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Sand Binder Systems

Technical Paper

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Part IX: The Acrylic-Epoxy/SO_2 Cold Box Process

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

The term "cold box process" relates to the production of foundry sand cores and/or molds at ambient temperature.

This specialized technique utilizes a vaporized or gaseous chemical that operates as a catalyst or co-reactant in order to cure (polymerize) a resin binder film, which has been spread uniformly over the surface of the sand and compacted into a box-like structure known as a core box. When the coating has fully cured, each sand grain is firmly joined to others in contact with it.

There are several different types of cold box processes. They all use thermosetting resins in conjunction with a variety of catalysts or co-reactants. This article will deal primarily with the one that uses sulfur dioxide (SO_2) gas as the curing agent and acrylic-epoxy resins as the sand binder.

Evolution of the SO2 Process

"Original" SO_2 Process – There are several SO_2-gassed binder systems called "The SO_2 Process." It first came to the U.S. from Europe in 1975. Termed the Sapic Process, it used a phenolic modified furan binder with a silane additive to increase handling strength and an organic peroxide reacted with SO_2 to cure the resin. The system is noted for excellent shakeout and hot strength along with a fairly good bench life.

However, the system has always had productivity problems due to excessive resin wipe-off core/mold curing that requires the tooling should be warmed to 125°F, the sand temperature controlled between 80–100°F, and the purge air heated to at least 220°F. When a furan/SO_2 core is cured it changes the color of the resin coating to black, clearly indicating where polymerization had occurred.

Eventually it was found that substituting an epoxy resin and changing the peroxide type for the furan resin resulted in a system with more easily controlled curing characteristics that also improved casting properties. A few foundries continue to use the Furan/SO_2 system where shakeout is the main consideration, but it has been almost completely replaced by the Acrylic-Epoxy/SO_2 (A-E/SO_2) system.

The Free Radical Curing (FRC) Process - This used acrylic resin in place of phenolic modified furan and/or epoxy. It was introduced around 1983 and it became the fastest curing system in the industry. But despite its rapid cycle speeds it lacked sufficient hot strength to produce ferrous castings and even large aluminum castings were found to be a problem. Nonetheless, it was suspected that this system would have sufficient hot strength if it were modified by the use of epoxy, which turned out to be true. Modifying the acrylic with epoxy gave acceptable hot strength with only small sacrifice in curing speed. However, the amount of epoxy which had to be used was limited because of patents held by the company marketing the epoxy/SO_2 system.

It was also found that acrylic modification of the epoxy/SO_2 system enhanced the curing cycle, handling strength, and strip strength. But, ironically, the company that marketed the acrylic/SO_2 system had patent coverage on its system that limited the supply of acrylic used to modify the epoxy. The amount of acrylic that could legally be used was insufficient to give adequate stripping and handling strength to the epoxy/SO_2 system.

Thus, the epoxy system was no good without a large percentage of acrylic and the acrylic system was no good system unless it was modified with a significant amount of epoxy.

The A-E/SO_2 Cold Box Process - The solution to the dilemma of one binder not working without critical components found in the other was to combine the two technologies. The company that marketed the acrylic system acquired the patent rights from the one that made the epoxy type system in 1983. This gave birth to the Acrylic-Epoxy/SO_2 system. Since its introduction it has become the foundry industry's most versatile and fastest cycling cold box core/mold making system.

A-E/SO_2 Resins

This binder system is comprised of two distinctly different resins– an acrylic (best recognized as a shatterproof clear plastic substitute for glass) and an epoxy (known for its outstanding adhesive properties). Their combination results in physical properties that are truly synergistic since each clearly makes up for deficiencies in the physical properties of the other.

The acrylic offers rigidity, hardness, and rapid curing. It provides the critical out-of-box rigidity needed for rapid core stripping, rough handling, and sag prevention. It also contributes to improving shakeout and reclamation properties.

The epoxy contributes to toughness, abrasion resistance, and excellent handling characteristics. The superior cohesive and adhesive properties of epoxy provides an outstanding mechanism for both coating the sand and then bonding the grains together. Its flame retardant properties contribute to outstanding hot strength and excellent casting finish. The core/mold making benefits of epoxies include excellent release from the tooling and fast cure speed. The unmatched moisture resistance of epoxy resin makes core storage easier and provides resistance to humidity degradation.

Combining the two resins into a single binder results in a system that has the highest strength, the longest mixed sand bench life, and the best casting properties of all cold box systems. It also provides the resin formulator with two materials that can be proportioned to maximize specific core/mold making, handling, and casting properties. It offers the foundryman a system that can be customized for any specific operation.

System Properties

The A-E/$S0_2$ process is based on a two component system. Part A is an epoxy resin, blended with an organic hydroperoxide. Part B consists of acrylic resin, epoxy-resin, additives, and (sometimes) solvents. Once the sand is coated with the two components it is exposed to SO_2 gas, which cures the binder by way of a 2-stage mechanism. The acrylic portion is very rapidly polymerized through a "free radical cure" mechanism. In this portion of the system, the gas acts as a catalyst. The epoxy is cured when it absorbs the SO_2 gas. The SO_2 then acts as a co-reactant, becoming part of a chemical curing reaction during this phase of the polymerization reaction.

The acrylic component cures quickly and thoroughly (giving the system its early handling strength) and the epoxy reacts slowly (giving the system good release properties and eventually good hot strength properties).

Notably, this process contains no water or nitrogen, and the resin coated sand can be stored almost indefinitely. In addition, it can be used with virtually any type of sand.

Binder levels range from 0.5–2%, with 1.1% being typical. Several different versions of the binder have been formulated in order to better match specific metals and meet the needs of the individual user. For example, there are high hot strength binders available for iron and steel that exhibit excellent veining and improved erosion resistance. There are also systems available for aluminum and other nonferrous applications. Specific binder formulations provide good shakeout and improved core storage properties. There are even solvent-free versions of the system that reduce gas defects and meet the changing Volatile Organic Compound (VOC) Regulations.

Core/Mold Making - Once the sand is coated with the two resin components it is blown into a vented pattern, then gassed with sulfur dioxide.

Equipment manufacturers provide a variety of new gassing equipment (see Fig. 1) that provides blends of SO_2 and nitrogen (N_2) for curing the binder. The blends of SO_2/N_2 enable lesser amounts of SO_2 to be used, reducing the amount of SO_2 left in the core/mold.

Fig. 1: SO_2/N_2 gas generator for A-E/SO_2 process.

The SO_2 gas is followed by a dry air purge. The purge air thoroughly distributes the SO_2 throughout the tooling to ensure complete curing, then flushes residual A-E/SO_2 gas from the sand. Heated purge air can be used to more efficiently distribute and carry the SO_2 from the sand and out of the pattern.

As it is purged from the core/mold the SO_2 gas is sent to a packed tower scrubber, such as is shown in Fig. 2. Upon entering the scrubber atmosphere the SO_2 is neutralized by reaction with a 5% concentration of sodium hydroxide inside the scrubber. The neutralization reaction's product is an aqueous solution of sodium sulfate. This is discharged from the scrubber with a controlled pH of 8.5 and is usually acceptable for discharge into municipal sewage systems.

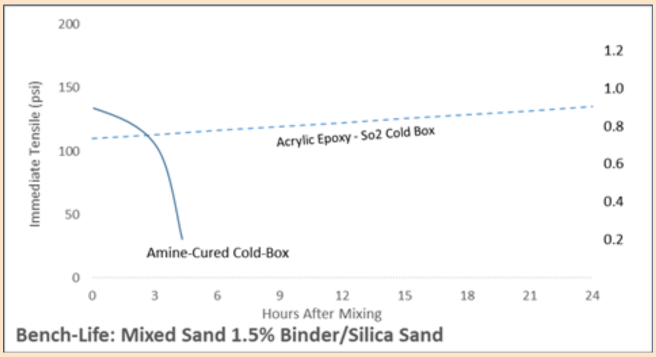
Fig. 2: Packed Tower Scrubber for neutralizing SO_2 gas from A-E/SO_2.

Core/Mold Making Properties - A sand trap installed between the E-A/SO_2 core machine and scrubber is often recommended. This is a very effective way to prevent fine sand particles from entering the scrubber.

The biggest advantage of the A-E/SO_2 process is the nearly indefinite bench life of the coated sand. Once the sand is mixed no reaction takes place until the sand is exposed to SO_2. The mixed sand will not harden in the mixer, sand hopper, or blow magazine. The acrylic-epoxy coated sand is remarkable in that it slides down the sides of hoppers without leaving caked material behind, minimizing hopper cleaning.

The most important advantage resulting from the system's indefinite bench life is its yield of high quality cores/molds. As shown by the negligible loss in strength producing capabilities indicated in Fig. 3, the coated sand does not get gummy during storage, resulting in constant sand flowability and blowability. This significantly reduces core scrap, lowers blow pressures, enhances uniform core/mold density, and lowers binder usage, since the binder level is not raised to compensate for weak, gummy sand. Core scrap is reduced because cores are not blown with sand that has aged beyond its usable bench life. One foundry reported that core scrap went from 7.7% to 2.2% when it switched from hot box to A-E/SO_2, and another stated that core scrap went from 4% to less than 1% since converting from a phenolic urethane cold box to the AE/SO_2 process.

Fig. 3: Loss in tensile strength due to bench life "aging" of foundry resin core systems.



The lack of change in coated sand properties and the resultant constant core strength results in easy start-up, even after prolonged production delays, or extended plant shut downs. The ability to instantly start and stop a manufacturing process is especially useful in synchronous manufacturing operations. There are considerable labor savings and huge productivity gains because start-up is not delayed by getting a new batch of coated sand ready, and shut-down is not prolonged by the need to empty coated sand from the blow magazines and hoppers.

Refractory Coating Application - Another attractive aspect of A-E/SO_2 for both synchronous manufacturing and just-in-time delivery is that cores/molds are immediately ready for metal casting or to accept a refractory coating after removal from the tooling. Virtually any type of refractory coating and application system can be used. Dry coatings, along with alcohol or water based coating systems, are successfully utilized in conjunction with dipping, brushing, spraying, and slushing.

If a water based system is used, the core/mold should be coated as soon as possible after removal from the pattern, and the coating should be dried immediately after application using maximum air flow to achieve low oven drying humidity and a temperature range of 200–350°F. Keeping the temperature and humidity as low as practical results in reduced core/mold breakage and better casting properties.

Refractory Drying Ovens - Drying ovens should be engineered and constructed to dry the coating quickly with maximum air volume and minimum temperature. The oven should have a "preheat zone" where the coating can be "flashed" from the surface of the sand with infrared or quartz heaters. The convection section should maintain minimal temperature with maximum air exchange to minimize humidity. Cores/molds that are oven dried have reduced handling strength before they have cooled to room temperature so the oven should incorporate a cooling zone at the end to reduce handling breakage of the hot cores.

Core/Mold Storage Properties - The storage properties of A-E/SO_2 cores/molds are as good as or better than those of any other cold box process. Although the binder system is affected by high humidity, it is above average for cold box systems and sufficient for virtually all core/mold storage situations.

Casting Properties & Applications

The A-E/SO_2 system offers excellent ferrous and nonferrous casting properties. It contains no water and some of the new systems contain no solvent. The solvent-free systems can reduce potential gas-related defects caused by molten metal contact with moisture or solvents in the binder.

The A-E/SO_2 process is used to produce simple and complex cores and molds for the production of aluminum, iron, and steel castings. Applications include motor blocks, diesel cylinder heads, pump parts, intake and exhaust manifolds, steering gear components, pistons, disc brake rotors, boiler castings, and structural parts.

The chemical composition of the A-E/SO_2 is conducive to all metal casting applications. The elemental chemistry of the binder consists of carbon, oxygen, and hydrogen. The cores/molds contain small amounts of sulfur after they are cured (0.02–0.025%), but still contain less than one-third as much as green sand and sulfonic acid catalyzed no-bake systems. The residual sulfur level depends on the amount of SO_2 used to cure the binder. Efforts are ongoing to develop systems that require less SO_2 to decrease the amount of SO_2 remaining in the finished core/mold.

Since there is no nitrogen in the system the need for iron oxide and other nitrogen scavengers in the sand mix is eliminated.

It is, of course, important to minimize the volume of gas generated by the binder during decomposition by minimizing the amount of resin used. The A-E/SO_2 operates at one of the lowest binder levels in the industry. Levels as low as 0.5%, based on sand weight, and are used to make highly intricate castings. Low binder levels are especially important when cores are complex and require good sand flowability, high tensile strength for handling, and extended bench life. Even though binder levels are important, it is just as important to minimize potential gas defects through good venting practices, proper core print design, and correct refractory coating procedures.

Core Deflection - A-E/SO_2 binders can be reformulated to reduce the threat of core distortion in the mold. The A-E/SO_2 may be formulated by changing the acrylic/epoxy ratios to minimize deflection at semi-permanent mold temperatures.

Shakeout - A-E/SO_2 exhibits its best shakeout properties when the casting temperatures at shakeout are controlled to 350–450°F. Sand removal can be increased up to 80% by shaking out in this temperature range. This enables foundry engineers to design the casting process to shakeout the cores in a just-in-time or synchronous manufacturing system. This also reduces shakeout time and retained sand, and streamlines the casting process.

The positive aspects of the system include:

- Elimination of nitrogen related defects.
- No formaldehyde increases employee safety and facilitates compliance with OSHA standards.
- Elimination of non-productive labor for cleaning sand hoppers, sand magazines, blow tubes, and sand mixers.
- Excellent shakeout properties and reduction of the possibility of hot tears.
- Reduction or elimination of veining defects.
- Maximum productivity due to elimination of start-up or shut-down of equipment holding mixed sand.
- Consistent core/mold quality due to sand bench life.

Sand Reuse and Reclamation

Green Sand - A-E/SO_2 shakeout sand has excellent physical and chemical compatibility with green sand systems. The resin burns out relatively well during metal casting, and this contributes to a sand entering into the green sand system that has a low Loss On Ignition (LOI) value. Because the binder is free of nitrogen it eliminates the concern about nitrogen build-up in the recycled sand.

Mechanical Reclamation - The A-E/SO_2 binder can be easily reclaimed mechanically. The relatively low amount of lustrous carbon remaining on the grains results in high rebonding strength, and the system's zero nitrogen content eliminates concern about nitrogen build-up in the recycled sand.

Thermal Reclamation - Thermal reclamation is often preferred because it eliminates the organics left on the sand. Thus it minimizes LOI and helps control gas related defects.

Thermal reclamation of A-E/SO_2 sand poses no special problems. Since it is an organic binder, it can contribute to the combustion process as it burns off of the sand. Shakeout sand from no-bake operations and in semi-permanent mold foundries can be readily reclaimed mechanically and thermally.

Modern thermal reclaimers are engineered to ensure that the binder decomposition products are totally converted to carbon dioxide, carbon monoxide, and water during combustion, thereby removing all potential for VOC emissions.

Environmental Benefits

As the metalcasting industry moves toward more semi-permanent molding and aluminum sand casting applications the A-E/SO_2 offers a system for these processes that is free of isocyanates or formaldehyde as decomposition products from binders. This is a significant benefit over other organic cold box processes.

The A-E/SO_2 process is producing cores and castings in over 100 foundries worldwide. Its advantages are well documented, yet there is reluctance to implement the process due to the handling and control of SO_2 gas.

Worker Exposure and Control - Sulfur dioxide has a pungent, irritating odor and an odor threshold of less than 0.5 ppm. Employee exposure must be controlled to less than 2 ppm over an eight hour time weighted average, and it may not exceed 5 ppm during any 15 minute period. While these levels are low, they are similar to those recommended for the amine catalysts used in the phenolic urethane cold box process. They are significantly lower than the control needed for formaldehyde emissions from heat-cured hot box operations. In addition, the irritating odor of the SO_2 makes the user pay attention to good cold box gas sealing and containment practices.

Control of SO_2 has been well documented in several tooling manuals and in an industrial hygiene appraisal presented in the American Foundrymen's Society Transactions. Basic controls such as the installation of double seals on parting lines, proper seal hardness selection, and proper maintenance will prevent leaks from occurring during cure and purge cycles.

The core storage area is the other place for potential worker exposure to SO_2. Residual gas might be left in the core and mold after it is ejected from the tooling. Two steps to reduce SO_2 exposure from freshly made cores and molds have been found effective and have been utilized over the last thirty years. The first employs blenders that mix nitrogen with the SO_2 gas. This provides a wide range of SO_2/N_2 blends for curing A-E/SO_2 cores/molds, and results in considerably less residual SO_2 in the core at completion of the gassing cycle. The second is the result of binder modifications that have resulted in less residual SO_2. Combining both methods can reduce the residual SO_2 to well below the 2 ppm maximum Personal Exposure Level. When using blended SO_2 and nitrogen, the foundry must measure the concentration being blended. This may be accomplished through the use of infrared testing of the core gas stream.

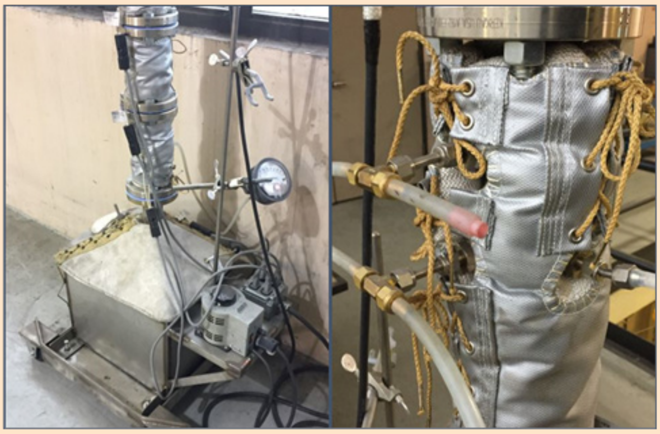
Sand Disposal

There are no waste streams generated from the clean-up of sand mixers, sand hoppers, and sand magazines. The disposal of waste coated sand and cleaning materials is not a problem. Nevertheless, cores cured with the A-E/SO_2 system and the uncured mixed sand have been tested using the Federal Toxic Characteristic Leachate Procedure (TCLP) criteria. The results show that uncured coated sand and cured waste cores do not exceed U. S. guidelines for metals and organics.

Air Emissions

Air emissions from the A-E/SO_2 process during both ferrous and nonferrous casting production have been measured by hood stack studies. Utilizing the equipment shown in Fig. 4, the types of air emissions and the quantity of the decomposition products produced during pouring and cooling are identified and quantified.

Fig. 4: Hood stack apparatus and gas effluent sampling ports.



The hood stack technique is the recognized method for collecting point source emissions. The procedure calls for collecting airborne decomposition emissions from molds less than 24 hours old. The hood stack test uses Class 30 gray iron at 2,600°F as the ignition source and sampling begins immediately upon completion of metal pouring.

Essentially all emissions are drawn up through the chimney, which is fitted with appropriate sampling devices. A constant flow rate is maintained using a variable speed fan that ensured minimal dilution of the effluent at the bottom of the hood. Sampling of the air stream is accomplished using methods developed for stack sampling.

The concentrations of decomposition products measured during the hood stack studies do not represent employee exposure, and should not be compared to work place exposure limits. The data, however, may be extrapolated to provide an approximation of potential emission rates found during pouring and cooling.

Conclusion

The metalcasting industry continues to routinely make conversions from heat-cured processes to cold box systems because they provide better dimensional accuracy and predictability. Non-heated pattern processes also save energy and contribute to a better work environment. However, when a new casting design calls for a high production, precision sand casting method the A-E/SO_2 process is selected more and more often because it reduces costs, streamlines casting production, and meets or exceeds the current or anticipated environmental regulations.

References

Fig 1 & 2: Gaylord Foundry Equipment Inc.
Fig 3 & 4: ASK owned pictures

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