

Since the 1970s, the integration of nobake binders into green sand systems has been investigated significantly. By updating a previous conclusion, closure to the dilemma might be at hand.

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ince 1979, the growth of chemical binders-particularly phenolic urethane binders-has been phenomenal. Although usage of most chemical binders has increased during the last 25 years, the use of phenolic urethane binders has grown at the fastest rate. In 1971 the U.S. metalcasting industry used only 2.7 million lbs. of coldbox and nobake phenolic urethanes. In 2003, 150 million lbs. of both resins were projected to have been consumed in the U.S. Estimated worldwide use is considered to be greater than 300 million lbs.

These newer binder systems have helped to meet the increased demands of the metalcasting industry for a variety of reasons including improved dimensional accuracy, increased productivity and reduced energy consumption.

However, spanning the same time period has been an ongoing controversy about the effect of recycled chemically bonded sands on green sand properties. In the 1970s, few reports were conducted on the topic. But over the last 25 years, more engineers have investigated the issue, mainly focusing on phenolic urethane binders, and in particular, whether their introduction into a green sand system affects rebonding properties.

One of the earlier studies (conducted in 1979) investigated the effects of chemical binder core sand contamination on the properties of a bentonitebonded green sand. Although the results were relevant at that time, the study was updated this year, reviewing the same tests with additional parameters. Also, the updated investigation studied three different metalcasting facilities and how phenolic urethane binders affect their green sand systems.

This article examines both the 1979 and updated studies of such binders as well as results of other investigations found during this 25-year span.

Binding Past Knowledge

Amid further studies of phenolic urethane binders' performance, some of the investigations have contested one another. Despite this closer examination and a dichotomy of information, one important question remained: "What effect will core butts and shakeout core sands have on green sand properties as they enter a green sand molding system?"

Several investigators have looked into possible chemical-related effects of core sand contamination on green sand properties. One study concluded that although specific change to a green sand system might be slight—and in some cases even advantageous—the long-term effects might be grave. In those cases where an effect was noticed, it was felt that condensed resin distillates (a byproduct of binder pyrolysis) impeded the bonding effectiveness of bentonite. The effects observed were most apparent in the de-

> terioration of both green compression and wet tensile strengths of the molding sands.

> Other investigations have declared the benefits of mixing, such as little-to-no difference between the rebonding characteristics of 100% recycled phenolic urethane coldbox (PUCB) process sand and new sand. A similar study revealed that 15% particulated core sand from both phenolic hot box and PUCB cores could be blended into a green sand system with minimal effect on molding properties. The losson-ignition (LOI) values of the particulated sands were 2.13%. A different investigation also focused on the effects of core sand dilution with PUCB binders. This study concluded that

Table 1. Moisture Content of New/Recycled Sand Blends

	% Contamination								
Binder System	1%	5%	10%	25%	50%	100%	Average	Std. Dev.	
FNB-Phos	2.70	2.72	2.82	2.74	2.84	2.72	2.76%	0.05%	
FNB-TSA	2.94	2.86	2.88	2.86	2.88	2.88	2.88%	0.03%	
FNB-BSA	3.00	2.96	2.74	2.82	3.00	2.80	2.89%	0.10%	
Phenolic Nobake	2.70	2.64	2.76	2.94	3.00	2.85	2.82%	0.13%	
Phenolic Urethane	2.96	2.96	2.96	2.82	2.84	2.70	2.87%	0.10%	
Silicate Nobake	3.00	2.84	3.00	2.98	3.00	2.86	2.95%	0.07%	
Standard Green San	d System N	Aoisture Cor	ntent: 2.87	% ± 0.11%					

Table 2. Available Clay Content of New/Recycled Sand Blends (Determined from IMC Charts)

	% Contamination								
Binder System	1%	5%	10%	25%	50%	100%	Average	Std. Dev.	
FNB-Phos	5.50	5.60	5.60	5.30	6.10	5.50	5.60%	0.24%	
FNB-TSA	5.60	5.30	5.70	5.80	5.70	5.80	5.65%	0.17%	
FNB-BSA	6.00	6.10	5.60	5.70	6.00	6.20	5.93%	0.21%	
Phenolic Nobake	5.80	5.50	5.70	6.10	6.10	6.00	5.87%	0.22%	
Phenolic Urethane	5.70	6.00	6.00	5.80	5.70	5.50	5.78%	0.18%	
Silicate Nobake	6.00	6.00	6.20	6.10	6.00	6.50	6.13%	0.18%	
Standard Green San	d System A	wailable Cla	ay: 5.80% ±	0.20%					

	% Contamination								
Binder System	1%	5%	10%	25%	50%	100%	Average	Std. Dev.	
FNB-Phos	3.20	3.60	3.60	3.20	3.90	3.30	3.47%	0.26%	
FNB-TSA	3.10	3.30	3.00	3.80	3.50	3.60	3.38%	0.28%	
FNB-BSA	3.80	3.90	3.50	3.40	4.10	4.40	3.85%	0.34%	
Phenolic Nobake	3.90	3.70	3.80	4.00	3.80	4.10	3.88%	0.13%	
Phenolic Urethane	3.90	4.00	4.10	3.80	3.70	4.10	3.93%	0.15%	
Silicate Nobake	4.00	3.90	4.00	3.70	3.60	3.90	3.85%	0.15%	
Standard Green San	nd System E	Bonding Cla	y: 3.90% ±	0.10%					

Table 4. Available Clay Content of New/Recycled Sand Blends (Determined by Methylene Blue Titration)

	% Contamination									
Binder System	1%	5%	10%	25%	50%	100%	Average	Std. Dev.		
FNB-Phos	7.60	7.80	8.00	7.60	8.00	7.60	7.80	0.18		
FNB-TSA	7.80	7.80	7.80	7.80	8.00	7.80	7.84	0.08		
FNB-BSA	8.00	7.60	8.00	7.80	7.80	7.80	7.80	0.13		
Phenolic Nobake	7.60	7.60	7.40	7.80	7.60	8.00	7.68	0.20		
Phenolic Urethane	7.80	7.80	7.80	7.60	7.80	7.60	7.72	0.10		
Silicate Nobake	8.20	8.20	8.60	8.60	8.40	8.60	8.48	0.16		
Standard Green San	d System A	Available (M	B) Clay: 7.8	3% ± 0.20						

the spent PUCB sands, regardless of LOI value, had no effect on green properties of the molding sand.

Still, examinations have been performed announcing that mixing core and green sands will have significant effects on molding properties. Because the curing mechanisms of all chemical binders involve various modes of acidbase catalysis, concern exists on how residual pH changes from shakeout core sands affect clay-bonded sand properties. Past studies have revealed that pH significantly affects green sand properties. These studies note that as the pH value of green sand increased, green compression strength decreased while dry strength, permeability and flowability increased.

Reconditioning of green sand systems has been said to be one of the most difficult steps in molding-sand technology. Bentonite and water preferentially settle on the molding sand grains already coated with clay. Long and intensive mulling is required before recycled core sands assume the same properties as those of the base molding sand. Table

One investigation found that incorporating lustrous carbon forming additives at high levels to improve the refractoriness of sands often leads to the buildup of an oily film, which further reduces bentonite swelling capacity. Lustrous carbon, several engineers have claimed, hinders green sand properties, and some note high-percentage LOI sands had such a coating.

However, lustrous carbon doesn't burn in a LOI test, hence, lustrous carbon and LOI values are not related. Therefore, the intermediate LOI values were likely the result of some other pyrolysis condensate residues. If these condensates from intermediate thermal decomposition levels produce a slippery or oily film on the sand grains, then one would expect to see reduced ability for bentonites to bond to sand surfaces. This may be partially overcome by additional mulling.

The pH and lustrous carbon dilemmas will be discussed later in this article.

In addition to chemical contamination, another factor affecting green sand properties is the physical effect from additional core sand entering a green sand system. These sands may be more difficult to mull with bentonite if they contain pyrolysis condensate residues. If appropriate tests are not run to make up for deficiencies in bentonite content, loss of bonding properties could result.

Then and Now

By updating the research from 25 years ago, a more detailed approach can be taken in regards to this controversial topic. The 1979 study dealt exclusively with residual chemical effects, such as acidity and basicity contributions from recovered shakeout sand. It did not examine physical interactions, such as pyrolysis condensate residues on sand grain surfaces and/or condensate residues on bentonite particles from binder decomposition. That study showed that recycled nobake core sand additions up to a 50% substitution rate and after exposure to casting temperatures had littleto-no effect on green sand properties. In all cases, optimum green sand properties were

achieved after 25 min. of mulling.

With a few exceptions, green sand properties, such as compactability and green compressive strength, for the bentonite-bonded coldbox recycled shakeout sand were essentially equivalent to those of the new base sand. Although some slight shifts in performance were observed, these deviations were usually within one standard deviation of the average base green sand system properties.

In the current study, the results from 1979 were reviewed to determine the effect of deliberate additions of recycled shakeout core sands and the effects on the properties of the new bentonite-bonded molding sand. To investigate these effects, varying amounts of recycled nobake sands were added to fresh sand mixtures to determine possible interactions between the recycled core sand and new sand system. Green compressive strength, shear strength, compactability and permeability were measured in an attempt to determine potential chemical interac-

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	% Contamination									
Binder System	1%	5%	10%	25%	50%	100%	Average	Std. Dev.		
FNB-Phos	46.00	46.00	55.50	48.00	48.00	47.25	48.46	3.25		
FNB-TSA	52.00	53.00	50.00	51.00	50.00	47.25	50.54	1.82		
FNB-BSA	49.50	49.75	48.50	49.75	49.00	45.75	48.71	1.40		
Phenolic Nobake	50.00	48.75	50.00	47.50	46.75	42.50	47.58	2.57		
Phenolic Urethane	53.00	52.75	51.00	50.75	49.50	47.00	50.67	2.03		
Silicate Nobake	53.00	51.00	46.25	44.75	46.25	33.75	45.83	6.13		
Standard Green Sar	d System (Compactabi	lity: 54% ±	4%						

Table 6. Effect of Core Sand Contamination on Green Compression Strength

tions. Other properties measured were moisture, available clay, mean available clay and bonding clay contents.

The procedure used was divided into two phases. The first phase consisted of generating shakeout sand from chemically bonded molds after performing casting trials. The second phase evaluated the effects of the recycled sands when added in vari-

ous proportions to a new sand-claywater mixture.

The sand was a blend of new sand and recycled core sands obtained during casting shakeout. Recycled core sand contaminant levels of 1%, 5%, 10%, 25%, 50% and 100% were evaluated. (The 1979 research did not include contaminant levels of 1% and 100%).

The Current Event

With the addition of the 1% and 100% contaminant levels, one finding was as noticeable in the current study as in 1979—almost all of the binder systems for the various properties studied were found to be within a standard deviation of 1 (Tables 1-7). This proves that the properties of a contaminated system are similar to those of a standard base green sand system. The only property where more than two binder systems exceeded the 1 standard deviation level was permeability, which had a standard deviation of 10 (Table 8). Tables 9 and 10 examine various

	% Contamination								
Binder System	1%	5%	10%	25%	50%	100%	Average	Std. Dev.	
FNB-Phos	19.00	19.30	17.50	16.90	21.00	17.35	18.51	1.42	
FNB-TSA	15.65	16.40	17.20	19.30	18.05	19.05	17.61	1.33	
FNB-BSA	18.95	20.90	18.00	17.70	18.87	24.20	19.77	2.23	
Phenolic Nobake	20.50	19.95	19.75	21.50	20.65	22.50	20.81	0.94	
Phenolic Urethane	18.65	19.20	21.20	19.40	19.00	16.65	19.02	1.33	
Silicate Nobake	19.80	20.13	21.95	19.93	19.50	24.85	21.03	1.88	
Standard Green San	id System (Green Comp	ression Stre	ength: 19.0	psi ± 1.0 p	si			

properties of recycled core sand and new green sand.

When this investigation was moved to three metalcasting facilities (A, B and C) the results were all similar. Facilities A and B, both of which use rigid flasks, run nearly identical green sand properties, whereas facility C, which utilizes vertically parted molds, requires more robust green sand properties. Even though two entirely different base sands were used at facilities A and B, the physical properties of the green sand system were remarkably similar.

Facilities B and C reported that PUCB shakeout sand re-entering their green sand systems did not present any problems. Both PUCB shakeout sands had relatively low LOI values and both facilities treated spent PUCB shakeout sand entering the sand system as a new sand addition; they added the appropriate amount of bond and water to compensate for the PUCB sands. These findings are likely due to the fact that facilities B and C use aromatic and aliphatic solvents, which are normally associated with PUCB systems.

On the contrary, facility A used a system based on bio-diesel solvents due to a "brittle-sand" condition that resulted in casting surface deterioration. After converting to the new system, the facility no longer needed to add new sand to the green sand system to restore properties and, like facilities B and C, did not report any green sand property deterioration.

Truth Be Told

By evaluating the reports from the three facilities as well as the updated laboratory research, these investigations advance the argument that nobake sands do not significantly affect molding characteristics of a green sand system.

pH level—Even though certain nobake binders may contain strong acids or bases in either the resin or the catalyst, it is evident that after the binders have

undergone curing and casting, they impart very little of their original acidic or basic character to the reclaimed sand.

When such sands enter into a green sand molding system, they do not significantly reduce the bonding effectiveness or molding properties of bentonite clays in the mix, thus, there is no correlation between residual pH and green properties.

There are several reasons why residual binders on reclaimed nobake sand do not impart appreciable acidic or basic impurity functionality to a green sand system. In some cases, during the curing reaction between resin and catalyst, acidic or basic substances react to form neutral salts, which are relatively nonreactive with bentonite clays.

In addition, acidic or basic

 Table 7. Effect of Core Sand Contamination on Green Shear Strength

	% Contamination								
Binder System	1%	5%	10%	25%	50%	100%	Average	Std. Dev.	
FNB-Phos	4.80	4.90	5.50	3.60	5.40	4.50	4.78	0.63	
FNB-TSA	4.35	5.30	4.10	5.15	5.05	5.00	4.83	0.44	
FNB-BSA	4.70	5.27	4.57	5.37	5.27	5.90	5.18	0.44	
Phenolic Nobake	5.50	6.45	5.20	5.60	5.10	4.75	5.43	0.53	
Phenolic Urethane	4.35	5.60	5.60	5.20	5.70	4.50	5.16	0.54	
Silicate Nobake	5.75	5.75	5.65	5.45	4.93	5.00	5.42	0.34	
Standard Green San	d System (Green Shear	Strength: 5	5.10 psi ± 0	.70 psi				

Table 8. Effect of Core Sand Contamination on Permeability

	% Contamination								
Binder System	1%	5%	10%	25%	50%	100%	Average	Std. Dev.	
FNB-Phos	112.00	112.00	117.00	82.00	94.00	72.00	98.17	16.84	
FNB-TSA	103.00	100.00	85.00	91.00	85.00	78.00	90.33	8.79	
FNB-BSA	91.00	91.00	88.00	83.00	94.00	75.00	87.00	6.35	
Phenolic Nobake	110.00	112.00	112.00	111.00	97.00	85.00	104.50	10.18	
Phenolic Urethane	113.00	114.00	108.00	108.00	111.00	77.00	105.17	12.80	
Silicate Nobake	102.00	105.00	98.00	107.00	109.00	79.00	100.00	10.03	
Standard Green Sar	nd System I	Permeability	/ Index: 107	7 ± 10.0					

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catalysts in a nobake system are normally used in such small amounts that after casting and reclamation, only a minimal amount of residual catalyst remains on the sand. It appears likely that in instances where there have been reports of decreased green sand

properties because of suspected PUCB contamination, pyrolytic condensate residues on either sand grain surfaces or bentonite particles, from incomplete pyrolysis, may affect resultant green sand properties. These condensates may impede the swelling action of bentonite and, for a given mulling time, the smearing action of bentonite particles needed to develop green sand properties.

Lustrous Carbon—Lustrous carbon defects have been blamed as a cause of many contamination problems. Some investigators of core sand contamination have concluded that lustrous carbon is one cause of reported deterioration green sand molding properties. Lustrous carbon, a brittle material measuring 0.0001 in., forms at the moldmetal interface in binder systems that contain high levels of carbon and relatively low levels of oxygen. It cannot coat sand grain surfaces.

As additional metal flows into the mold, these films may become dislodged and be flushed ahead of the leading edge of the incoming metal stream. If the films are not dissolved in the metal or oxidized, solidification can proceed against these accumulations, resulting in surface wrinkling characteristics of lustrous carbon defects.

However, the lustrous carbon-forming tendencies of certain chemical binders are harmful only if large amounts of

carbon films form and then are dislodged from the moldmetal interface during pouring. When this happens, wrinkling and surface laps result. If the lustrous carbon films are not dislodged during filling of the mold cavity, lustrous carbon formation may actually improve casting surface finish.

As such, the deposits do not have a LOI value because they will not burn in a traditional LOI test. Based

Table 9, Recy	vcled Shake	eout Core Sa	nd Properties

Core Sand System Contaminant	рН	ADV	Loss on Ignition (%)
Furan Nobake—Phosphoric acid	2.8	-15.2	0.81
Furan Nobake—Toluene Sulfonic acid	4.3	+3.2	0.78
Furan Nobake—Benzene Sulfonic acid	5.2	+4.0	1.08
Phenolic Nobake—Benzene Sulfonic acid	5.2	+5.2	1.03
Phenolic Urethane Nobake (PUN)	7.0	+3.8	0.62
Silicate Nobake (SNB)	8.5	+5.4	0.17*
New Sand Base Reference	6.3	+3.0	0.06

*Conventional LOI determination is not applicable to inorganic systems.

on the proposed mechanism of lustrous carbon formation, lustrous carbon films from PUCB binders cannot be responsible for some reports of diminished green sand properties. If and when green sand properties deteriorate from PUCB binders, it probably results from unique thermal circumstances occurring within the core during casting, not lustrous carbon. Such problems may be overcome by employing longer mulling cycles.

Useful Sand to the Core

Despite the 25 controversial years regarding green sand contamination, this recent investigation augments the theory that both recycled core and green sands are compatible in the same system. Although this study showed that reclaimed nobake core sand had little acidic or basic interaction with bentonite clays, such sand should be treated as new, unbonded sand.

However, there are a number of methods that may be used if green sand properties need to be restored. These include:

increasing mulling time;

Table 10. Standard New Green Sand Properties

Base Sand System Parameters: 3% moisture, 6% seacoal,

8% Western Bentonite, 10 minute mulling time

1—From IMC Sand-Clay-Water Control Charts

2—Determined from Methylene Blue Titration

Property

Moisture

Bonding Clay 1

Available Clay 1

Green Shear

Permeability

Compactability

Available (MB) Clay 2

Green Compressive

- increasingwestern bentonite levels;
- increasing mold venting to help release gaseous decomposition products;
- reducing binder content in cores;
- scalping or removing core butts from the shakeout system;

Average Value

2.87%

3.9%

5.8%

39 ml

5.1 psi

19 psi

107

54

Standard Deviation

0.11

0.10

0.20

1

0.7

1

10

4

• if possible, reducing core weight to provide higher levels of thermal breakdown. Other factors that metalcasters using PUCB binders should consider are that, in the investigation, PUCB binders formu-

lated with aromatic

and aliphatic sol-

vents generally did not result in green sand property deterioration. In instances where the deterioration of green sand properties is linked to the use of standard PUCB binders, the facility should consider coldbox binder systems that use bio-diesel solvents.

Further, appropriate additions of new bentonite clay and water should be made to adjust total clay back to its original value. Thermal conditions within the mold may result in incomplete combustion of PUCB decomposition gases during pouring. Condensate residues generated from such conditions may inhibit the ability of bentonite particles to effectively coat sand grains.

Lastly, past studies have claimed the addition of small amounts of sodium carbonate or soda ash (Na₂CO₃) to a bentonite green sand system has helped improve the bonding action of bentonite clays as well as soda ashes' ability to cleanse sand grain surfaces.

Although green sand systems might falter as a result of other conditions, after this thorough examination, no indication was found that recycled chemically bonded sands have any deleterious effect on the properties of a green sand system. *MC*

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For More Information

"Evaluating Refractory Coatings for PUCB Binders: A Practical Approach," S.G. Baker, 2002 AFS Transactions paper No. 02-026.

"Influence of Nobake Core Sand Contamination on the Properties of Green Molding Sands," R.L. Naro, T. Zeh and J. Plummer, 1979 AFS Transactions, vol. 98, p. 39-46.

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