

Phenolic Urethane Cold-box Binders – A Study of Global Properties, Variables, Causes and Effects

M. Stancliffe

Ashland Casting Solutions, Kidderminster, England

Abstract

The complexity of phenolic urethane cold-box binder materials, properties, processes and applications around the world make the development of binders to cover the expanding range of global industry requirements a challenge. The recent shifts in geographic casting production are continually raising new combinations of property requirements or more difficult combinations of conditions under which phenolic urethane cold-box binders must deliver these customer requirements. A model study was undertaken to link customer requirements, from a more general or global perspective, to verifiable phenolic urethane cold-box core making product and process design characteristics. Design for Six Sigma (a registered trademark of Motorola, Inc.) techniques and tools were applied and an experimental design was developed to provide the basis for the systematic evaluation of the factors binder composition, binder level, global sand source, and global location of test piece manufacture and testing. Testing included typical core-making properties and test castings. The results were analyzed using statistical methods and effects, and the contribution of the design factors to the variation of the test results is discussed.

Key words: Cold-box, sand binders, sand testing

Introduction

The history and development of phenolic urethane cold-box (PUCB) binders has seen many twists and turns as new technology advancements come and in some cases go. Successful phenolic urethane cold-box binders are those that deliver the optimal performance in the maximum number of properties while not having any properties that are clear “show stoppers.” It is extremely rare that any adjustment in phenolic urethane cold-box technology will only result in property improvements. There are almost always one or more property compromises. A thorough knowledge of all foundry applications and processes as well as a well defined ingredient/property relationship matrix is required. Also required is a knowledge of geographic-specific factors such as local sand sources and qualities and environmental conditions and their modified requirements from the binder. Phenolic urethane cold-box binders have evolved into their current form and have been the result of many trial-and-error-type experiments and trials. In addition the requirements of foundries on phenolic urethane cold-box binders have changed and become much stricter in their expectations of productivity and scrap levels. Finally, the ability to investigate and test core-making and casting properties have greatly improved over recent years. In addition, experimental design and statistical analysis techniques, such as those employed within the Design for Six Sigma (a registered trademark of Motorola, Inc.) concept, have also improved the quality and reliability of the data analysis and interpretation.

The authors have undertaken to map out the various differences and commonalities resulting from binder composition and different sands through equipment settings and test methodology to differences in ambient environmental conditions around the world. [1]

Consideration Of Experimental Factors

Sand binders are often underestimated as to their influence throughout the foundry process and the quality and efficiencies in producing metal castings. Focusing on making savings in one isolated area may well have a bigger cost penalty in another area.

The phenolic urethane cold-box binder system is a two-part binder system. Part 1 typically comprises a phenolic resin, solvents and performance additives. Part 2 contains isocyanate, solvents and performance additives. The binder, when cured, is best described as a phenolic urethane polymer which has profound impact on core mechanical properties, resilience of the core to atmospheric conditions and, of course, the performance of the core when it interacts with the liquid metal. Depending on the type of phenolic resin and the isocyanate, a large spectrum of different phenolic urethane polymers can be created. Solvent technology is also being viewed as critically important for the performance of the binder, both at core making and during subsequent stages of storage and at casting. Solvents make up 20% - 40% of the total binder composition and provide the basis for many property variations.

Performance additives generally account for only a small portion of the entire binder composition, but result in “big” effects. As these additives are also very costly it was viewed that the approach to this re-assessment of the technology should not include the effects of additives or at least keeps their effects to a low and standardized level within any comparison.

The fact that a typical phenolic-urethane bonded core may consist of 99% by weight of sand and only 1% by weight of binder suggests that the sand source and quality might play a major part in the resultant properties of the resulting core and possibly has an impact on the final casting as well.

In terms of core making process controls and variations, resin addition (i.e., the “binder level”) is known to have an important effect, as does the physical location in the world of the core machine due to extreme variations in ambient conditions. Based on the above, five variables of immediate interest and global impact were identified:

- Sand
- Binder solvents
- Binder polymer
- Resin addition
- Location of manufacture and test

Designed Experiments

Design of experiment techniques provide an approach to efficiently designing complex, large-scale experiments which will improve the understanding of the relationship between product and process parameters and the desired performance characteristics.

For the performance comparison of different phenolic urethane cold-box binders on different global sands the following factors and levels were applied in the study:

1. Sand source
Four subangular silica sands with AFS GFN 50-60 were chosen from various locations around the world. The analysis data for each sand is shown in Figures 1 and 2 and Table 1. Sands were picked that were fairly similar as the effects of big differences in sand quality are well documented.[2,3] The object of this study was to look for more subtle differences that can still have a significant effect on phenolic urethane cold-box binder performance.
2. Binder solvent package
Phenolic urethane cold-box binders require an appropriately designed solvent package that solvates the phenolic resin, the polyisocyanate and the curing phenolic urethane polymer. Whilst this can be a complex blend of solvents each with varying properties, in this case, two specific and simplified packages were chosen to

provide a comparison of the two main solvent package families currently employed in phenolic urethane cold-box binder technology. Solvent systems based mainly on aromatic hydrocarbon solvents and ester solvents were considered, denoted S1 and S2, respectively.

3. Phenolic urethane polymer

A significant proportion of phenolic urethane cold-box technology relates to the design of the phenolic base resin and the subsequent phenolic urethane polymer when reacted with a typical grade of isocyanate. For the purpose of this experimental design, two globally successful and yet different phenolic base resins were utilized, of specific interest to the authors, denoted in this case as B1 and B2.

Combined with the two solvent package types, this resulted in four different binders. Each binder was optimized in formulation ratios to give a maximum immediate strength within a specified viscosity range. Viscosity was limited because it controls the property of mixed sand flowability which could influence or mask performance due to variations in equipment design. Each formulation was also limited by having to achieve a practical level of cold temperature stability without separation.

4. Resin addition

2 levels: 1% and 1.5%, measured as weight percent of binder based on sand, of Part I and Part II applied at a ratio of 1:1. The adjustment of binder additions is known to have significant effects, both advantageous and disadvantageous on several properties.

5. Location of test piece manufacture and test

Three test laboratories in the U.S., Europe and Asia. By the inclusion of three testing facilities in different locations, the comparative level of contribution to variation in certain properties could be established in proportion to the other factors examined. By allowing these differences into the experimental design we can at least pinpoint worst cases to their location and start to investigate and hopefully eliminate their cause.

The experimental design was a L16 mixed 2-4 level Taguchi design based on a fractional factorial experiment which allows an experiment to be conducted with only a fraction of all possible experimental combinations of parameter values.

The core-making and casting tests employed to comparatively evaluate the performance of the various factors are described below.

Core-making tests:

Immediate tensile strength [4]
 Immediate transverse strength [4]
 Tensile strength at 24 h [4]
 3-hr mixed sand bench life [4]
 Tensile strength @ 90%RH [4]
 Release and resin wipe-off [6]
 Amine consumption [6]
 Curing efficiency [6]

Casting tests:

Gray iron erosion wedge casting [5 7]
 Gray iron penetration casting [5]
 Gray iron warpage block casting [8]
 Aluminum shake-out casting [9]
 Hot distortion [8]

Veining, penetration, erosion and surface finish were visually rated using a scale of 1 to 5 with 1 as the “best” and 5 as the “worst.” Warpage was measured as deflection of the core cavity in the resulting casting.

Analysis of Variation

The raw data gained from the experiments were statistically analyzed using analysis of variation (ANOVA) techniques. A design factor with a large difference, in contribution to the total variation, from one level to another indicates that the factor is a significant contributor to the performance characteristic in question. Contributions derived from the results of the core- making and casting tests are shown in Figure 3.

All factors had a significant effect on at least one and usually more core-making properties. The binder level had the largest effect on the greatest number of properties. The variation from the different sands had a surprisingly smaller effect than expected on many of these properties. Sand variation had the greatest effect on benchlife performance on immediate tensile strength.

The variation between test locations was fairly consistent in most properties. Any testing that includes exposure to humidity features an inherently larger error than testing under normal conditions. Humidity resistance was also clearly a property greatly affected by binder formulation variations. The results of resin wipe-off testing indicate that prediction of this property is least reliable. The larger variation associated with the two release and transversal test locations was immediately investigated and verified and found to be due to a design / part specification difference in the test piece manufacturing equipment resulting in an immediate benefit from this experiment.

The contribution to variation arising from the casting tests and evaluation of casting properties resulted in a very different picture. Most notably the error contribution is considerably larger. Some casting properties were mostly sand specific, while others were affected by all factors. The contribution of binder technology and binder level was significant in properties such as erosion resistance and core warpage on casting and the binder level clearly dominated shake-out. Veining proved to be

completely independent of phenolic urethane cold-box binder choice and addition, and largely dependent upon the sand.

Effects

The significance of each factor and level can be visualized in an Effects plot which shows the effect of each level per factor per test measurement discussed in Figures 4-8.

Phenolic base resin B1 gave rise to better erosion performance than B2. Dalin sand had a very beneficial effect on veining. The lower level of purity in the Dalin sand is a likely reason for this. Phenolic base resin B2 had a lower level of core warpage on casting than resin B1, which is opposite to the comparison of erosion resistance. Nugent sand had an unusually low level of core warpage on casting. Solvent package S1 and Arena sand gave rise to improved levels of shake-out performance.

Additional Properties and Tests

Once the general structure of this experiment had been designed, additional tests were run and their results introduced providing further depth to the effects of the various factors. For example:

Hot distortion tests were performed on the sand, resin and % factors. The hot distortion, or hot deformation test, involves the measurement of deflection of one end of a sand core test piece when a gas flame is applied to the centre of a bar shaped sand core test piece. This test has long been the discussion topic of foundries and binder manufacturers alike as to the relationship of different parts of the graphs with particular casting properties. An example of the hot distortion curve typical for a PU bonded core is shown in Figure 9. The curve contains 3 distinct measures: maximum distortion height (upward deflection of the core); time to zero distortion (return of the core end to its original position); time to failure (excessive sagging or breakage of the core).

The effect plots for each of the graph measurements are shown in Figure 9. The plots for each measurement on the graph clearly responded very differently to the different levels for each factor. The plots can be used almost like finger prints which can be compared to the casting effect plots in Figures 7 and 8 to find a reasonable match. Out of all the casting plots only core warpage on casting, not surprisingly, resulted in a good match and only in the measurement of time to zero deformation.

Conclusion

The enormous amount of data within this study and the subsequent statistical analysis has already generated a wealth of information as well as several directions for future study. The data and analysis presented is only a sample of what was obtained and further mining of this data along with additional experimentation will be required to extract full value.

The knowledge accrued forms a secure foundation on which further experiments in sand, binder and process variables can be based and added to. Future binder development can only benefit from studies such as this, providing more secure knowledge of phenolic urethane cold-box binder performance and the factors which can be adjusted to more accurately deliver customer requirements, regardless of global location and sand used.

References

1. Copyright 2006 American Foundry Society (www.afsinc.org): Stancliffe M; Kroker J; Wang X; "Phenolic Urethane Cold-box Binders-Using Design for Six Sigma Methodology to Evaluate Core Making Needs for the Global Market," AFS Transactions (2006)
2. Carey P, Swartzlander, M W, "Sand Binder Systems Part II – Resin/Sand Interactions", *Foundry M & T* (1988).
3. Garner T E, "Mineralogy of Foundry Sands and its Effects on Performance and Properties", *AFS Transactions* (1977).
4. "Mold and Core Test Handbook," 3rd Ed, American Foundrymen's Society, Des Plaines, IL.
5. Tordoff W L, Tenaglia R D, 25th Anniversary Paper: "Testing Casting Evaluation of Chemical Binder Systems", *AFS Transactions* (2006).
6. Blackburn P A, Henry C M, "A More Productive Phenolic Urethane Coldbox Process", *AFS Transactions* (1996).
7. Henry C M, Showman R E, Kahles D, Nikolai M., "Process Variables Affecting the Erosion Resistance of Phenolic-Urethane Cold Box Cores", *AFS Transactions* (2003).
8. Rigel J A, Sturtz G P, "Developing New PUCB Binders for Aluminum Casting Applications", *AFS Transactions* (2005).
9. Henry C M, Showman R E, Wandke G, "Process Variables Affecting Al Casting Shakeout of Coldbox Cores", *AFS Transactions* (1999).

Tables

Table 1. Compositional analysis by X.R.F.

XRF TEST RESULTS				
	Dalin Industrial	Arena C-55	Congleton HST 50	Nugent 480
	%	%	%	%
SiO ₂	91.70	95.38	97.67	95.41
Al ₂ O ₃	4.46	2.37	1.16	2.46
K ₂ O	2.24	1.45	0.69	1.25
Na ₂ O	0.86	0.32	0.11	0.45
Fe ₂ O ₃	0.28	0.06	0.22	0.25
CaO	0.20	0.12	<0.05	0.21
MgO	0.08	0.05	0.07	0.10
TiO ₂	0.07	<0.05	<0.05	<0.05
Cr ₂ O ₃	<0.05	<0.05	<0.05	<0.05
Mn ₃ O ₄	<0.05	<0.05	<0.05	<0.05
BaO	0.05	<0.05	<0.05	<0.05
ZnO	<0.05	<0.05	<0.05	<0.05
V ₂ O ₅	<0.05	<0.05	<0.05	<0.05
P ₂ O ₅	<0.05	<0.05	<0.05	<0.05
ZrO ₂	<0.05	<0.05	<0.05	<0.05
SrO	<0.05	<0.05	<0.05	<0.05

Figures

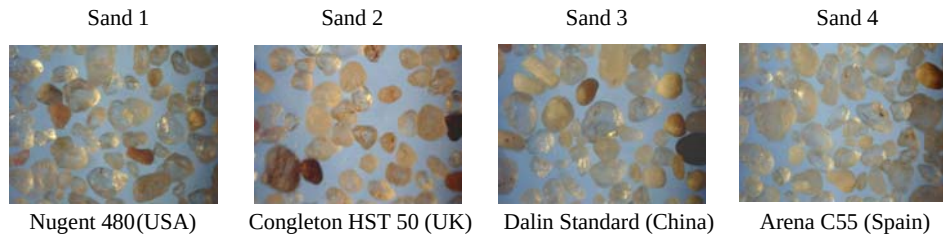


Figure 1: Micrographs of the four sands used in the experiment.

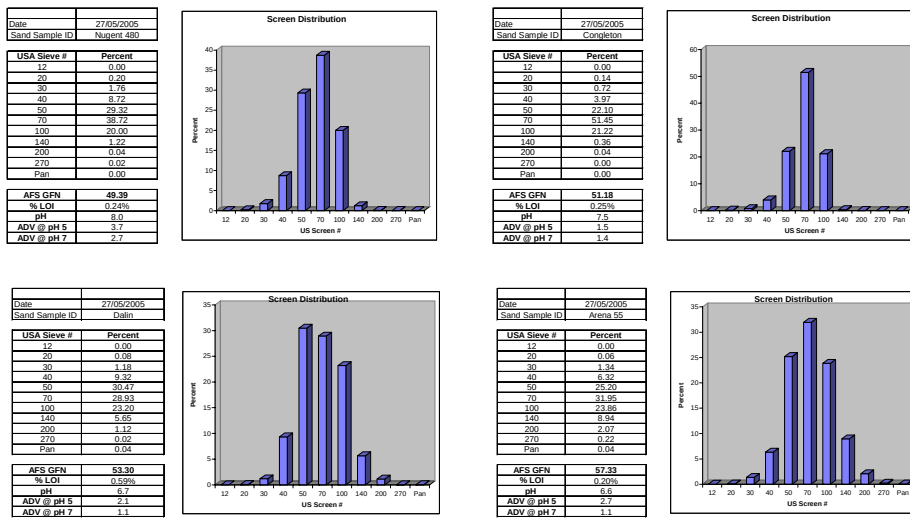


Figure 2: Sand granulometry, physical and chemical analysis data.

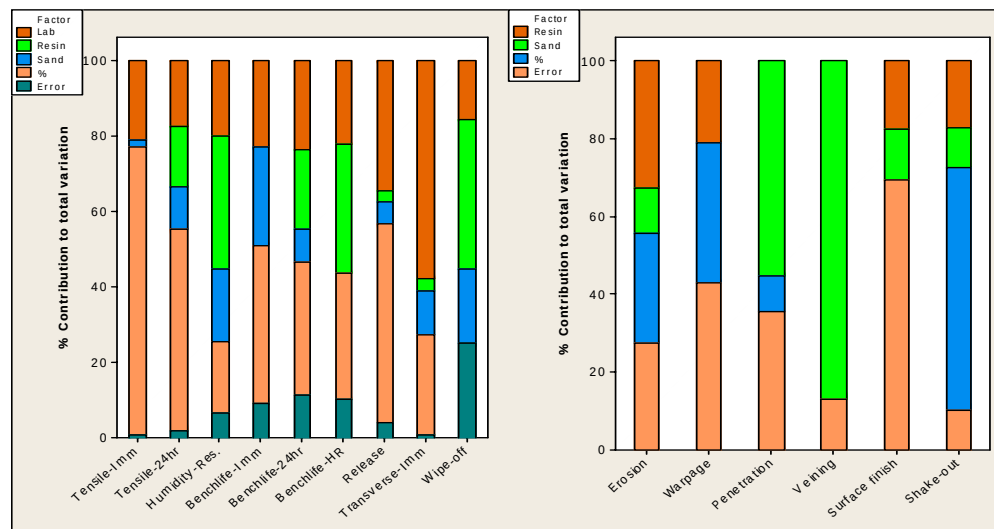


Figure 3: Contribution to variation vs. factor per casting property.¹

All tensile strengths measured at the European location were unusually high. Reasons for this may include equipment design as the processing parameters were generally considered quite similar.

Resin B1 gave higher 24hr tensile strengths than B2. Solvent Package S2 gave superior humidity resistance than S1 and the interaction of B1 and S2 gave the highest performance. The same trend was observed in humidity resistance testing.

Dalin sand gave noticeably poorer 24hr and 24hr@90% RH tensile strengths.

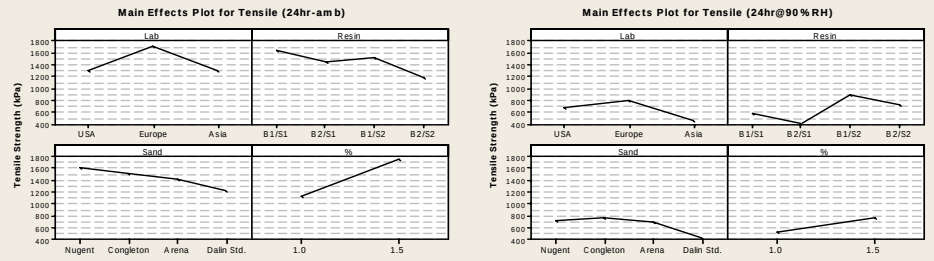


Figure 4: Effect plots for core strength properties.

Benchlife properties were much lower in the Asian testing location. Ambient environmental conditions showed no obvious correlation as to why. Free amine levels in the vicinity of the stored sand could be responsible.

Solvent package S2 gave rise to higher benchlife performance in terms of 24hr and 24hr@90% RH conditions. Nugent and Congleton sands were generally better in benchlife performance even though both sands pH's measured higher than the Arena and Dalin sands. No correlation with ADV was observed.

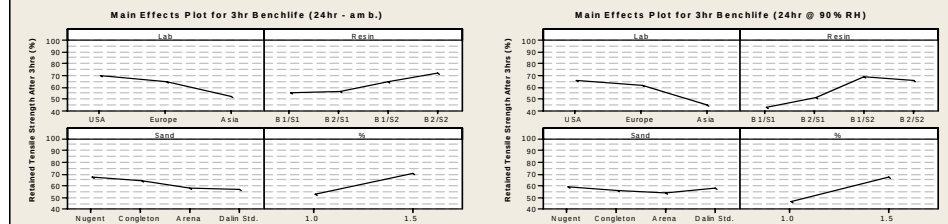


Figure 5: Effect plots for benchlife properties.

The difference between USA and European test equipment has been identified as a difference in part specification which resulted in the difference in test data obtained.

Solvent package S1 gave higher transverse strengths than S2.

Nugent and Congleton sand gave higher transverse strengths than Arena and Dalin sands. This difference was not observed in the tensile data.

Resin B1/S1 and Arena sand both gave unusually high levels of resin wipe-off.

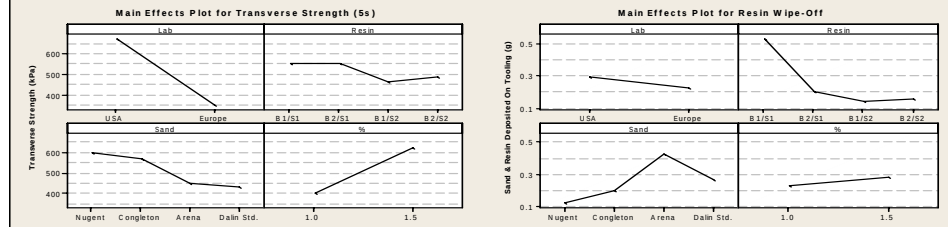


Figure 6: Effect plots for tooling properties.

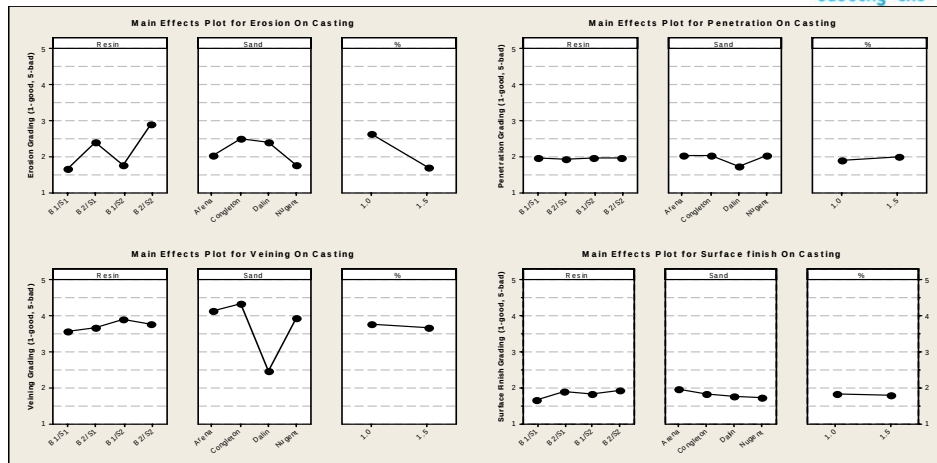


Figure 7: Effect plots for casting quality properties.



Figure 8: Core warpage on casting and shake-out performance.

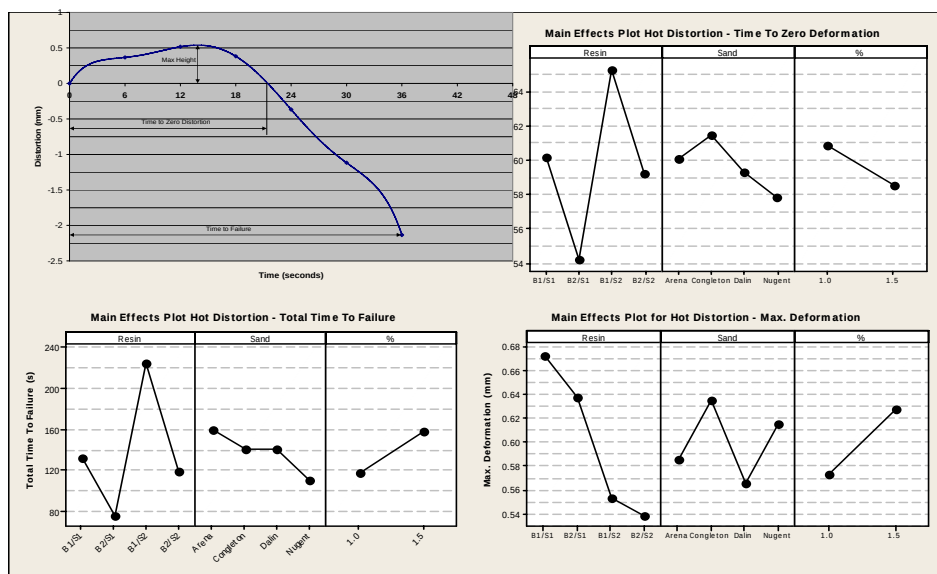


Figure 9: Typical hot distortion behavior & effects plots / measurement

Author's E-mail Address: mstancliffe@ashland.com