lose their flowability steadily once coated, with a resultant loss in density and tensile strength that accompanies the loss in compactibility.

Loss On Ignition – The Loss-On-Ignition (LOI) test measures the amount of combustible materials present in the raw or coated or reclaimed sand. LOI of the coated sand indicates the amount of binder and catalyst present on the sand. LOI of the reclaimed sand is a useful check to determine 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.

Moisture– Moisture in the sand dilutes the acid catalyst and slows the condensation-type curing reaction. Sand with a moisture level above 0.2% significantly slows the cure rate, lowers cured strength, decreases flowability, and produces inferior through-cure properties.

High ambient relative humidity slows the apparent rate of cure. Because the furan condensation cure mechanism produces water, it must be evaporated to achieve complete through-cure.

Silane Additions

Silane can be used in the FNB system to significantly increase strength and to improve its moisture and humidity resistance. Its role is to act as a coupling agent between the inorganic sand grain surface and the organic binder. It can be added to the resin when manufactured, but is sometimes added as a third component because the silane tends to "fade," or lose its effectiveness during storage. The major disadvantage of the silane additive is its very high cost.

No Bake Core and Mold Handling

Quick setting no-bake binders with their predictable strip times are well suited for use on any type of manual or automated conveyorized production line. During the six decades that no-bakes have been in use there have been many innovative, efficient core/mold desings used in foundries.

Here are some examples of no-bake handling systems:

Basic Roller Conveyor Loop

Fig. 2 shows a roller conveyor system used with no-bake resin. This is a basic configuration that can be used to efficiently produce cores and molds with any of the quick setting no-bake systems.

Straight-line Roller Conveyor

Fig. 3 illustrates how maximum productivity can be achieved within a small area of the shop floor using a manual, straight-line roller conveyor with a side loop for returning patterns to the mixer for refilling. An automated rollover incorporates a vibrator built in to help strip the molds from the pattern box just as it cures.

8 Station Turntable

Fig. 4 shows an 8-station turntable producing no-bake molds. This process can be very efficient for high speed production of similar sized molds.

Fig. 2 – Basic loop roller conveyor

Fig. 3 – Highly efficient straight-line roller conveyor

Fig. 4 – Eight-station carousel turntable

Casting Properties and Shakeout

FNBs provide excellent dimensional accuracy and a high degree of resistance to sand/metal interface defects such as veining, erosion, and penetration. They exhibit the necessary combination of high tensile, along with the excellent hot strength, needed for flaskless no-bake molding.

FNB binder decomposes readily during the metalcasting operation. This leads to superior shakeout along with easy mechanical or thermal reclamation.

Since the properties offered by expensive, high-quality furan binders are not needed by all foundries, various modifications have been made to zero water/zero nitrogen furan resins. Various co-polymer blends and dilutent-extender modifications are commonly made to the base of high-grade furan resin to balance price and performance properties. Foundrymen paying a premium price for a low water content binder should remember that there is usually far more water in the catalyst, and sometimes in the sand, than there is in the resin. Although modifiers lower cost, they can cause detrimental side effects, such as increased nitrogen or hydrogen gas evolution and less hot strength.

Reclamation

Nearly all foundries using significant amounts of FNB either mechanically or thermally reclaim their sand because it is economically advantageous, minimizes disposal problems and, in some cases, actually improves the characteristics of the sand itself.
FNB is noted for its outstanding shakeout and excellent reclamation characteristics. If a consistent screen distribution, constant grain fineness number, reasonable magnetic levels, and low LOI values are maintained, FNB sand reuse percentages in excess of 90% are common with mechanical reclamation. A reuse level of 100% is possible with thermal reclamation, or with a thermal/mechanical combination.

Thermal and mechanical reclamation can pose special problems. Lake sand and, to a lesser degree, bank sand often contain a significant amount of calcium carbonate resulting from fine particles of sea shells, etc. Carbonate-containing sands pose special problems for acid catalyzed binder systems. When the carbonate materials are heated and oxidized during the metalcasting process and/or during thermal reclamation, they convert the carbonates to water soluble and very alkaline lime, or calcium oxide (CaO). The presence of lime in the sand obviously must be neutralized by the acid catalyst before it can start to cure the resin.

In thermal reclamation nearly all of the carbonates are converted to lime; but in mechanical reclamation, the amount of the carbonate material converted to lime by the heat from the metal casting operation varies dramatically, depending on casting size, sand to metal ratios, sand exposure temperatures, etc. This is a problem because the ADV of the sand exiting the reclaimer varies based on the quantity of the lime conversion in the heat exposed sand. To compensate for this, the catalyst amounts must also vary.

Furans In The Future

FNBs are recognized as the “first true no-bake binder system.” They have been modified extensively during their six decades of foundry application, and are currently undergoing further modifications:

- Reductions of already low phenol levels are being implemented to minimize employee exposure and control phenol leachate.
- Reduction of nitrogen levels to eliminate gas related defects.
- Development of new and drastically modified zero nitrogen Furan systems such as Reacted-Type (Polymeric); Furfuryl Alcohol – Reactive Compound Blends; Ketone Aldehyde Resins – FA Blend; and Phenol Modified Furan No-Bake.
- Further improving the already excellent reclamation properties.
- Improving reactivity of the resins to reduce acid catalyst requirements.

Some Definitions on Formaldehyde Exposure

Free formaldehyde levels in the workplace have become a very important consideration for FNB utilization, especially when noting that the limits are continually being revised downward. Any discussion of exposure requires many unfamiliar terms, which need to be defined.

Time Weighted Average (TWA)

A cumulative period of time, not necessarily continuous, during which a sample of a substance is captured to determine a worker's exposure.

Permissible Exposure Limit (PEW)

The time weighted average for the maximum allowable concentration of a substance that a worker can be exposed to during an eight-hour period.

Action Level

A concentration of a substance, normally stated in parts per million (ppm), that requires annual training and/or special monitoring.

Permissible Exposure Limit (PEP)

Exposure to formaldehyde, as defined in the OSHA Formaldehyde Standard, is currently regulated to a concentration that exceeds 0.75 parts of formaldehyde per million parts of air (0.75 ppm) as an eight-hour Time Weighted Average (TWA). At the Action Level of 0.50 ppm, employers are required to provide annual training, periodic monitoring (every six months), and medical surveillance. At a level of 0.10 ppm, workers are only subject to the annual training requirement of the formaldehyde standard.

FNB Pros and Cons

ADVANTAGES

- High tensile strength for given resin content.
- Good casting dimensional accuracy.
- Predictable polymerization shrinkage.
- High hot strength combined with excellent shakeout.
- Fresh sand mix has excellent flowability.
- Lower smoke and odor during casting than organic solvent-based systems.
- Wide ranging binder selection offers alternatives to balance cost versus performance.
- Wide range of acid availability with various catalytic reactivity.
- Highly reactive binder can use milder acids, such as phosphoric.
- High reactivity extends low temperature range of coating and curing.
- Low viscosity resin minimizes low temperature handling and coating problems.
- Color change indicates rapid cure – a warning of insufficient work-time for hot sand.
- Agriculturally based raw material.

DISADVANTAGES

- Uses corrosive acid catalyst.
- Work/strip times very sensitive to sand temperature.
- Relatively high resin cost.
- Extenders that lower cost generally reduce properties.
- Subject to loss of properties if over catalyzed.
- Experienced raw material shortages in the past.
- Nitrogen and sulfur residues pose potential reclamation problems.
- Acidic sand surface is generated when mechanically reclaimed.
- Some formulations contain phenol and potential leachability problems.
- Brittle coating, but can be modified with plasticizers to improve flexibility.

References

Fig. 1 & 2: ASK owned pictures
Fig. 3 & 4: Palmer Mfg.

The authors would like to thank Bill Scott, Scott Consulting, and Bill McKillip, Advanced Resin Systems, for their assistance in producing this article.

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