New Coldbox Binder System for Improved Productivity

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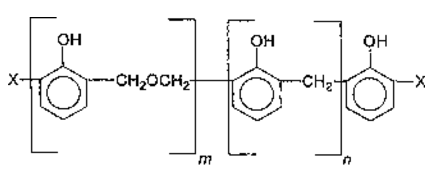
ABSTRACT

A new solvent system based on methyl esters of vegetable oils, when used to formulate phenolic urethane resins, shows a reduction in volatile emissions and improved process performance. Pattern release, for both coldbox and nobake cores and molds, is significantly improved. Humidity resistance and dip and dry tensile of coldbox systems are improved. In coldbox core production, increased cure efficiency has resulted in greater productivity in high-production operations.

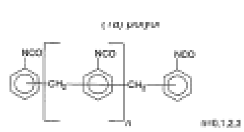
BACKGROUND

Since the introduction of phenolic urethanes in the late 1960s, phenolic urethane binder systems have been improved in performance and increased in complexity and sophistication of design. This has led, in part, to the increased usage of these systems in the United States. Consumption of both the nobake and coldbox versions of this system now exceeds 130 million pounds annually. Phenolic urethanes account for the largest market share of any nobake (over 45%) or coldbox (more than 85%) system in use.

Some of the reasons why phenolic urethane systems are so popular are their versatility. Nobake systems are used to produce castings of all sizes and shapes in all types of metal. Work and strip times can be varied over a wide range to meet almost any production requirement. This system has the highest work-to-strip time ratio of any nobake system, due to a unique latent reaction mechanism. This feature allows metalcasters to work with the sand longer and strip sooner, again equating to greater productivity.



(1a) polyol



(Ib) polyisocyanate

Fig. 1. Active ingredients in a PUCE resin.

Coldbox systems have become the most widely used process for a variety of reasons. Phenolic urethane coldbox (PUCB) is a known system, first introduced in 1968. The foundry industry has the benefit of 30 years of improvements to the system. The system provides good tensile strength needed for delicate cores and is relatively insensitive to sand type. This system provides good hot strength and dimensional accuracy. PUCB sand is reclaimable. The system is always associated with high productivity.

Many of the new developments with phenolic urethanes have been focused on improved environmental characteristics and productivity enhancements. These developments include the removal of lead and the reduction of free formaldehyde from Part I resins, and reduced naphthalene content in both resin and coreactant components. Systems that feature lower volatile organic compounds (VOCs) have also been introduced.

Productivity enhancements include better bench life, greater humidity resistance, resistance to degradation from aqueous core coatings (so-called dip and dry characteristics) and improved release from the tooling or pattern.

Despite these advancements, the need for greater productivity and better environmental characteristics has led to the development of yet the next phase of improvements for phenolic urethanes.

CHEMICAL CHARACTERISTICS OF COLDBOX RESINS

All phenolic urethanes are three-part systems consisting of a modified phenolic resin Part I, polymeric isocyanate Part II, and tertiary amine catalyst Part III.

The "active" ingredients in a PUCB resin system consist of a polyol and a polyisocyanate. The polyol representing one of the components is a phenol-formaldehyde resin exhibiting benzyl ether character. These resins display the general formula shown in Fig. la, in which the sum of m and n is at least two, and the ratio of m:n is at least 1:1 (x = -H or $-CH_2OH$).

The polyisocyanate is an oligomeric product of 2,4'- and 4,4'-diphenylmethanediisocyanate (commonly referred to as MDI), and has the structure shown in Fig. lb.

Both the phenolic resin component and the polymeric isocyanate are traditionally dissolved in organic solvents, due to the very high viscosity of both materials.

However, the difference in polarity of the polyisocyanate and phenolic resin limits the choice of appropriate solvents that are compatible with both components. This compatibility is necessary to achieve complete reaction and curing of the binder, as well as the speed of cure.

Polar solvents like dibasic esters and dioctyl adipate are, for example, very appropriate for phenolic resins, but less so for isocyanates. The situation is exactly the reverse when nonpolar solvents are used. The preferred nonpolar solvents are high-boiling aromatic hydrocarbons (generally in the form of mixtures) exhibiting a boiling range above 150C at atmospheric pressure.

Despite all the advantages that phenolic urethane binders offer to the foundry industry, the aromatic solvents that used to be considered indispensable in them have created serious disadvantages, due to emissions in production and storage of cores and molds, and particularly during pouring, cooling and shakeout operations. The nonpolar aromatic solvents are rich in both VOCs and hazardous air pollutants (HAPs), both of which are carefully regulated by the Federal Environmental Protection Agency's Title V permit program as outlined in the Clean Air Act Amendments of 1990.

At the high temperatures encountered during the casting operation, the binder components are subjected to a pyrolysis process involving creation of new, stable compounds. In the presence of aromatic hydrocarbons, this pyrolysis process generates benzene, toluene and xylenes, which exhibit particularly great thermal stability. The focus of this paper is the development of new coldbox binder systems[1] to improve this environmental weakness.

Instead of the previously favored high-boiling aromatic hydrocarbons, plant-based solvents (methyl esters of vegetable oils) were used for the resins and coreactants. Aside from the ecological advantages of these odorless, environmentally friendly, nonpolluting and $C0_2$-neutral natural products, the new solvents meet all physical requirements for phenolic urethane binder systems. They are high boiling, sufficiently low in viscosity, odorless, and are classified as innocuous at the workplace. They are furthermore nonflammable, a property that considerably simplifies transportation and storage of the resin and coreactant solutions prepared from them. Table 1 shows typical physical properties of a methyl ester solvent.

Table 1.
VOC Comparison

Component	% VOC	System VOC (@ 55/45)	% Reduction (vs. Conv.)
Conventional Part I	41.7	-	
Conventional Part II	22.6		
Conventional System Combined		33.1	
New Part I	26.8		
New Part II	2.0		
New System Combined		15.6	52.7

VOC'S AND EMISSIONS

As mentioned earlier, a deficiency of the PUCE process is that it is a solvent-based system. In traditional systems, the use of aromatic hydrocarbons as the solvent of choice has led to relatively high VOC content. Typical VOC content for traditional coldbox systems range from 40-50% in the Part I and from 20-30% in Part II. Table 2 shows a VOC content comparison between a conventional PUCB system and the new methyl ester technology. Note that VOCs are shown for the individual components, as well as for the combined system calculated at a 55/45 ratio. The new methyl ester technology results in a VOC reduction of over 50%.

If benzene is considered a lead component for the emissions that arise when molding sand binders are exposed to thermal stress, pyrolysis of coldbox systems containing various combinations of solvents shows radical differences in the emission results.

In tests conducted in Europe using German PUCB formulations, remarkable differences have been seen and are documented here. The binders shown in Fig. 2 and Table 3 specifically represent a classic system containing aromatic solvents, the first stage of development with a reduced level of aromatics, and a system that is free of aromatic solvents and based on the methyl ester technology. The plot shows the individual benzene emissions produced by pyrolysis under inert gas at various temperatures. The slightly shaded bar represents the classic coldbox system; and the white bar, the new methyl ester technology.

Table 2.
Methyl Ester Physical Properties

Characteristic	Typical Value
Appearance	Yellow liquid
Moisture, 0/0	0.1 max
Viscosity @ 40°C, cSt	4.6
Flash Point, °C	190
Density, lb/gal	7.30

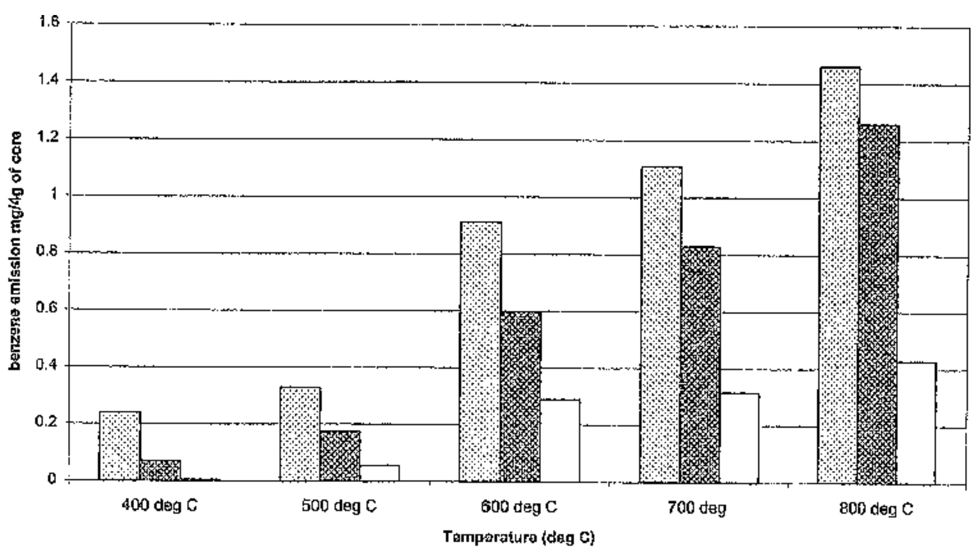


Fig. 2. Benzene emissions produced by pyrolysis under inert gas; 1.6% total binder (50/50); silica sand. Light gray bars = standard; dark gray bars = low VOC; white bars = new.

Table 3.
Benzene Emissions (mg/4 g)

Temp.	Standard System	Low VOC System	New System
400C	0.24	0.07	0.005
500C	0.329	0.174	0.055
600C	0.911	0.594	0.289
700C	1.11	0.829	0.316
800C	1.46	1.259	0.429

Notes: 1.6% total resin (50/50 ratio) on silica sand (gfn 46). Pyrolysis under nitrogen, at different temperatures. Weighed sample: 4 g of pulverized core material. Benzene emission (mg/4 g core).

This difference clearly shows that the workplace exposure of the employee at the shakeout station is lower when the new system is in use. Furthermore, the environmental burden is reduced. This has been demonstrated by measurements made in the hoodstack of a foundry, as shown in Table 4. The levels at the shakeout station and in the hoodstack, through which the exhaust air leaves the foundry, are listed.

These emission measurements led to identical results in a number of foundries: the BTX (benzene, toluene and xylene) emission levels were decreased by 25-50%, depending on the operating conditions, with the new methyl ester-based formulas.

Reduction in benzene emissions has not yet been as well documented in the U.S. Limited hoodstack testing conducted at a midwestern ductile iron foundry has shown a modest 5% reduction in benzene, but a more significant 18% reduction in VOCs, and is shown on Table 5. Additional work is presently underway.

Table 4.
Pouring Measurements

	Shakeout (mg/m^3)		Hoodstack (mg/m^3)	
	Standard System	*New System*	*Standard System*	*New System*
Benzene	10.82	6.37	13.48	7.00
Toluene	7.10	3.54	9.81	5.36
Xylene	7.77	6.09	12.99	5.10
Phenol	14.22	6.60	18.85	7.61

Table 5.
U.S. Hoodstack Measurements

	Pounds Benzene/Ton Iron	Pounds VOC/Ton Iron
Conventional coldbox	0.055	0.27
New coldbox	0.052	0.22
% reduction	5.45%	18.5%

Table 6.
V8 Diesel Head Core

System	No. of Blows Before Release Application
Standard	15
New	70

STRENGTH DEVELOPMENT

The plots in Figs. 3-5 show the tensile strength development provided by the new coldbox system, in comparison to those in a standard system.

In general, out-of-box strengths are similar to those of standard systems, with the exception of immediate and early strengths. However, the somewhat lower initial strengths developed with the methyl ester systems are compensated for by easier release from the tooling. No deleterious effects from this phenomenon have been observed in actual foundry practice.

Furthermore, as can be seen in Figs. 4 and 5, improvements in resistance to degradation, to exposure, to high humidity and aqueous core coatings are seen with the new system.

IMPROVED RELEASE OF CORES FROM TOOLING

During the mixing operation, the sand grains are coated with a film of binder consisting of resin and coreactant. During the blow cycle, when the corebox is filled, the sand grain strikes the surface of the corebox at high speed. This impingement against the surface of the corebox causes the binder layers to spall off the grain, and simultaneously deposit on the surface of the corebox.

In the case of conventional coldbox binder systems, attempts were made in the past to diminish this negative effect by including release agents in the resin and activator formulations.

Deposition of binder residues on the corebox surface below the blow inlet has been minimized by use of vegetable oil methyl esters as solvents. This provides for excellent release of the core from the tooling. A lower fraction of core breakage, longer runs and reduced consumption of external release agents result.

Table 6 shows the increase in the number of blows achieved before use of an external release agent is required for both conventional and new systems, from a foundry producing diesel engine heads and blocks.

The previously described reduction of binder residue deposition below the blow tubes leads to an increase in productivity, due to the lower cleaning requirements in series production of cores.

IMPROVED CURE EFFICIENCY

An unexpected benefit of the new solvent technology was improved cure efficiency. Methyl esters act to increase the transport of amine gas throughout the core faster than aromatic solvents, a phenomenon referred to as bulk cure.

Foundry results consistently have shown cycle time reductions of 5% or more due to this effect resulting in greater core production. The improved bulk cure efficiency with the new system is shown in Fig. 6.

THERMAL CHARACTERISTICS

PUCB systems exhibit a markedly stronger tendency to soften during pouring than do hotbox and shell molded components. The cause of this behavior lies in the fact that solvents, particularly aromatic solvents, migrate from the surface to the interior of mold and core components when the latter are exposed to thermal stress, and can form a solvent condensation zone that softens the polyurethane binder links. The results are erosion, increased finning, scabbing and inaccurate casting dimensions.

In the new coldbox systems, the vegetable oil methyl esters polymerize when enough heat is present. This polymerization of the solvent stabilizes the polyurethane links and increases the strength levels in the high temperature range.

The results, in practice, are impressive. No scabbing or erosion defects have been observed, to date. The tendency for finning is markedly reduced, and the dimensional accuracy of the castings is very good.

GAS DEVELOPMENT

Liberation of gas in core and mold sands can lead to defective castings under certain circumstances, for example, at high binder levels, when gas evolution occurs at an early stage, or when the silica sand exhibits low gas permeability. The dipping method developed by Levelink, Julien and De Man[2] and described in the literature represents a very practice-relevant test method involving measurement of the gas pressure in a sand test core surrounded by molten metal, over a period of time, to produce a curve.

A comparison of the gas pressure curves obtained using the dipping method shows marked differences. In the new coldbox systems, the powerful initial gas burst that otherwise occurs at a relatively early stage is weakened and its time of occurrence shifted slightly. Figure 7 shows a comparison between a conventional (Gasharz 5366 and Aktivator 5333) and a new coldbox system (Gasharz 6348 and Aktivator 6324), where the test cores were exposed to the dipping test in an uncoated condition.

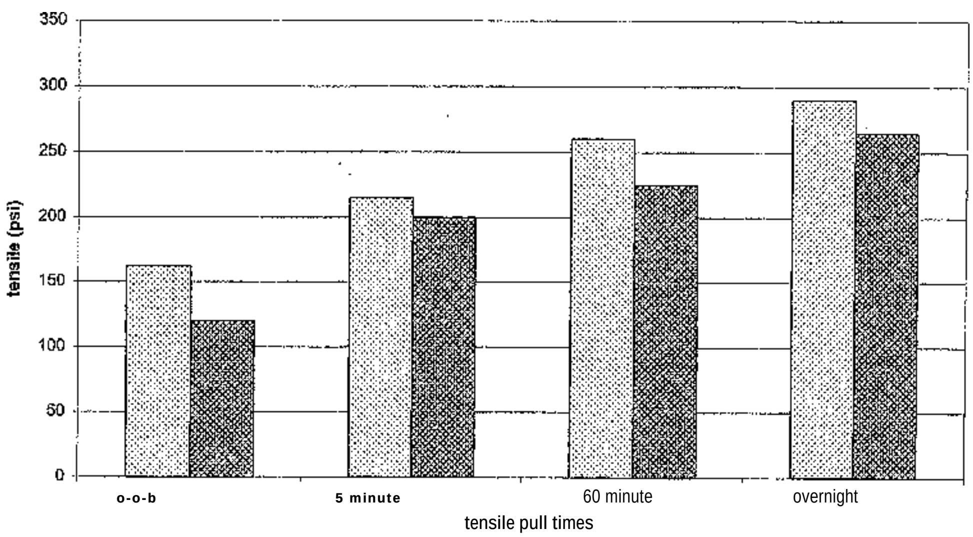


Fig. 3. Tensile strength development; 1.45% total binder (55/45); lake sand @ 70F). Light gray bars = standard; dark gray bars = new.

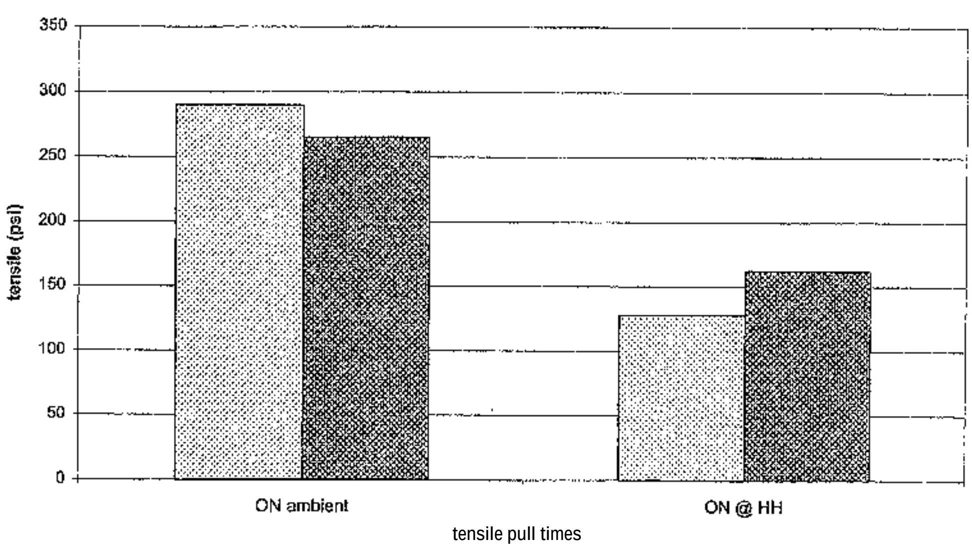


Fig. 4. Humidity resistance; 1.45% total binder (55/45); lake sand @ 70F; 93F L7a 89% RH. Light gray bars = standard; dark gray bars = new.

The differences are even greater in the case of coated cores, as shown in Figs. 8 and 9. Figure 8 shows the results of a dipping test using a coating with very high gas permeability. The high gas permeability of the coating permits the gases developed in the core to escape in front of the column of molten metal.

Typical defects (gas bubbles) are minimized by this coating behavior. Figure 9 shows the results of an otherwise identical test using a coating exhibiting low gas permeability. A glance shows that the conventional coldbox system quickly develops a high gas pressure in the core. In such a case, the coating must be well anchored to the core, since it could otherwise spall off and lead to formation of a gas pressure scab. Under the same circumstances, the new coldbox system features a slower rise in the gas pressure, which reaches its peak at a time when the initial casting skin has already formed.

APPLICATIONS TO NOBAKE SYSTEMS

Clearly, the use of methyl ester to replace aromatic solvents, in part or total, can be extended to PUNB (nobake) systems, as well.

While clearly a topic for a separate publication, we will make the following observations and comments.

In general, PUNS binders that employ methyl esters to replace part or all of the aromatic solvents exhibit strength and performance characteristics similar to standard or conventional binders. They may be used with conventional activators and give the same work and strip time ratios as the conventional systems.

Tensile strength development is similar to standard systems, as well. What is different is a marked reduction in solvent odor during mixing due to the substitution of the low-odor methyl esters for aromatic solvents.

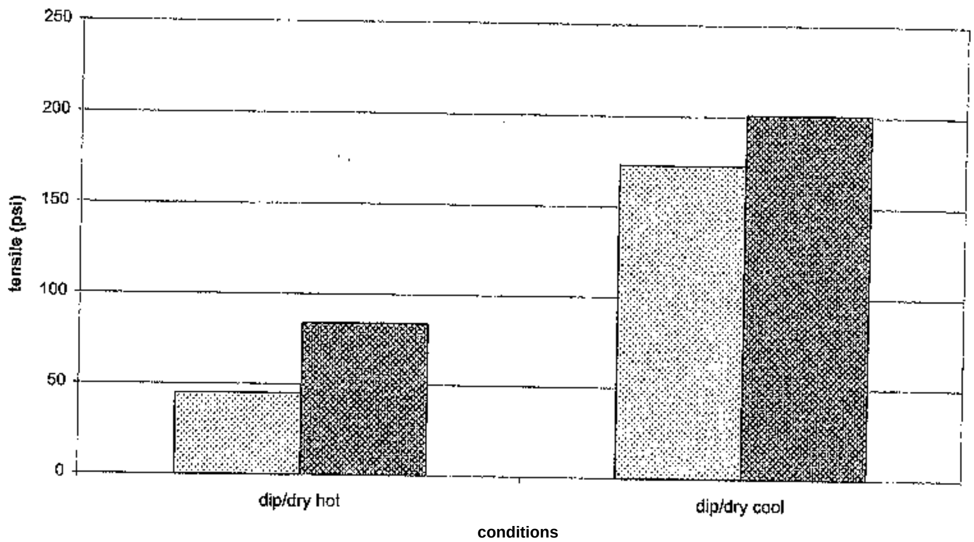


Fig. 5. Dip and dry conditions; 1.45% total binder (55/45); lake sand @ 70F;; automotive coating @ 23° Be. Light gray bars = standard; dark gray bars = new.

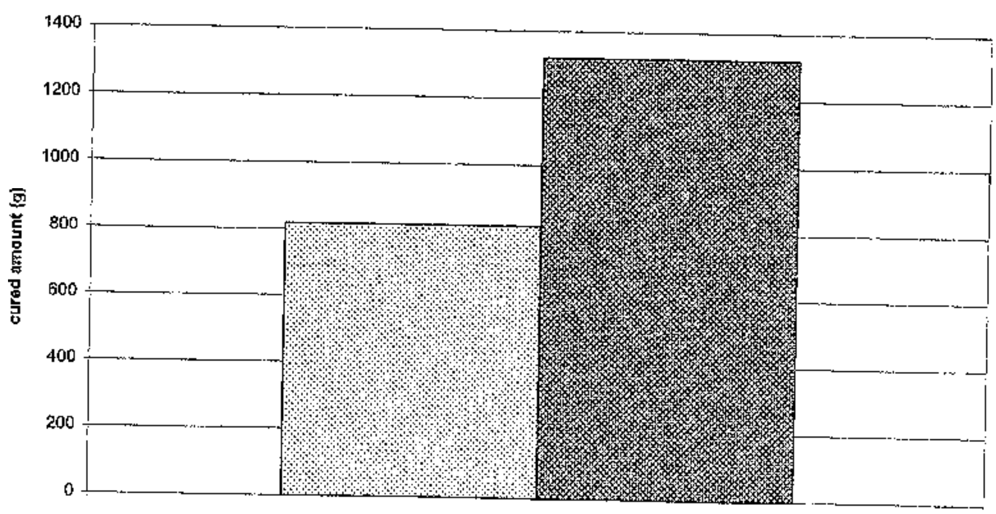


Fig. 6. Bulk cure characteristics; 1.45% total binder (55/45); lake sand @ 70F;; 30 psi @ 0.2 ml/4 sec. Light gray bars = standard; dark gray bars = new.

VOC reductions in the order of 50% may be achieved by complete substitution of the aromatic solvent by methyl esters.

At the time of this writing, reclamation properties are still being evaluated. Due to the higher boiling points and lower evaporation rates of methyl esters, their buildup characteristics in reclaimed sands are different, and dependent upon a number of factors, such as sand-to-metal ratios, pouring temperature, reclamation system type and efficiency, to name a few.

Caution should be employed during use, so problems with buildup on reclaimed sand do not occur.

SUMMARY

In addition to the considerable reductions in VOC emissions during core making and storage operations, this new coldbox system offers notable technological advantages. Practical results in Europe confirm reductions of between 25-50% in emissions of benzene, toluene and xylene.

The excellent release of cores from the tooling, along with decreased application of external release agents and improved cure efficiency, contribute to increased core production.

Test Mixtures:	
Silica sand AFS 41	100 PBW
Gasharz 6348	0,8 PBW
Activator 6324	0,8 PBW
Pouring temperature 1502°C	

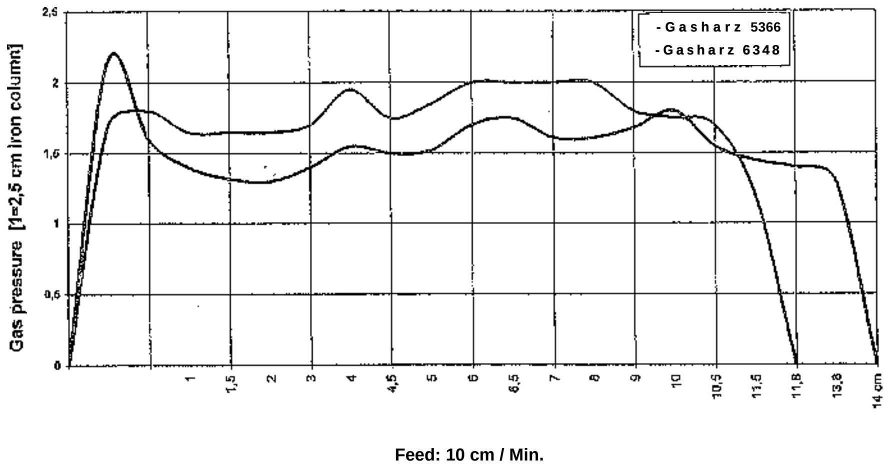


Fig. 7. Gas pressure curves for uncoated cores.

Test Mixture:			
Silica sand AFS 41	100 PBW	Silica sand AFS 41	100 PBW
Gasharz 5366	0,8 PBW	Gasharz 6348	0,8 PBW
Activator 5333	0,8 P8W	Activator 6324	0,8 PBW
Coating: Arkopal 6286 (high permeability)			
Pouring temperature 1500°C			

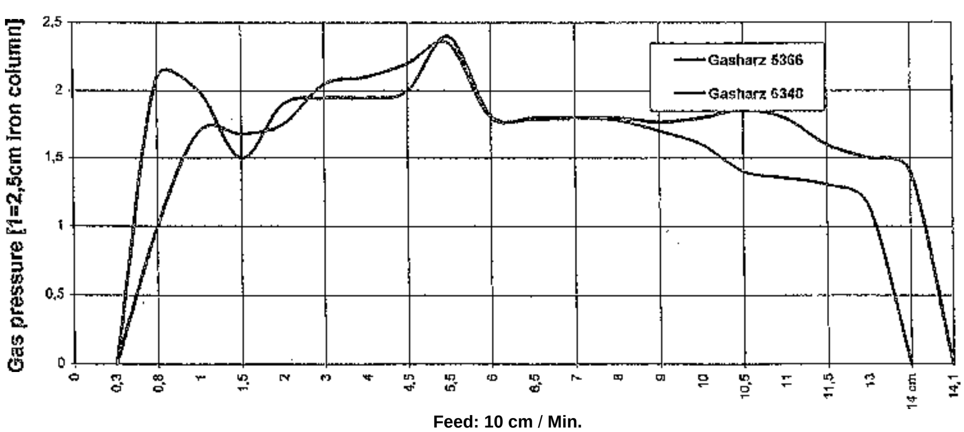


Fig. 8. Gas pressure curves for high-permeability coated cores.

Test Mixture:			
Silica sand AFS 41	100 PBW	Silicasand AFS 41	100 PBW
Gasharz 5366	0,8 PBW	Gasharz 63x8	0,8 PBW
Aktivator 5333	0,8 PBW	Aktivator 324	0,8 PBW
Coating: Arkopal 6172/I (lax permeability) Pouring temperature			

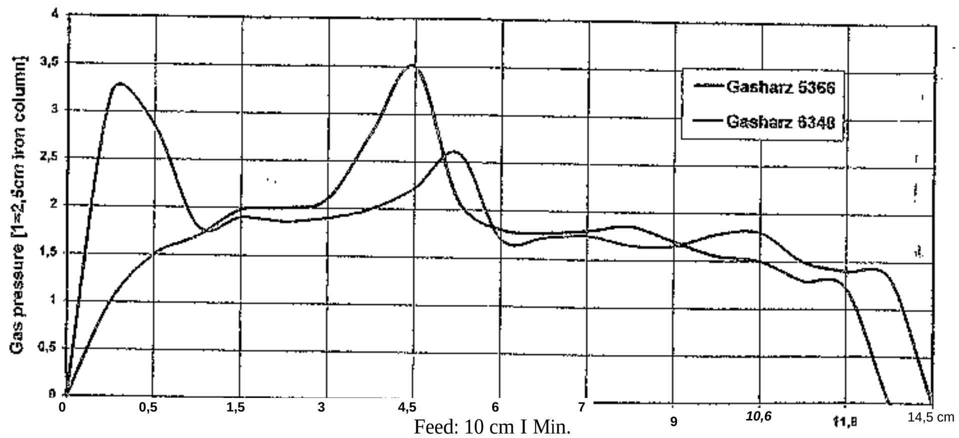


Fig. 9. Gas pressure curves for low-permeability coated cores.

The secondary strengthening of the methyl ester solvent prevents the usual softening of the polyurethane bond during pouring, thereby reducing veining and improving thermal accuracy of the castings.

All the previously described improved properties of phenolic urethane coldbox systems, such as strength development, good bench life, resistance to aqueous core coatings and humidity degradation, remain the same or are improved in the new systems.

Finally, after escape of the residual amine, cores produced with the new system are virtually odorless.