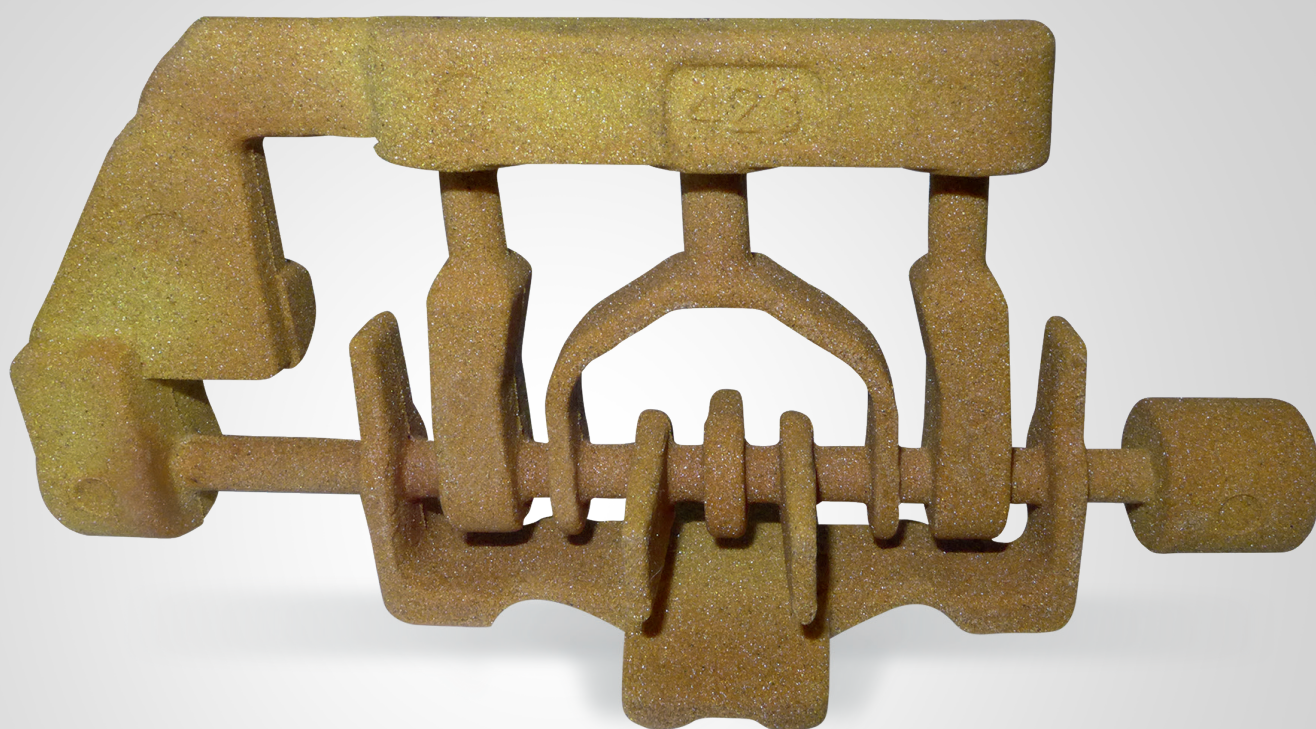Authors: P. R. Carey, L. Roubitchek & J. Green

Sand Binder Systems

ASKCHEMICALS

Part VI: The Shell Process

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

The shell process was developed in Germany during World War II by Dr. Johannes Croning. Even today, in many parts of the world it is referred to as the Croning Process or C Process. Croning's new procedure was limited to making molds, but it enabled the molds to be produced with relatively uniform thickness and dimensional accuracy that was better than alternative molding techniques then available.

The Germans used the shell process during the War to produce molds for mortars, artillery shells, and other projectiles. Interestingly enough, the Germans attempted to keep this process a secret even after the war. However, in 1947, the process was discovered by investigators and placed in the public domain as war booty providing the foundry industry with a revolutionary new mold making process.

The original Croning Process physically blended raw sand with powdered phenolic resin and powdered hexamethylenetetramine (hexa). This mixture was then gravity fed onto a preheated pattern. The heat from the pattern melted the resin coating and activated the hexa to partially advance the resin and fuse the sand grains together. After a sufficient wall thickness was formed (invested), the pattern was inverted and the unfused, inactivated sand dropped away from the partially cured sand that remained on the still-warm pattern surface.

The contoured shell of semicured sand, along with the pattern, were then placed into an oven, and after a specific cure cycle the rigid sand mold was pried off of the pattern. An investment/dump box was eventually attached to the pattern as a container for catching and reusing the inactivated sand mixture that fell away from the mold surface.

Since the early Croning shell process was a dry blend of sand, resin, and hexa it could only be used for making molds by gravity feeding or for producing cores by hand ramming the powdery mixture into the core box. Air transporting or blowing the sand into a core box resulted in unacceptable separation of the resin components from the sand. Consequently, in the early stages of the shell process the dry blend of sand, resin, and hexa was utilized, almost exclusively, for producing shell molds.

However, many suppliers and users began improving the shell process. In the mid-1950's, a liquid shell resin was developed by dissolving the powdered resin into an alcohol solvent, enabling foundrymen to produce a blowable, dust-free resin coated sand that made very strong cores and molds. Later, refinements to the shell process included the introduction of warm air into the coating device to hasten solvent evaporation and, eventually, coating hot sand with resin dissolved in water diluted solvent led to water-borne hot coating.

One of the most dramatic improvements to the shell process came in 1955 when a form of metallic soap (calcium stearate) was incorporated into the coated sand as a flowability additive and release agent. As shown in Fig. 1, using 2.5 to 5% calcium stearate, based on resin solids weight, nearly doubles strength and significantly increases the density of the shell sand.

Fig. 1 – Effect of adding calcium stearate.
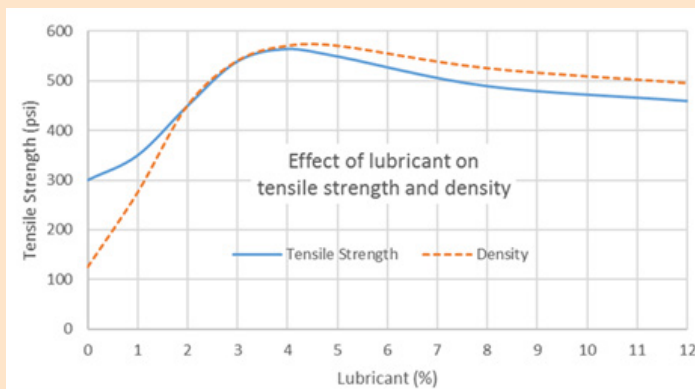
The hot coat process began in the late 1960's utilizing both waterborne and particulated (crushed) shell resin. By the early 1970's solvent-free, flake resins were developed for the hot coating process. Today, over 80% of all shell resins used in North America are in flake form. Solid flake phenolic novolak resins used in the shell process have the advantages of being:

1. Non-flammable.
2. Virtually free from VOCs.
3. Easier to handle than the viscous liquid counterparts.
4. Able to produce freely flowing resin coated sand, which results in very dense cores and molds.
5. Able to melt quickly and coat uniformly.

The shell process is well suited to economically produce large hollow cores. It works well for specialty applications such as pipe hub cores that use a unique core shooter to make it.

Making high quality castings from contoured shell molds is one of the most economically advantageous aspects of the shell process. The sand's outstanding flowability, excellent hot strength, and high density produces very strong molds. This means a relatively thin mold can be utilized to economically cast a number of large, complex castings in a single mold. Because the molds have a contoured surface, the drag half can easily be embedded in raw sand to support the drag during pouring. The molds can also be cast vertically by placing them in a flask and filling the void between the two mold halves and the tub-like flask with raw sand or steel shot. This type of mold making procedure has been used for the production of nodular iron crankshafts.

The Shell Process in Foundries

As listed in Table 1, more foundries utilize the shell process to produce resin sand cores and molds than any other technique. The shell process is also extensively applied worldwide.

Table 1	
Total number of north american foundries	3,110
Foundries using a core process	2,901
Foundries using shell process cores	1,274
Foundries using shell process molds	283

Today, the hot coated shell sand process using flake phenolic resin bears little resemblance to the process invented during World War II.

Types of Sand Used for the Shell Process

One of the remarkable aspects of the Shell Process is its ability to successfully utilize almost any type of aggregate used in the foundry to make cores and molds. Shells curing operation is virtually unaffected by almost any type of sand contaminant or unusual sand surface chemistry. In North America, olivine, high and low acid demand sands, and even thermally high acid demand re-claimed lake sand works very well with shell. In Japan where there really is no good foundry sand, foundrymen utilize the shell process to coat reclaimed local sands and imported sands from Australia.

Coating the Sand

Although alcohol-borne shell resin is still used to coat shell sand by the warm coating technique, illustrated in Fig. 2, most shell resin coated sand is now produced by the hot coat technique shown in Fig. 3.

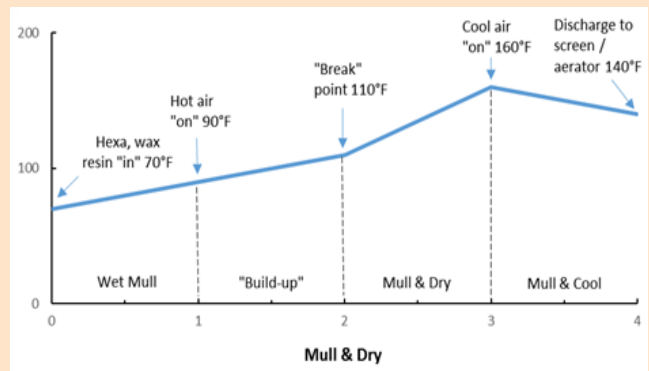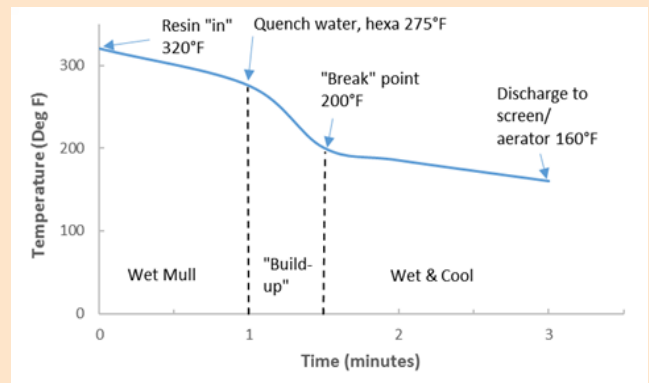**Fig. 2 – Typical cycle for applying resin to sand by the warm coating process.**

Fig. 3 – Time-temperature curve for the hot coat process coating cycle.

The hot-coat process preheats the sand to approximately 300°F, then mixes the hot sand with the solid phenolic novolak flake resin and calcium stearate. The resin melts thoroughly during the wet-mull portion of the coating cycle and covers the individual grains of sand, decreasing the temperature of the sand by about 25°F. A water solution of hexa is then dispensed into the coating device so that it can mix with the resin on the sand. The water quenches and cools the sand. When the quench water is added the hot resin/sand mixture becomes gummy. The coating device completes the sand coating and then breaks down the gummy sand mass into dry lumps. Then the still warm, but dry, coated sand is discharged onto a vibratory screen. It is particulated as it passes through various sized openings and cooled to ambient temperature with large volumes of air during the screening process. After being screened the coated sand is packaged for shipment.

Cooling the dry, coated sand to ambient temperature eliminates any tendency for the sand grains to sinter, or lump, together after packaging.

With the packaging improvements made to the flaked resins over the years, it is now even more important that proper time and temperature controls accompany the hot-coating procedure. Much shell sand is now coated with computer controlled mullers. With

this type of advanced control hot coated sand can be produced in 3–4 minute cycles with batch-to-batch variations so slight that tensile strength and stick point vary less than the accuracy of the testing equipment. Today, shell-coated sand is flowable and dust-free and can be stored indefinitely if it is kept cool and dry.

If lumping or sintering of coated sand occurs, it is usually caused by a combination of high storage temperaures, high humidity, and physically exerted pressure from stacking the bags too high.

Curing the Shell Resin Coated Sand

The chemistry of the shell process is straightforward: phenolic novolak resin + hexamethylenetetramine(hexa) + heat = cured core/mold

When the resin coated shell process sand is exposed to the heat from the pattern, several chemical reactions and physical transitions take place as shown by the three phases of the coating process illustrated in Fig. 4.

Phase I: The thermoplastic resin begins to melt, causing the viscosity of the coating to drop. The hexa mixed into the gelled resin begins to decompose into ammonia and formaldehyde.

Phase II: The thermoplastic B-Stage of the resin begins to polymerize and advance toward the thermosetting C-Stage as the formaldehyde from the hexa reacts with the phenol, liberating a small quantity of water as a by-product. As the binder flows between the sand grains it bridges them together.

Phase III: The phenolic novolak resin becomes thoroughly cured as the phenol consumes the liberated formaldehyde. A transition from a meltable thermoplastic to a rigid thermosetting plastic is virtually complete at this point. The color of the surface of the core/mold is now a golden yellow– a clear indication of a strong, thoroughly cured core or mold. If heat is continually applied to the surface beyond this point the resin post cures and turns brown. Now the bonds between the sand grains become too rigid and the core or mold becomes weaker. If heat is applied still longer the surface begins to thermally decompose and turn black– a clear indication of condition excessive curing. This must be avoided.

Overexposure to elevated curing temperatures will burn and carbonize the surface to the core or mold. This can lead to penetration defects on the casting surface along with a physical weakening of the core or mold. The ideal curing results in a surface that is light brown or dark golden in color.

Fig. 4 – Curve showing conversion of shell resin from thermoplastic to thermoset state.
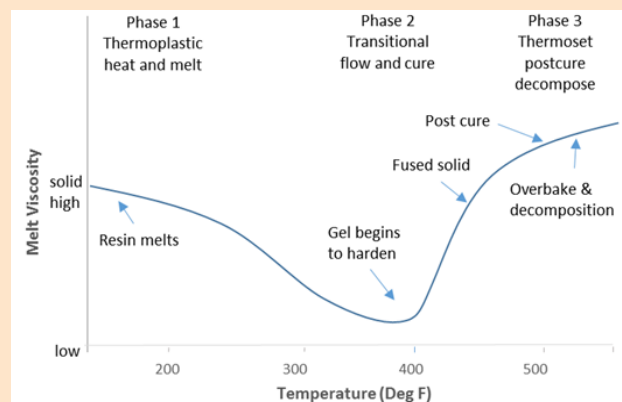
Producing the Cores and Molds

There have been spectacular equipment innovations and significant resin developments in the shell process. However, the fundamental sequence for producing a shell core or mold remains essentially the same as outlined in the five steps below:

1. Dump or Blow– Dump the sand onto a pattern for molding or blow the sand into the core box.
2. Invest– Allow the coated sand time to increase in temperature and build-up to the appropriate thickness.
3. Drain– Turn the pattern over or invert the core box to allow the unreacted sand to fall away from the heated pattern surface and be collected for reprocessing.
4. Rock– In some cases the machine rocks back and forth facilitating better removal of the unfused sand.
5. Dwell– Give the uniform, contoured thickness of shell sand the appropriate time to cure while in contact with the heated tooling surface.
6. Strip or Eject– Remove the cured mold or core.

The shell process appears simple as it repeats the sequence of blow (or dump) / invest / drain / cure / strip during the production cycle. However, both the chemical and physical aspects of the cure are complex and need to be controlled and monitored. The core/mold must be removed as soon as possible because the heat that melts the coating and fuses the sand grains together will begin to thermally decompose the binder coating as soon as the chemical reaction is complete. Temperature control, uniform heating of the pattern, and proper dwell time are as important to making quality shell cores and molds as is the resin formulation, the coating procedure, and the coated sand itself.

Temperature Considerations

Pattern surface temperature and dwell time determine the thickness of the shell developed during the invest portion of the cycle. Maintaining the tooling at the ideal operating temperature range builds-up the appropriate shell sand wall thickness without thermally decomposing the binder. That temperature range is 475–525°F. Process extremes are 400°F minimum to 600°F maximum. Operating within these temperature limits, in addition to building the appropriate shell wall thickness, allows for optimum resin flow. During the final curing stage, the resin at the sand surface undergoes minimal thermal decomposition.

When aluminum patterns are used, the pattern surface temperature should be maintained below 500°F.

Higher pattern temperatures of 525–600°F are, however, often used successfully to make small cores. Little surface definition is lost by decomposition of the resin at the pattern interface during the relatively brief cure cycle needed for smaller cores– which many times are made solid and eliminate the rock and drain part of the core making cycle.

Problems begin to occur when the pattern temperature is in excess of 550° F, and, of course, become more pronounced as the temperature increases, for the following reasons:

1. High temperature in combination with low thermal conductivity of sand, does not allow enough time to invest the necessary shell thickness without decomposing the surface.
2. Shell thickness becomes non-uniform resulting in a thick section of undercured sand that very often tends to generate excess gas and/or delaminate (peel).
3. Resin cures so quickly that it does not flow well enough to form the resin bridges necessary for optimum tensile strength.
4. High temperature will increase operator discomfort.

Peelback

As the cores become larger, a problem unique to the shell process is sometimes encountered. This is known as peelback (a delamination or separation of the partially cured sand from the more thoroughly cured sand at the pattern face). Uniform temperature over the surface of the pattern is perhaps even more important than the specific operating temperature because it, more than any other single factor, may induce peelback. It occurs as a layer of partially cured shell that is passing through the low-melt-viscosity stage begins falling or peeling away from the layer of more fully cured sand in contact with the heated pattern. The shape of the curve during the liquid phase indicates how strong a resin bridge will be formed between the sand grains. The area enclosed by the curve and the solid-to-liquid phase change line is an indicator of the tendency for that coated sand to peel. The greater the area, the more likely the sand coating is to peel. The longer the coating remains in the liquid state, the farther the resin will be able to flow and form the strength-producing resin bridges. Unfortunately, the longer the resin remains in the liquid phase, the greater the tendency to peel.

Sophisticated short-flow resin formulations, hot coating, and the addition of salicylic acid to the resin have minimized the peel tendency. However, even the best shell sand will peel if there is a pattern surface temperature variation of more than 50°F. Peelback will also occur if water, usually caused by excessive moisture in the compressed air system that is used to transport and blow the sand into the core box, changes the ordinarily uniform thermal transfer characteristic of the coated sand or generates steam at the pattern-sand interface.

A significant contributor to peelback is moisture. Moisture, from any source, will turn to steam during the shell cycle and contribute to peelback. Moisture is generated as a by-product of the phenolic novolak curing reaction, and although the amount is not significant by itself, it still adds to the total. Moisture can enter into the cycle from moist blow air. It also can be condensed onto the coated sand during hot, humid times of the year– especially if the sand is considerably cooler than the ambient temperature. Cold sand is a significant contributor to peelback.

The use of salicylic acid to produce a faster cure, improvements in resin technology, and higher melt point resins have combined to minimize this old, nagging problem in the shell core and mold making process.

Run-Ins

Because the shell process makes a hollow core, foundrymen sometimes experience run-in problems with metal filling the hollow core because of thermal cracking, a failed core surface where excessive peel has occurred, or the metal seepage in the vicinity of the open-end of the core. To prevent run-ins from occurring cores are often made thicker or sometimes filled with no-bake sand. In addition, the ends can be sealed by placing some shell sand into the hollow core and inverting it onto a hot plate to cure the sand.

Additives

Various sand additives may be used during the coating operation. They include iron oxide to prevent thermal cracking, provide chill, and minimize gas related defects; potassium fluoroborate for magnesium casting operations; plasticizers to prevent thermal cracking; 1–3% kaolinite clay to improve hot strength, provide chill, and eliminate the orange peel defect on steel casting surfaces; and a long list of proprietary additions.

Tooling

Because the shell process generally operates in excess of 450°F, and requires a uniform transfer of heat into the coated sand, gray iron is the usual material utilized in shell patterns. Gray iron patterns combine good heat capacity along with acceptable thermal conductivity and recovery. The hardness of iron also provides resistance to damage from scratching with sharp instruments and from sand erosion. Compacted graphite iron and nodular iron, however, are now recognized as even better materials than gray iron because of their superior resistance to damage from thermal cycling. Meehanite Type C iron is also an excellent choice for shell patterns because of its excellent wear resistance.

A recommended chemical analysis of iron used for casting shell patterns and related tooling items would be: carbon = 3.20–4.30; silicon = 1.94–2.10; manganese = 0.80–0.90; phosphorous = 0.12 max; and sulfur = 0.12 max.

Since a uniform pattern temperature is required the contoured boxes must be contoured maintaining a thickness of at least ¾ in. Patterns should be equipped with heat-conductive inserts that extend through the iron pattern to the heat source when areas protrude away from the heat source more than two inches. Beryllium copper or manganese bronze are excellent insert materials.

Core boxes should be relieved 1/32 in. on the parting line face and 1/2 in. away from the core cavity. When core boxes contain more than one cavity, a minimum of 3/4 in. should be maintained between cavities.

Shell mold pattern should be designed to result in a minimum bonding surface around the perimeter of the shell mold for efficiently gluing the two mold halves together.

Care should be taken in mounting and locating burners so that the tooling can maintain a uniform surface temperature of ± 25°F in the ideal operating range of 475 to 525°F.

Environmental Considerations

Phenol: For many years there has been considerable concern regarding environmental problems associated with phenolic based foundry resin binders. Shell process resins, as well as resins from many other chemical binder processes, are phenol based and can pose potential phenol leaching problems. However, controlled tests show that waste sand from shell cores and shell molds often contains less leachable phenols than waste sand from other commonly used core and mold processes.

Which foundry waste sands contain phenol? Any waste from a foundry core or mold process that uses organic binders or additives contains phenol. Phenols can be formed as a result of high temperature, or thermal decomposition of organic binders. Waste sands from the shell process generally have the lowest leachable phenol values.

Why do shell molds and cores yield the lowest leachable phenol levels when the base resin contains free phenol and the percentage of resin used in the shell process is often higher than the other systems? The answer lies, at least partially, in the low sand to metal ratios commonly found in shell molding (0.3:1 to 1:1) and the even lower sand to metal ratio, typical of hollow shell cores. The low ratios can contribute to a nearly complete burn-out of the binder during pouring. The result is that there is little phenol left to leach out of the shakeout sand!

The high density of shell cores and molds further enhance heat transfer because frequent grain contacts improves the thermal conductivity and burn-out. In addition, shell molds are generally thoroughly exposed to air during pouring and solidification. This is another factor which contributes to a more complete thermal decomposition of the binder and burn-out of the phenol.

Formaldehyde: In June 1992 the final new ruling on occupational exposure to formaldehyde was issued by the Occupational Safety and Health Administration (OSHA). It contained several new requirements for employers relative to formaldehyde in the work place. The ruling lowered the permissible exposure level (PEL) for formaldehyde from 1 part per million (ppm) to 0.75 ppm. In addition, the new ruling mandates annual employee training for all employees exposed to formaldehyde at levels at or between 0.1 and 0.5 ppm

for an eight hour time weighted average. The new ruling has had, and will continue to have, a significant effect on foundries using binder systems containing and emitting formaldehyde.

It is important to point out that shell resins contain essentially zero formaldehyde, but with the addition of the hexa catalyst there is ammonia and formaldehyde introduced into the process. Ammonia and formaldehyde are both liberated when the hexa decomposes during the sand coating operation, as well as in the curing cycle of the core and mold, and during the pouring and shakeout stages of the casting operation. It is important to point out that the quantitative emissions of phenol, ammonia, water, formaldehyde, and 1.3-benzodioxane are almost always well below currently established Threshold Limit Value (TLV) of 0.75 ppm. However, the exact level of any component from any process in a foundry environment is a function of the efficiency of the venti¬ation system and foundry operating conditions.

From environmental and performance standpoints today's shell resins are being constantly improved. Examples of ongoing research efforts include:

1. Further reduction of the free phenol content of the resin, which is currently less than 3%.
2. Higher melting point resins for improved peel resistance.
3. Lower melting point resins for better resin flow during the coating operation and faster sand buildup during the core and mold making operations.
4. Lower and zero hexa resins.
5. Vinsol replacements.
6. Faster curing.
7. Reduced smoke and odor.

An important point to consider regarding shell resins in the flake form and shell coated sand is that they do not contain any organic solvents and are, therefore, very low in Volatile Organic Compounds (VOC) emissions. This is a notable advantage for foundries making efforts to comply with the Clean Air Act Amendment.

Waste Minimization

Waste minimization and disposal is of great significance to the manufacturing industry and to foundries in particular. How can the shell process assist in the achievement of waste disposal minimization goals? There are four areas in which use of the shell process minimizes waste.

First, resin coated shell sand has an almost indefinite bench life. This eliminates the need for disposal of mixed sand generated in core and mold processes because the binder's limited bench life.

Second, cured shell sand cores and molds have an almost indefinite shelf life and are relatively unaffected by storage at high temperature and high humidity conditions. This eliminates disposal of cores or molds that have lost strength in storage.

Third, most shell cores are hollow. This results in considerably less sand needed to make a given casting than if it were a solid core. Generating less process sand means less sand needs to be reclaimed or disposed of.

Fourth, shell molds and cores are severely scorched during the casting operation, thereby generating a sand easily introduced into a green sand system or one that is easy to reclaim or reutilize.

Reclamation

It's well recognized that thermally reclaimed green sand and reclaimed sand from other core and mold making processes can be readily recoated and reused in the shell process. This is because the chemistry of the shell prcess is not significantly affected by acidic or basic components in the sand. The reuse of reclaimed sand in the shell process is a significant advantage to foundries in which sand disposal costs and/or new sand purchase costs are significant.

Shell Process Casting Properties

Shell is well known for its superior hot strength, but this not the only positive aspect of the process.

Superior Casting Finish – Resin coated shell sand is dry and free flowing. This produces cores and molds of high density that result in superior casting finish. The free flow characteristic of shell process sand can provide the required quality casting finish with a coarser, more permeable sand then might be required using an alternative process. Additionally, the dry, free-flowing nature of the resin coated shell sand allows cores to be densely blown with lower blow pressure than might be required for other systems. This generally results in less wear on the tooling surfaces.

Excellent Dimensional Tolerance and Predictability – Shell process cores and molds have higher hot strength and develop more physical strength than any other commonly used core making process. The superior hot strength and physical integrity gives the shell process its well-recognized advantage of producing castings with very precise dimensional tolerances. The shell process is the first choice of automotive foundrymen when casting critical internal passageways such as water jackets in automotive cylinder heads.

Reduced Level of Gas Defects – Although shell cores, and especially shell molds, utilize a higher binder level than alternative organic systems, the use of thin-walled, hollow shell cores offers an outstanding natural vent path for them, even when finer sands are used. Many foundrymen have found the use of hollow shell cores, combined with the increased permeability of coarser sands yield castings without significant gas defect problems.

Additives, such as iron oxides and clays also can be incorporated into all types of shell sand formulations for additional resistance to veining and casting porosity.

Although the relatively thin, contoured shell mold provides a nearly perfect path for gas to escape from the mold, gas related casting defects occasionally plague steel foundries using shell molds and/or cores, especially steel foundries pouring low carbon grades. These gas defects are often attributed to nitrogen levels in the resin coated shell sands. Grades of low nitrogen resin coated sands are now available in standard resin coated sand grades and that can eliminate or significantly reduce nitrogen related gas defects attributable to the binder.

This new family of low odor shell resins work with hexa levels lower than 4%. Hot distortion values along with other physical properties compare favorably to the conventional types of shell resin as shown in Table II.

Table II: Comparison of Conventional vs. Low-Hexa & Odor Shell Sand		
Resin Coated Sand Type	Conventional	Low-odor-hexa Type
Hexa level (%)	14	4
Melt point (F)	211	213
Hot tensile (psi) 3 min	533	388
Cold tensile (psi) 3 min	690	580
Odor at Coremaking	Strong	Mild
Loss on Ignition	2.99	2.98
Zircon Sand (Source 1992 AFS Transactions, Page 453)		

Testing

Conventional 1/4 in. dogbone specimen tensile testing, both for hot and cold tensile measurements are basic for shell process and testing. The stick point, or melt point, test is used to measure the softening point of the resin coating. Loss On Ignition and GFN testing is also common control tests associated with the shell process.

The Real Cost of the Shell Process

The relatively high cost of pre-coated sand on a perton basis can easily lead to an erroneous economic evaluation of what it actually costs to make the casting with cores and molds made in a shell sand process. Cost comparisons with other processes should be made on the basis of the actual amount of coated sand used to produce the casting along with the actual direct and indirect costs for everything it takes to make it. Costs for all process materials and materials handling also need to be factored in.

Refractory coating costs, for example, are significant and often overlooked. Shell is the process that is most likely not to require a refractory coating. The costs for refractory coating material, application equipment and maintenance, direct application labor along with material handling labor, and coating related defects are some of the often overlooked items. Savings from the elimination of additives, waste coated sand expenses, the value of the sand saved with hollow cores and contoured molds, and especially reduced cleaning room costs are some of the hidden benefits of the shell process.

Commercially Coated Shell Sand

A network of pre-coated shell process sand suppliers has been developed in North America. These specialized companies supply coated sand to foundries on a ready-to-use basis, thereby eliminating the need for individual foundries to purchase, operate, and maintain coating equipment. The need to develop coating expertise, bear environmental compliance costs, and deal with many of the environmental issues relating to coating the sand are also eliminated. As of 1995 approximately 60 to 65% of all shell process sand consumed by North American foundries is supplied by commercial sand coaters.

Conclusion

The shell process remains the most widely used process in North America and has an even broader base worldwide. However, it is recognized that there is no single best process for the production of all foundry cores and molds. For jobs that involve relatively low production volumes, no-bake processes may be less expensive to use because of the relatively low tooling cost. Core weight, core production considerations, casting quality, and environmental factors must all be taken into account when a specific core or mold process is chosen. The shell process has a relatively long machine cycle, and when compared to process such as cold box, can be far less productive. Unquestionably, the unique properties of the shell process and the high quality of the castings it produces insure its future.

References

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