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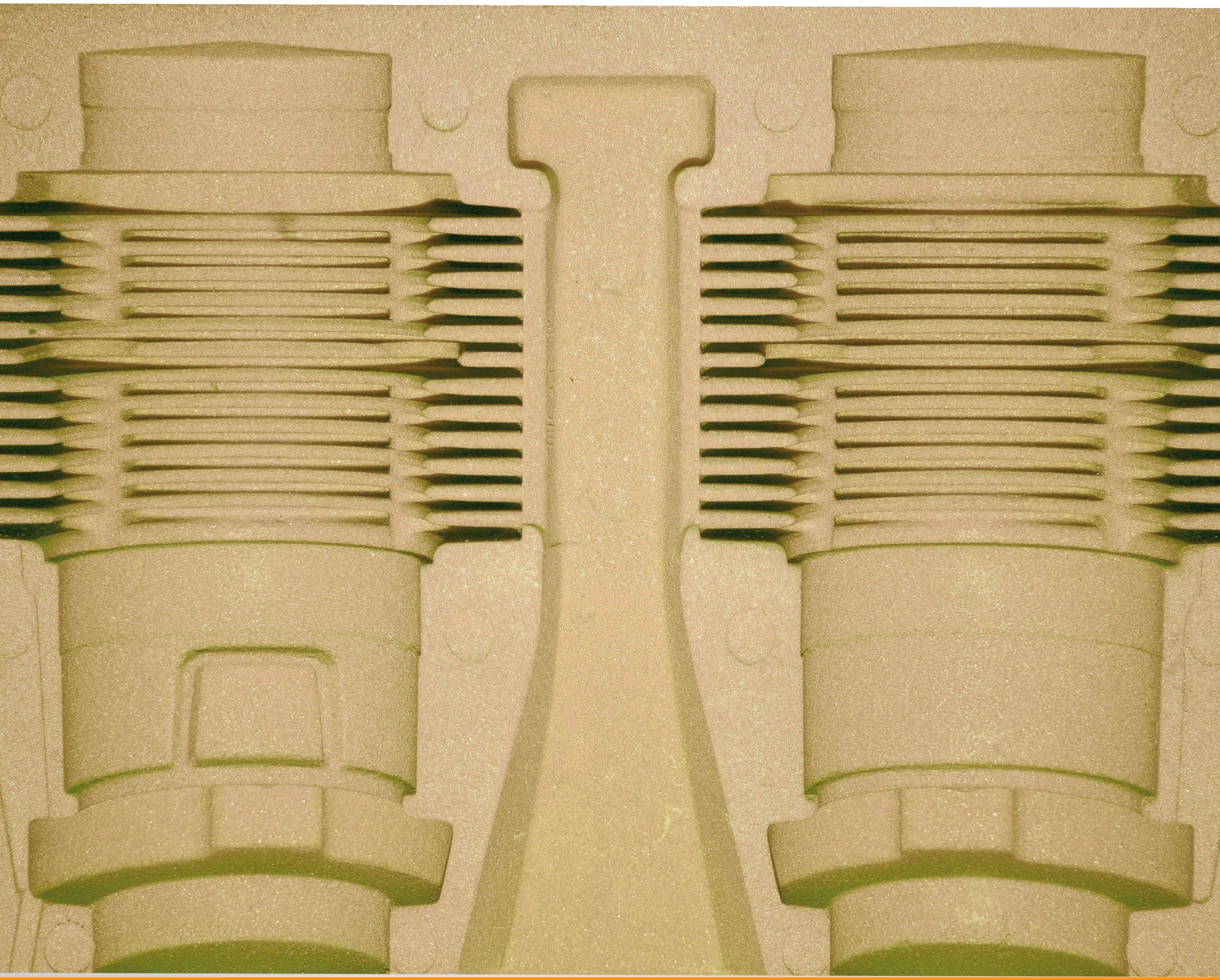
Sand Binder Systems



Technical Paper

Part XII: Hot Box, Warm Box, and Core Oil

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

HOT BOX

Early furan technology was the beginning for the fast-curing hot box process used today. First attempts to utilize furan as a hot box binder to replace core oil and shell used chlorine gas as a catalyst. Because of problems encountered with catalysts, core machines, and resin technology, the process was not really successful until the late 1950s. Three factors made the process acceptable:

- Machine modifications permitted a wet sand mix to be blown into a high temperature.
- Vertically or horizontally parted corebox.
- Permitting higher production rates.

Acid catalyzed, furfuryl alcohol no-bake had gained acceptance as a foundry binder and was chemically modified for use in a heated corebox.

Most importantly, a mildly acidic, chloride salt catalyst was used to give the needed combination of coated sand bench life, cure speed in the corebox, and tensile strength.

The Process

Here is the basis for the furan process: furan resin, phenolic resin, or a mixture of both + acid salt catalyst + 450–550°F = cured resin + water.

Hot box binders have a unique curing cycle. After sand has been coated, it is blown into a heated corebox. The "wet mix" begins to cure as soon as it contacts with the hot pattern. At the operating temperature of the hot box process, the catalyst forms a strong acid that causes the resin to polymerize in a reaction that produces water as a byproduct.

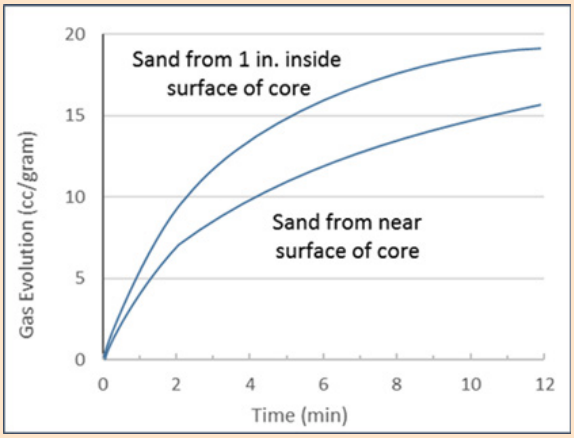
At normal pattern operating temperatures (450–550°F) the core will form a hardened, shell-like skin at the rate of 1/16 in. for every 5 sec it remains in the heated tooling. Once the core surface has enough strength to withstand the force of ejector pins, it is pushed from the cavity.

The hot box cure (dwell) part of the cycle, intended to "skin" the core over to permit ejection, is almost always too brief to completely cure the core. "Through-cure" therefore depends on residual heat in the core to continue curing after removal from the pattern. The cure is sustained and completed by residual heat in the core and that generated by the mildly exothermic chemical reaction that occurs as the resin cures. Post curing might be necessary for cores having a thickness greater than 2 in.

Because the machine cure cycle is short, it's a good idea to keep the sand hot as long as possible to maximize through-cure. Many foundries have high velocity exhaust hoods to carry away fumes and cool cores for easy handling and storage. This rapid cooling may stop through-cure and result in unacceptable cores. A lower velocity exhaust system still can carry away the fumes, but will not cool the cores too quickly.

To insure optimum cure and minimize gas evolution, hot box cores should be held for at least 2 hrs. before they are exposed to molten metal so that the cure reaches completion and core moisture evaporates.

Fig. 1: Comparison of gas evolution from undercured and fully cured phenolic hot box sand taken from the same core.



Catalysts

Selection of the proper catalyst(s) is most important in getting the hot box system to work correctly. Though many foundries may use the same resin, the catalyst must be matched to sand and environmental variations. Core geometry and size are also major considerations.

Catalyst selection is based on the acid demand value (ADV) and other chemical properties of the sand. As ambient or sand temperatures change, a change in catalyst might also be appropriate. Locations with seasonal climate changes may use winter and summer catalysts. An ambient temperature change of 20°F and/or variations of +/- 5 in the ADV of the sand probably call for catalyst adjustment. Blending or mixing catalysts may help. Sand heaters/coolers help to minimize hot box performance fluctuations related to temperature variation.

Typical hot box catalysts are aqueous solutions of ammonium chloride or ammonium nitrate (acid salts) and urea. They are sometimes buffered with ammonium hydroxide to prevent premature curing of coated sand in the storage hopper. The typical amount of catalyst used is 20% BOR (based on resin weight).

The bench life of mixed hot box sand is dependent on water loss from the sand mix. Exposed sand will crust more readily than unexposed sand. In bygone days, wet burlap was placed on top of hoppers to minimize evaporation. Today, the problem is more easily handled with the use of on-demand mixers and minimization of the quantity of pre-coated sand.

Types of Resin

Most conventional hot box resins are classified as furan or phenolic types. The furans contain furfuryl alcohol. The phenolics contain phenol and the furan-modified phenolics contain both. All conventional hot box binders contain urea and formaldehyde.

The furan hot box resin cures faster than phenolics and can be ejected from the corebox with greater frequency. Furan resin also provides superior shakeout, has less odor, and presents fewer disposal problems. Typical resin content is 1.5–2.0%.

Conventional hot box resins contain 2–10% free formaldehyde and 6–13% nitrogen (the catalyst contains 15–25% nitrogen). The formaldehyde odor is irritating and most apparent at the sand mixer and the coremaking station. High nitrogen levels in the resin and catalyst can lead to problems with "ammoniacal nitrogen."

Ammoniacal nitrogen is especially troublesome in ferrous casting operations. It forms quickly and dissociates easily at metal-pouring temperatures into monatomic nitrogen and hydrogen. In the monatomic state, both gases are soluble in the metal, and can cause porosity defects. A simple, inexpensive test for checking the ammoniacal nitrogen content of sand is available.

To minimize the negative effects of formaldehyde and nitrogen, new hot box systems have been introduced that decrease both. The new systems are easily substitutable and offer distinct advantages over conventional hot box systems. Their disadvantages are higher cost and lower reactivity.

Resin Storage

Hot box resins have a limited shelf life, though most of the catalysts do not. Since resin viscosity increases with time and temperature, containers should be stored in a cool place and older drums should be used first.

Phenolics have an especially short shelf life and should not be stored more than a month before they are used. A phenolic bulk resin storage tank should be water-cooled. The tank should have a large emergency dumping port built into its bottom so that the contents can be emptied quickly if resin starts to react exothermically and gel during storage.

Operational Considerations

There is an inverse relationship between hot and cold strength in a hot box system. The higher the hot strength, the lower the cold strength, and vice versa. Hot strength determines productivity because it dictates when the core can be stripped. Cold strength is necessary for coating, drying, and assembly. This becomes an important point in matching the resin with the catalyst.

The temperature of the catalyzed coated sand should be maintained at 70–80°F. When hot box sand is less than 70°F, it will tend to stick in the hoppers, lose flowability, and be slower to cure. If the raw sand temperature is less than 70°F, then it should be "dry mulled" and brought to 70°F before catalyst and resin are added.

Sand above 95°F will harden prematurely in the hoppers and become difficult to blow. On a hot day, when a foundry operates with hot sand and high temperature conditions, the tendency is to add water to the mix and/or to reduce catalyst in an attempt to improve sand bench life. Both actions can be mistakes.

If water is used, it should be added to the sand and mulled for 2 min so that it cools the sand before resin and catalyst are added. This produces cooler sand only if the mulling action does not add more heat than the evaporating water removes.

Never allow wet, resin-coated sand to rest on hopper flat spots or in sand magazine dead spots. It will dry out and break into lumps that will lodge in the blow tubes. Blow plates, blow tubes, hoppers, and sand magazines should be water cooled.

Blow pressures used to produce good cores are usually in the 70–100 psi range, but should be set at the minimum that will produce a uniformly dense core. The generally accepted optimum blow pressure is 80 psi.

Blow times should be as short as possible. For best results, the dew point of blow air should be less than 0°F at atmospheric pressure. A regenerative desiccant air dryer will maintain that dew point easily. Cores not fully blown often are the product of incorrect blow pressure, poor rigging, plugged blow tubes, and/or partially plugged exhaust vents, and especially parting line leaks.

Core wash application should be delayed until the core has cooled to near room temperature. A water-based wash dried in an oven is good from the post curing standpoint since oven drying, in effect, postures the core.

Venting

In addition to conventional slot and screen vents, parting line vents are used in many hot box patterns. The following points are important:

- Brass screen vent openings should be 0.004 in. minimum and 0.010 in. maximum so that sand does not blow through them.
- Slotted vents are used with 0.010–0.020 in. maximum openings.
- Woven wire and screen vents work well on flat surfaces and offer more open vent area than slotted vents.
- Vent passageways leading to the atmosphere must be free of obstructions and kept open.

Ejector Pins

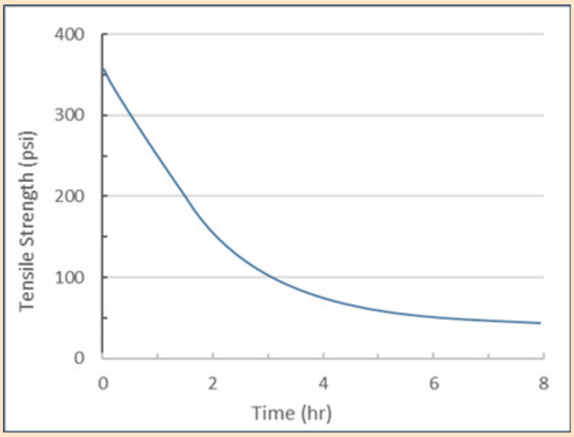
Hot box cores fit snugly in the corebox and spring-activated ejector pins are often used to push the cores from the box. Following are a few good rules for ejector pins:

- Minimum diameter of ejector pins should be 3/8 in.
- Pins should be located in the deepest pockets of the patterns and as close to any vertical draw as possible.
- Irregular areas need more pins.
- All pins must be activated at the same time.
- Pins should be long enough to raise the core completely out of the box.
- Mechanically operated, straight, or headless pins (tapered after 1 in.), fastened onto a bottom ejector plate, are the best for high productivity.
- Clearance around stripper pins should be 0.006–0.008 in.

Effects of High Humidity

Hot box binder systems are affected severely by high humidity, especially on hot days. Because the cold tensile strength of hot box cores is very high, the effects of humidity degradation go relatively unnoticed. A hot box core could lose as much as 150 psi of tensile due to exposure to 100% relative humidity. Core oil, silicone, and additives blended into the mix to improve flowability and release also improve humidity resistance.

Fig. 2: Effect of 100% relative humidity on a basic hot box system.



Sand Coating

Weak cores can be traced to incorrectly mulled sand more often than is realized. The following are some common mulling mistakes:

- Not recognizing that sand and/or resin below 60°F needs longer mulling time and sand over 90°F needs less.
- Adding resin before adding catalyst.
- Adding the resin before the catalyst has been distributed over the sand.

Pattern Temperature

Pattern temperature should not vary more than 50°F across the surface. Measure it at the highest and lowest points across the pattern.

Most shops run hot box pattern temperatures of 450–550°F, but the ideal temperature range is 425–475°F. The biggest mistake foundrymen make with temperature is to have it as high as possible. The result is burnt core surfaces and a friable core.

The core's surface color shows how thoroughly it is cured and is an excellent guideline. The surface should be slightly yellow or very light brown– not dark brown and especially not black. Black means the core is over cured.

Color variation over the core's surface indicates pattern surface temperature variation or a pattern temperature/dwell time combination that is burning thin sections in order to adequately cure thicker sections.

Sand segregation is especially troublesome for the hot box process. This affects permeability along with heat transfer and often produces low to high extremes in sand pH.

Process Advantages

The hot box process has limitations, but it also has many subtle advantages, including the following:

- Because the sand is coated (not mulled), simple paddle or continuous mixers are adequate.
- Seasonal temperature variations can be compensated for with catalyst changes or the addition of up to 0.25% water (based on sand weight) to counteract the effects of high temperature. Mixing 0.2–0.4 lb. of 28% ammonium hydroxide per ton of sand with the catalyst is an effective bench life extender.
- Sticking in the core box is controllable with proper use of a water-emulsified silicone release agent applied to the pattern. Internal release agents, added to the sand just before it is discharged from the muller, further improve release.

Conclusion

Material cost and productivity are factors that determine the selection of a binder process, but shortages, pollution factors, and open time on core machines often dictate process selection. Other factors include a foundry's experience with a system or the availability of patterns or equipment to run a specific binder. The use of reclamation and various compatibilities are also considerations. However, environmental issues, such as formaldehyde in the coremaking area, are special problems and are commanding the attention of users and manufacturers of hot box systems.

WARM BOX

The warm box process is used by many high production foundries and is considered a good substitute for hot box systems. At first, the process might appear to simply be another hot box system. It uses the same coating equipment, processing procedures, and production techniques as conventional furan and phenolic hot box. It is, however, distinctly different. Besides dramatic differences in catalyst and resin chemistry, there are important variations in processing characteristics.

The Resin

The typical warm box binder contains less than 8% water, 70% furfuryl alcohol, and less than 2.5% nitrogen. Because the resin/sand mix exhibits rigid thermosetting properties when fully cured, little or no post-strip distortion or sagging occurs during and after stripping. The hot tensile and cold tensile strengths of warm box sand are similar to hot box sand, but the warm box does it all at lower binder levels, sometimes up to 20% less than the resin content of conventional hot box systems.

Catalysts

Warm box catalysts are typically copper salts of toluene sulfonic acid dissolved in a combination of water and alcohol (usually methanol). The catalyst may also contain some copper chloride. Catalyst level is generally 20–35%, based on resin weight. These catalysts impart an excellent "latent" characteristic to the curing mechanism– they are hardly reactive at room temperature, but form a strong acid when heated, thereby promoting a through-curing action starting at about 150°F.

The alcohol solvent in the catalyst can result in a flash point that requires it to be red labeled, but alcohol-free formulations are available to eliminate the need for red labeling.

Operational Aspects

Optimum pattern operating temperatures are 300–450°F. The recommended uniform surface operating temperature of 400°F is about 100°F lower than that for conventional hot box systems.

Lower operating temperatures result in less tooling warpage and extend tooling life.

Under the mistaken belief that hotter is better, many core machine operators, even during an initial demonstration of the system, want to raise the pattern temperature to 500°F. This is the temperature used with the hot box process and it causes many advantages of warm box to literally go up in smoke.

Since the sand mix changes color during curing, from a light green-yellow to a dark green, the machine operator has a visual aid to get the best curing for a particular job.

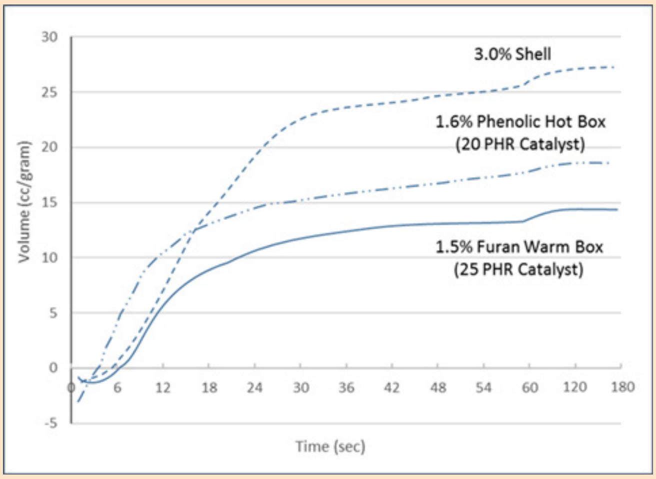
Low resin viscosity (as low as 100 cps at 72°F) and catalyst latency combine to produce highly flowable sand. This yields an operating advantage during the 2–3 hrs. bench life. However, viscosity will increase if stored at high temperatures for extended periods.

High ADV sand and cooler sand (less than 70°F) will increase bench life, but low ADV sands and high storage temperatures (above 100°F) can reduce the bench life of this acid-catalyzed system. Curing problems related to high ADV sands can be partially compensated for by a change in catalyst formulation and/or quantity.

A significant reduction in blow pressure (compared to hot box) and potential use of bigger diameter blow tubes (to eliminate rifling of sand into core-box cavities) are benefits derived from the latent catalyst and low viscosity characterized by the warm box system.

Powder additives are not usually used with the warm box system– an obvious indicator of the lack of lustrous carbon formation, high hot strength, and, as shown in Fig. 3, the relatively low volume of gas evolution.

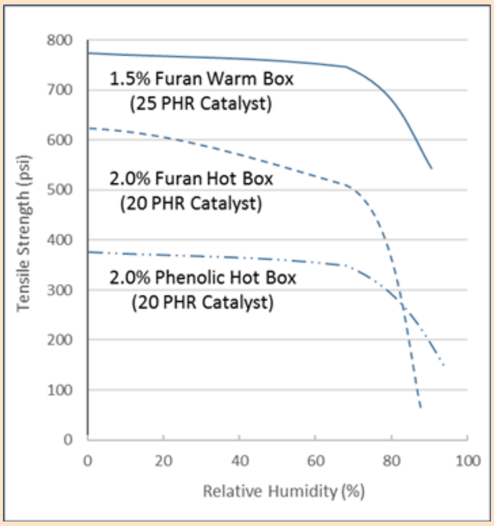
Fig. 3: Comparison of typical gas volume evolved by different foundry binder systems.



Humidity Considerations

Warm box cores have excellent humidity resistance, but, as shown in Fig. 4, they lose significant strength when exposed to very humid conditions. The combination of temperature greater than 90°F with 90–100% relative humidity is tough on any core binder.

Fig. 4: Retained strength for 60 GFN cores after 48 hour exposure to various relative humidity levels. Specimens cured for 30 sec. at 475°F.



Warm Box System Advantages

Warm box systems offer the following process advantages:

- The combination of high reactivity furan resin and strong acid catalyst produces a short cycle time.
- Cores do not usually require post curing.
- The free flowing, highly blowable sand mix often increases core density enough to eliminate wash.
- Lower pattern temperatures result in processing advantages and energy savings.
- Both resin and catalyst have outstanding storage life.
- Lower blow pressure reduces tooling wear and lessens resin wipeoff, yielding cleaner tooling surfaces, less vent plugging, and less down time.
- The free formaldehyde in the resin is less than 2.5%.
- Newer warm box systems have free formaldehyde levels of less than 0.1%.
- There is no formaldehyde in the catalyst.
- Spent sand meets present EPA standards.

Warm Box System Cost

With all these apparent advantages, why wasn't the warm box system more widely used upon introduction? The answer was cost and, to a lesser extent, past developmental problems.

The system's cost is relatively high. Compared to phenolic hot box, it might be 2–3 times higher for the resin and 3–7 times higher for the catalyst. The coated sand cost comparison varies, but is almost always much higher for the warm box process.

Replacing solid shell cores with warm box is one exception. It's often possible to economically justify the replacement of a solid shell sand core with a warm box core because of relatively high shell sand cost, combined with drastic improvement in cycle time.

Most process substitutions are evaluated on the basis of a quality improvement and/or lower cost. However, no matter how many benefits warm box has, its high material costs were difficult to offset by hard-to-quantify improvements in productivity, quality, tooling benefits, reduction of waste sand, and the value of scrap castings.

Today, environmental regulations have pushed coremakers toward using warm box resin over hot box in most regions.

Conclusions

There is now a place in the foundry industry for the warm box process. Many developmental problems experienced in earlier evaluations of the warm box system have been resolved. The system has a number of ecological advantages compared to competitive high production systems, although volatile organic compound (VOC) problems pose difficulties in some regions.

Unfortunately, until the cost of warm box binders is competitive with other processes, and until the uncertainty about the supply of furan decreases, choosing to run a warm box process and will likely be based on a unique, environmental problem-solving or processing advantage.

CORE OIL

Core oil is the oldest of the resin binders used today, dating back to the 1600s. The earliest core oils were made from raw linseed oil and mixed with sand to make cores and molds. Chemists in the early 1900s discovered that linseed binders not only required heat, but also needed oxygen to polymerize. Therefore, they began to add more easily oxidized vegetable and animal oils to facilitate the drying reaction.

Today, most vegetable core oils are based on an oxidizing type of curing mechanism. These oxidizing resins are about one third drying oil (linseed, tall, soy bean, cotton, etc., and/or esters, fatty acid, alkyd, etc.), a third petroleum resin (fast to slow polymerizing olefins), and a third solvent (kerosene, mineral spirits, naphtha, etc.), with a small percentage of metallic dryer catalyst, a wetting agent, and some release agent added. A modern core oil resin may contain up to 20 different ingredients to improve specific processing, curing, and handling properties.

Core oils generate smoke and odor because of VOCs in the binder. The EPA has forced some foundries to shut down their core oil process ovens because of neighborhood complaints. Several core oil manufactures, therefore, have produced solvent less and water-emulsified systems for environmental compliance. These newer systems are effective in reducing smoke and odor, but generally require a longer baking cycle.

Undercured coated sand generates excessive quantities of gas, so complete cure in a minimum period of time is important. Dryers (liquid catalysts) reduce cure time and improve through-cure. Dryers are available that can be added to the muller with the binder. These are effective when heavy through-core sections need to be baked. Check with your supplier to see if you can utilize dryers or a faster baking oil.

How the System Works

All core oils are used in combination with water and cereal to produce a sand core with "green strength," a handling property that permits the wet sand mix to be blown or hand rammed into a vented corebox at room temperature and retain its strength when removed from the pattern.

The uncured, plastic-like cores are usually placed onto a flat board or a dryer plate (a supporting structure to maintain the shape of the core) for oven drying. The cores are then placed into an oven for curing.

The core oil process is a fast way to produce cores or molds. Except for the subsequent drying operation, the cores are, in effect, made almost as fast as they are blown.

Core Oil System Components

Resin - Linseed or vegetable are most commonly used in the core oil process. However, resole phenolic (for steel applications), alkyd (faster drying and higher strength), and urea formaldehyde (nonferrous application) have also been utilized.

Cereal - Core mixes generally contain 1% or less cereal, based on sand weight. The cereal is kept to a minimum because it generates a significant quantity of gas during the casting operation. Normally when more green strength is required for core stripping and/or handling, the cereal is mulled along with the water for a longer time. Small additions of southern (calcium-type) bentonite (up to 0.5% based on sand weight) are a successful supplement to cereal for developing green strength, and they emit far less gas. Unfortunately, bentonite extends required mulling time.

Water - Water is added to the mix to activate the cereal and create green strength. The amount must be controlled to develop optimum properties. Baked strength, green strength, and baked rate are influenced by moisture content.

Additives - Nearly everything imaginable has been added to core oil mixes. The fewer the additives, the better. A core oil formulation usually is a mixture of ingredients added to the mix one at a time over the years to correct sporadically occurring problems that long ago have been solved by other means or simply forgotten.

Sequence of Muller Additions to Core Oil Sands

	All at Once	1. Cereal 2. Oil 3. Water	1. Cereal 2. Water 3. Oil	1. Oil 2. Cereal 3. Water	1. Oil 2. Water 3. Cereal	1. Water 2. Oil 3. Cereal	1. Water 2. Cereal 3. Oil
Green Strength	1.0	0.3	1.5	0.5	0.6	0.5	1.1
Tensile	280	195	362	250	210	200	330
Scratch	89	80	97	84	84	86	91

1% Cereal, 1% Oil, 1.5% Water, 90-min bake at 400°F, Silica sand.

Operational Aspects

A number of points about the core oil system should be recognized and understood before working with it:

- Basic Formulation – A standard core oil mix contains about 1% cereal, 1–3.5% water, 1% binder, and a small quantity of a flowability/release agent.
- Mixing Order – The sequence of additions to the muller has a significant effect on core oil sand properties. The best mixing order to the sand is: 1) cereal and dry additives; 2) water; 3) oil; and 4) flowability / release agent.
- Mulling Procedure – 1) All dry ingredients are dispersed evenly; 2) Water is mulled into the cereal until maximum green strength has been achieved (established by testing); 3) Oil is mixed until it begins to form a creamy emulsion; 4) A conditioning and release agent (kerosene is generally used, but both heating oil or low sulfur diesel fuel are better because they have higher wax content), is added during the last few seconds before discharge.
- Oven Drying – Forced hot air is the principal means of curing core oil binders. Heat is the primary catalyst for the oil sand process.

Whether the binder cures by oxidation (vegetable oil) or by polymerization (urea formaldehyde and resole phenolic) doesn't mean much to the foundryman. He should be looking at factors that affect the core's curing. These include heat transfer, oven humidity, and overbaking / underbaking. The proper combination of oven temperature, drying humidity, and time determines final strength, dimensional stability, and surface finish of the core.

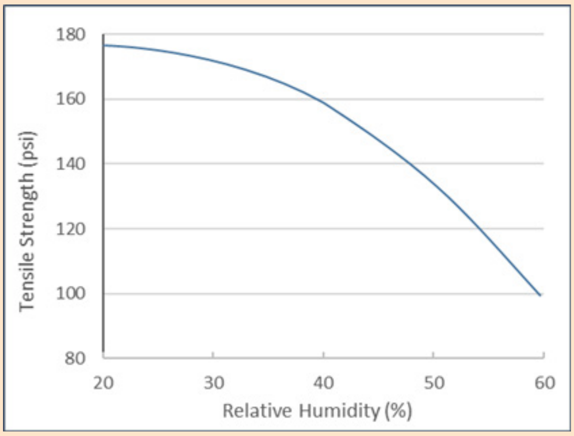
Mixing cores produced by other binder processes in the same drying oven with undercured oil sand cores usually weakens the non-oil cores because of the steam evolved from the water in the core oil.

Drying Procedures

To produce a better core faster, it's necessary to speed up water evaporation without excessively high temperatures that will decompose the surface of the sand before the inside temperature is where it must be for proper curing. That goal can be achieved in several ways:

- As shown in Fig. 5, it is advisable to keep oven humidity as low as possible to maximize tensile strength.
- Use a sand with an AFS Grain Fineness Number (GFN) as low as is acceptable for a given casting finish.
- Arrange cores on racks for good air circulation so oxidation can take place.
- Check oven temperatures to determine if heat distribution is uniform.
- Use only enough water and cereal to achieve the minimum green strength necessary. Each pound (or pint) of water added evolves about 28 f^{t3} of steam that must be removed.

Fig. 5: Tensile strength development based on oven relative humidity; 2-hr. baking at 400°F, 1.25% binder, 2% water, and 1% cereal.



Baking Temperature

Normally, the lower the baking temperature, the better the surface (Fig. 6). The practical baking range, however, is 400–450°F for reasons of oven cycle time.

Fig. 6: Effect of baking temperature on tensile strength.

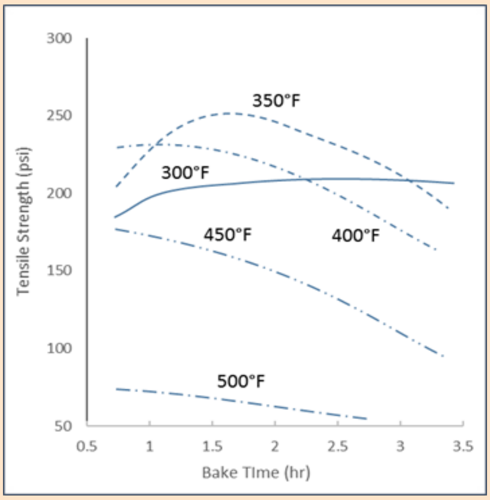
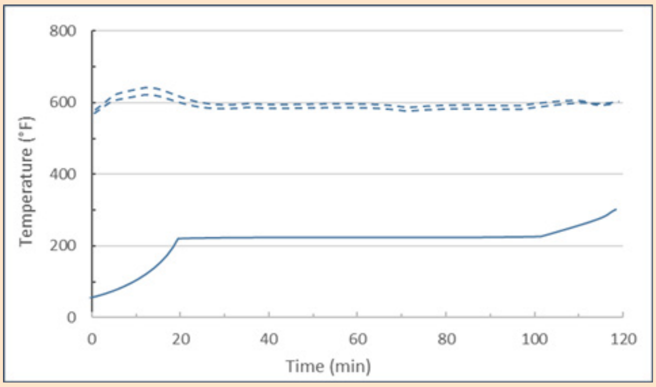


Fig. 7 illustrates the typical heating rate for an oil sand core made from sand, water, cereal, and binder. Note that 20 min. is needed to go from room-temperature to 212°F. It then takes 40 min. to get rid of the water before the temperature begins to climb toward the desired 400°F. Another 20 min. is needed to get to temperature. Thus, it takes nearly 90 min. to begin to cure.

Fig. 7: Typical heating rate for oil sand core of medium section thickness with 1.25% binder, 2% water, and 1% cereal.



Smokeless Oils

Core oils generate smoke and odor as they cure because of their chemical nature. The VOCs that might be contained in the formulations have proven to be special problems. Some foundries have been forced to shut down their core oil process ovens because of excessive odor and smoke emissions. Several-core oil manufacturers, therefore, have formulated solvent-less and water-emulsified systems to help comply with environmental requirements. These newer systems are effective in reducing smoke, odor, and VOC emissions, but generally require longer baking cycles.

Underbaking

Heat and excessive volumes of gas are evolved from undercured core oil during the casting operation. The solvent-containing unreacted binder literally fuels a fire inside the sand and burns. That heat increases the temperature at the sand metal interface to the point that it can cause severe burn-on defects by superheating the interfacial metal. In addition, rapidly expanding gas, formed during the combustion of the undercured binder, can vent from the core so rapidly that it actually might draw the superheated metal farther into the sand, causing massive penetration defects.

Conclusions

Many foundries utilized core oil at one time, but most were unable to afford the EPA required emission controls for batch-drying ovens. Some large, high-production foundries, however, are able to afford the cost controls for the high-capacity, tower-drying ovens and today account for most of the industry's core oil consumption.

Smaller operations that continue to use core oil do so because they have patterns for it. Larger foundries use this process to fill in their core oil process equipment capacity. Today the core oil process remains one of the foundry industry's "old standbys." Although no new core oil foundries are being built, predictions that core oil will disappear quickly are unlikely to come true because core oil process equipment is uncomplicated and rugged, its patterns are simple, and the process itself remains one of the fastest ways to produce small to medium sized cores.

References

All ASK owend figures

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