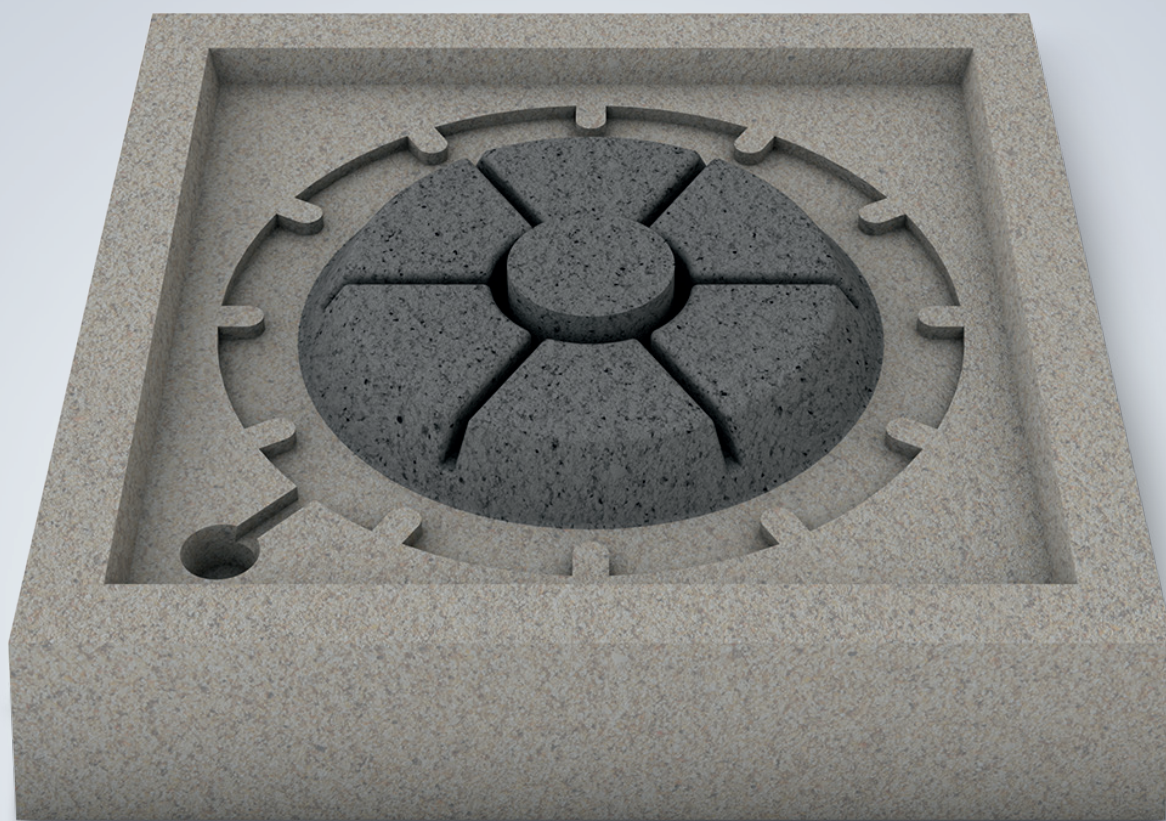


Authors: P. R. Carey & M. Swartzlander

Sand Binder Systems



Technical Paper

Part III: Urethane Binders

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

Urethane no-bake and cold box binders constitute nearly 50% of the resin binders used in North America. The cold box version is the largest selling system, and the no-bake versions are third, after the furan binders.

Unless a breakthrough occurs in inorganic binder technology, urethane systems will probably grow more than all of the other binder systems combined.

Grain Distribution First of the Modern No-Bakes

Oil-urethane binders are the first of the modern “no-bakes.” They evolved from the so-called “air-set,” “cold-set,” or “self-set oils” used in the early 1950s. The term “set” implied that coated sand would set up well enough for a pattern to be separated from it. But the core or mold required drying for long periods at elevated temperature to complete the cure and impart sufficient hot strength for a successful casting to be produced.

By today's standards air-set core and mold making was inconvenient, energy consuming, time consuming, and polluting. However, production with air-set systems was a tremendous improvement over the alternative clay and pitch-bonded systems in terms of dimensional accuracy, productivity, and castability.

Modern No-Bakes Multi-Step Curing Process

When the oil-urethane no-bake system was introduced and patented in 1965, it offered a core and mold making method to produce large castings without having to bake the sand. This new “no-bake” system utilized an oil resin that was reacted with polymeric isocyanate for a predictable “first stage through cure” that enabled stripping from the core box. Then the oil resin would cure further at room temperature, through extended contact with ambient air, to enable production of a large casting. In addition, subsequent exposure to elevated temperature for a relatively short time was an option that offered improved casting properties and enhanced productivity.

Through the years, oil-urethane systems were modified by using various types of hydroxyl-bearing resins that could react with isocyanate to generate specific sand coating and casting properties.

Today, oil-urethane no-bake systems persist as the choice when extended work times are needed for large cores and molds. Rapid curing phenolic urethane systems have become the standard for small and medium sized cores and molds when productivity is a prime consideration.

Oil-urethane no-bake resins (also known as oil-urethane, alkyd urethane, or polyester-urethane) are three component systems comprised of an oil-type resin (Part A), a liquid catalyst (Part B), and a polymeric MDI-type isocyanate (Part C).

The three-part system uses varying amounts of catalyst to achieve a predictable work/strip time. It can be made into a two-part system by pre-blending Parts A and B, but doing so removes the operating latitude that a third part catalyst adjustment offers.

Part A is generally used at 1–2% of sand weight. It is easily modified for better coating action, less smoke, better strip, and

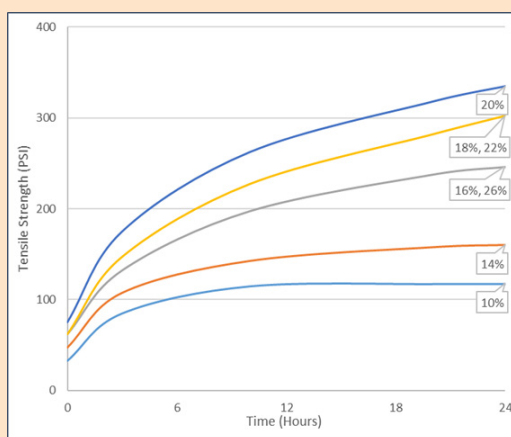
improved performance at extreme temperatures. The system has undergone extensive reformulating to reduce smoke and odor, and improve spent sand disposal.

The Part B catalyst, whether added as a separate component or pre-blended with Part A, is 2–10% by weight of Part A. It is a blend of amine and various metallic compounds. Lead, which had been the most effective metal catalyst, has been removed from the system for environmental reasons.

Part C is polymeric isocyanate, and it should always be used at 18–20% by weight of Part A. Changing this proportion is detrimental to strength, as shown in Fig. 1.

The Part C component contains 10% nitrogen, by weight. On the basis of 20% addition of Part C to the Part A resin, at a nominal 1.5% binder (based on sand weight), the weight percent of nitrogen to sand calculates at 0.03%. This is about the same amount of nitrogen contained in a low nitrogen furan no-bake system.

Fig. 1 - Effect of varying Part C, based on binder, of oil-urethane system with Parts A and B held constant.



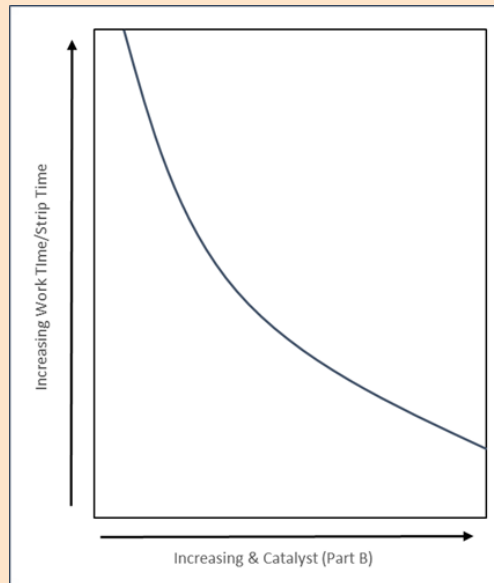
How the System Works

Although the oil-urethane no-bake system is easy to use, the chemical and curing mechanisms are difficult to understand because there are two separate curing stages and two chemical curing mechanisms.

Step 1 – The Urethane Reaction

When Parts A, B, and C are brought together on the sand, the polyisocyanate (Part C) quickly begins to cross link with the oil resin (Part A). The rate of the reaction is a function of both the temperature of the components and the level of the urethane catalyst (Part B), as shown in Fig. 2. This reaction produces a sand coating that provides sufficient bonding strength to enable pattern removal from the core or mold with enough bonded sand strength to prevent drooping or sagging. The speed of this initial reaction determines the strip time.

Fig. 2 – Effect of increasing oil-urethane system Part B (catalyst) on work time and strip time.



Step 2 – Oxidation

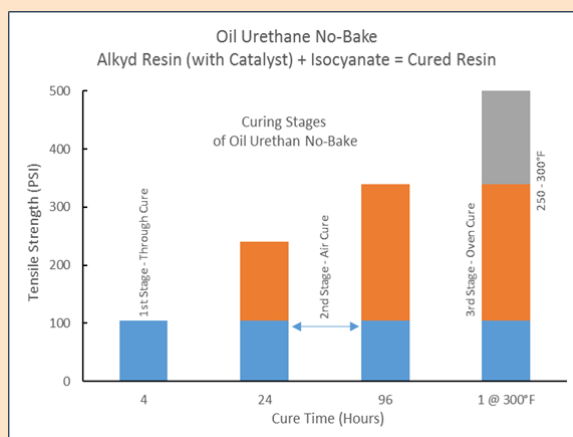
This step of the curing reaction is similar to the air drying of paint. Here, some of the remaining solvents evaporate while oxygen in the air combines with the oil resin component. At this point in the curing reaction, everything has happened at room temperature. The resin has formed a tough urethane bond with sufficient hot strength to make all but the most difficult metal castings.

Optional – Elevated Temperature Curing

Because complete polymerization (cure) is oxygen dependent, things that govern oxygen exposure to resin coated sand determine rate and degree of cure. Therefore, sand volume and surface, along with temperature and catalyst type and amount, are the prime factors that determine the time required for complete cure.

Metallic driers, along with other catalysts that might be present in Part B, accelerate oxygenation, or drying. The second stage, air cure, proceeds slowly at room temperature or quickly at elevated temperatures. For maximum cure and ultimate casting properties, the sand's resin coating should be heated to about 300°F in a forced air oven for about one hour. Figure 3 shows how elevated temperature exposure influences the degree of cure even after curing for 96 hours at room temperature.

Fig. 3 – Effect of baking at 300°F on oil-urethane tensile strength development, even after up to 96 hr. of room temperature cure.



The oxidation, or “air drying” reaction, determines how completely the coating is cured. The more complete the cure, the greater the strength and, in general, the better the casting properties.

The room temperature curing cycle produces a core or mold with strength and casting properties adequate for most situations. Therefore, oven drying is generally utilized only with certain large cores and molds, or in specific instances in which defects and/or dimensional accuracy is a problem.

Strip Characteristics

The speed of the initial reaction, known as the “urethane reaction,” determines the strip time.

The urethane reaction results in a plastic-like first stage cure that produces excellent stripping characteristics. Nevertheless, a release agent can be added by the supplier to the resin (part A) to further enhance the stripability of this system. The superior strip characteristics of the oil-urethane system along with its long work time, permit the use of larger, old wooden tooling that could not be used with any other no-bake process. It is the process of choice when very large castings, particularly of manganese steel, are produced.

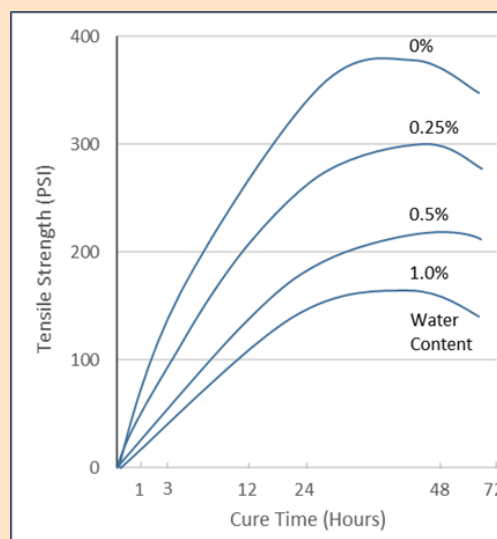
Sand Effects

The oil-urethane no-bake system is generally less sensitive to the chemical properties of sand than any of the other no-bake systems because of the nature of the curing reaction.

Moisture

A sand moisture level greater than 0.2% results in a slower cure rate and a significant loss in tensile strength (Fig. 4). High ambient relative humidity increases strip time and slightly decreases tensile strength. Water contamination of Part A is detrimental to the curing mechanism, and water contamination to Part C has very damaging effects on all aspects of the process. Part C must be kept dry— either under a nitrogen atmosphere or by having the aspirated air dried with silica gel as it enters the container to replace the volume of the liquid isocyanate being consumed in the process.

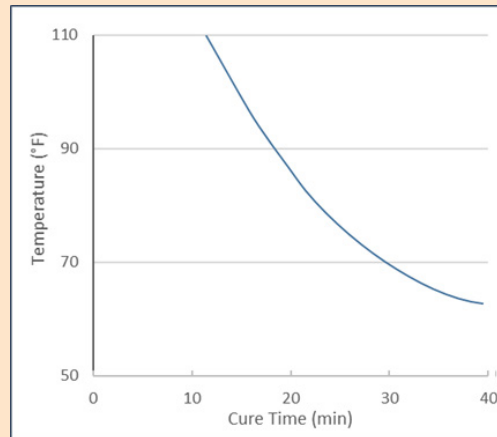
Fig. 4 – Effect of moisture in sand on strength development with 1.5% oil-urethane no-bake plus 20% Part C at 70°F, based on binder. Percent figures on each curve represent water content.



Temperature

Changes in sand temperature greatly affect the cure rate of the system (Fig. 5). A good operating range for this system is 80 to 90°F. It is an excellent idea to control both the sand and pattern surface temperature to about 85°F, and maintain the resin temperature at 75°F. In general, a one minute increase or decrease in strip time occurs with each degree Fahrenheit change in system temperature.

Fig. 5 – Effect of sand temperature on cure rate with 1.5% oil-urethane no-bake plus 20% Part C, based on binder.



Hot Strength

Hot strength of the oil-urethane no-bake system is low compared to that of most other organic no-bake systems. For most applications, the addition of 2–3% iron oxide to the sand mix improves this property and eliminates surface porosity and excessive lustrous carbon deposits. If additional hot strength is required, 1% kaolinite clay may be added with the iron oxide addition.

Core Wash Application

Nearly all types of refractory coatings and carriers are utilized with oil-urethane no-bake systems. It's best not to apply a water-based coating until 24 hours after stripping or after elevated temperature curing. A water-based coating should be dried immediately after application and an alcohol casting lit-off as soon as practical. In accordance with correct refractory coating application procedure, it should be applied to a sufficiently warmed surface— never to a cold one.

For large pieces, in which elevated temperature curing is impractical, coating application should be delayed for 24 hours after stripping. To ensure an advanced state of cure, the surface can be torched prior to coating application.

The first refractory coating application must penetrate the sand surface to a depth of two to three grains. If multiple coats are necessary, the first must be completely dry before the second is applied. Each refractory coat, after the first, should be thin and completely dry before another layer is applied.

It is best to use light off rather than water based refractory coatings, but Volatile Organic Compound (VOC) considerations are making this alternative less attractive.

Post Curing

Oven baking at 300–450°F for short periods, or a quick and careful torching promote further cross-linking of the resin system. This leads to improved tensile strength, better erosion resistance, and higher hot strength. Exposure to elevated temperature also can reduce the amount of potentially detrimental gas-producing solvent in the bonded sand.

Although it is beneficial to post cure the oil-urethane no-bake system to increase tensile strength, excessive post baking can result in binder decomposition on the core or mold surface. Excessive post cure is indicated by a blackened, carbonized sand surface. This should be avoided.

When using an oil-urethane no-bake system, wait three or four days before pouring very large castings. Use of a hot air purge from a forced air furnace will not only post cure the binder, but also eliminate condensed moisture and residual solvents from the coated sand.

With a forced air, large volume heater, mold and core surfaces can be dried conveniently and inexpensively. Hot air can be directed from a furnace into the mold cavity with flexible ducts inserted into the sprues. Riser openings should be covered loosely with tar paper or restricted in some way to slow air flow through the mold and force it into and through the sand.

Conclusion

The oil-urethane no-bake system, with its two-stage curing mechanism, results in unsurpassed stripping characteristics and offers foundrymen an excellent way to fabricate very large and complex cores and molds that require a long work time. Although use of the system will continue to decline, there will always be times when a large casting made from an old wooden pattern probably could not be made using anything else.

Polyester Polyol-Urethane System

This is a low hot strength urethane no-bake introduced into the foundry resin market in 1978. It found immediate application in aluminum, magnesium, and other light alloy foundries because it is an excellent alternative to the other harder-to-shakeout and relatively high hot strength no-bake systems. The system has the additional advantages of containing no phenol, no free formaldehyde, and no heavy metals. Other versions introduced were based on a polyester chemistry that was not as suited to foundry applications as the polyether binder systems.

Thus, the polyester polyol-urethane systems have almost faded from the market.

Polyether Polyol-Urethane System

Polyether-polyol/urethane no-bakes began as an alternative to the oil-urethane and the polyester polyol/urethane systems used in nonferrous casting applications in the late 1980s. Unlike the oil-urethane system, it does not require that a relatively slow reaction with oxygen take place in order to complete the cure. Therefore, it has faster and more predictable stripping and final curing characteristics. In addition, it does not require an elevated temperature post cure to achieve maximum properties. Unfortunately, the system does not offer the outstanding release characteristic of the slower-to-cure oil-urethane.

Stripping and curing characteristics are accelerated by basic sand conditions and retarded by acidic ones. Therefore, both low and high pH sands, along with the use of mechanically reclaimed sand, need to be examined carefully.

System Advantages of Polyether-Polyol-Urethane No-Bake:

- Outstanding shakeout
- No phenol
- No formaldehyde
- No solvent version
- High strength at lower binder levels (typical 0.7 to 1.5% BOS)
- Low viscosity components
- Excellent coated sand floability
- Low door
- Work time is 75% of strip time
- Develops 80-90% of its ultimate strength in 2-3 hr, but can be poured as soon as one hour after strip
- Easy to use 50/50 ratio
- Cure speeds can be varied by selecting different Part As
- Cure speed can be adjusted by adding liquid catalyst during the coating operation

The Catalyst System

Although the polyether/urethane system can be utilized as a three component system (resin, urethane coreactant and catalyst), it has been accepted as a convenient, two-part pre-catalyzed system. Suppliers can provide a range of pre-catalyzed resins with fast to slow strip and work times. This satisfies most requirements. When more precise control over the system's work and strip times is needed, the user has the option of adding catalyst as a third component to speed up any pre-catalyzed two component systems.

No Solvent Binders

A polyether/urethane system is available that contains reactive diluents that provide a completely VOC-free system. This minimizes gas-related defects and is a significant consideration in regions where air emissions are a particularly acute problem.

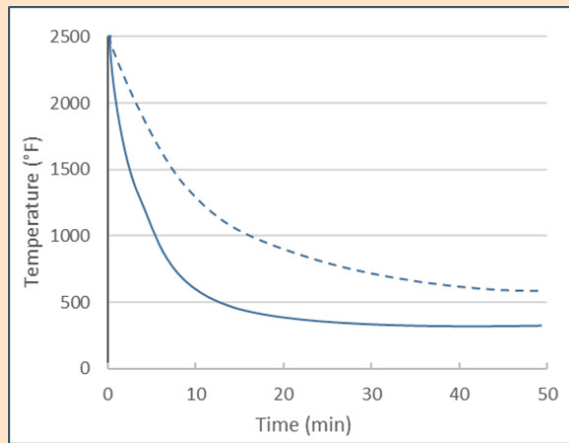
System Considerations

Polyether systems are not recommended for ferrous casting applications; suitability for copper-based applications should be determined on a case by case basis.

Overlooked Potential

The polyether-urethane no-bake system has never been fully recognized and applied to its full potential in non-ferrous applications. It has always been noted for its outstanding shakeout characteristic, as shown in Fig. 6. Looking at the list of advantages offered by the polyether-urethane system, it's difficult to understand why more operations don't utilize this system. With the notable feature of a solventless system added to its already impressive list of significant ecological and workplace advantages, this system deserves evaluation in all nonferrous operations.

Fig. 6 – Collapsibility of polyol urethane compared with that of phenolic urethane.



References

Fig. 1-6: ASK owned graphics

Please do not hesitate to contact us for further information:

Customer Service

Phone: +1 800 848 7485

Email: info.usa@ask-chemicals.com