Structurally Modified Cold-Box Systems with Improved Properties

The increase in complexity in the design and manufacture of castings over the past years has inevitably led to continuous improvement of the technological properties of the core binders used for them. For example, it was necessary to adapt the chemical curing process to match the short cycle times of the automatic peripheral systems in addition to enhancing the strength properties. The parallel demand to positively influence the environmental behaviour of the binders while enhancing their technical properties led to a revolution in the way modern organic binders are advanced, as in the case of the cold box process.

This process is based on formation of polyurethane under the catalytic effect of a tertiary amine. The two components, a gas-curing resin and the “activator” or curing agent, contain both additives and considerable amounts of solvents.

Such solvents not only serve as a vehicle for the highly viscous polyol resin, but also exert a significant effect on the progress of the chemical reaction and the properties of the sand mix as well as the cores fabricated from it. This third component of the system thus control technological properties such as the sand bench life, feasibility of using water-borne mood coatings, resistance of the cores to moisture, their collapse behaviour and other characteristics.

The fundamental improvements in the technological and environmentally relevant properties of the cold box process over the past years have focussed on the use of various solvents and their modifications. Thus, the three main types of solvents shown in the table are used in the author’s company.

<table>
<thead>
<tr>
<th>Classical aromatic hydrocarbons</th>
<th>Aliphatic compounds</th>
<th>Silicic acid esters</th>
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</thead>
<tbody>
<tr>
<td>In use since 1996</td>
<td>In use since 1999</td>
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<td>(unpolares Teil: nonpolar part, polares Teil: polar part)</td>
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<tr>
<td>$C_nH_{2n+1}$ $n = 3$ to $14$</td>
<td>$C_{16}$ $C_{19}$</td>
<td>$OR$ $OR$</td>
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<tr>
<td></td>
<td>$O$</td>
<td>$Si$ $OR$ $OR$</td>
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<td></td>
<td>$OCH_3$</td>
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Figure 1: Solvent evolution in the cold box process

Replacement of aromatic solvents by aliphatic compounds (methyl esters of fatty acids from plant-based oils) provided the cold box process with a definite technological advantage.

The reason for the superiority of these methyl esters over aromatic solvents may be found in the different polarity of such methyl esters of plant-based fatty acids. One finds an ideal combination of polar and nonpolar moieties in the molecule of a plant-based fatty acid.
methyl ester. This polarity has a marked effect on the technical properties of cores in a cold box system.

The polarity of a binder system is mainly determined by the polarity of the selected solvent. This property controls processes such as the diffusion of the amine throughout the core, and thus has an effect on the reactivity, amine demand and strength development. Furthermore, the polarity influences the storage life of the cores in humid environments and their stability when water-borne mould coats are applied. All these parameters are positively affected when methyl esters of plant-based fatty acids are used as solvents.\[1\]

Thus, the required amount of catalyst could be markedly decreased by use of these aliphatic systems. The gassing time could similarly be reduced, and the productivity accordingly increased (Figures 2 - 3).

In addition to their many technical advantages, the plant-based methyl esters also feature better environmental behaviour than that of aromatic compounds. In contrast to aromatic hydrocarbons, the plant-based methyl esters are low-odour liquids with a high boiling point (about 300 °C) and a high flash point. Their vapour pressures are accordingly very low. Because of this, the rate of vaporization of such solvents during fabrication and storage of cores is so low that nearly no solvent odour can be detected.

Use of plant-based fatty acid methyl esters instead of traditional solvents decreases the level of highly volatile components by nearly half, while simultaneously reducing the catalyst demand because of the higher reactivity of the new cold box systems. The sum of these two effects leads to a radical improvement in the workplace environment of the core making shop.

Exposure to heat during the casting process leads to formation of degradation products. Special attention is paid to BTX components (benzene, toluene and Xylene), since these can be liberated into the air because of their relatively high vapour pressures. A large number of pyrolysis studies and measurements in practice could verify that the use of gascuring resins and activators containing solvents based on methyl esters derived from rapeseed oil leads to a marked decrease in pollutant emissions in both aluminium foundries and in the field of iron casting (Figure 4).
The use of silicic acid esters in the cold box process was dictated by the necessity of reducing odours to a minimum. Although the pollutant (BTX) emissions could be markedly reduced by replacing the aromatic compounds with plant-based methyl esters, this benefit was not always reflected in the odour emissions. Both types of solvents exhibit nearly identical, high odour emission levels. Moreover, methyl esters of plant-based fatty acids produce heavy clouds of smoke when they degrade, a property considered particularly objectionable in the area of NE/L (nonferrous/light metals) gravity mould casting.

Use of a silicic acid ester-type solvent was found to offset both of these disadvantages. This solvent is tetraethyl silicate, a newcomer in the cold box process, but a material that has been used in the foundry industry for years in manufacture of investment casting compounds.

Ethyl silicates exhibit inorganic character, since their molecules contain silicon bonds instead of hydrocarbon links. Due to this structure, less pollutants and odoriferous substances are created. Measurements of the odour emissions in aluminium casting (Figure 5) and in iron foundries (Figure 6) verify the radical reduction in odour emissions when the new cold box systems are used.
Gaseous SiO is formed during thermal decomposition of this new cold box binder under reducing conditions, and migrates toward the surface of the flask. Upon contact with oxygen, this gas immediately oxidizes to form amorphous SiO\(_2\) (Figure 7), which is harmless to the environment and to health. The resultant deposits are not composed of alveolar dust and thus are not subject to the MAK (peak allowable workplace concentration) guidelines for quartz dusts (Figure 8).

The siliceous structure of the new solvent is similarly responsible for the good collapse properties in NE/L (nonferrous/light metals) casting, and particularly for the low level of condensate formation in gravity moulds. Due to the silicon bonds, less smoking is observed during the casting operation.

The improvements mentioned above could be achieved solely by replacement of solvents making up around 30 % to 40 % of the total cold box binder. Figure 9 makes it clear that the potential for improvement of several environmentally relevant parameters by solvent modification is nearly exhausted.
This is apparent from the example of odour emissions. Substitution of aliphatic by silicate solvents, markedly reducing the level of organic carbon, led to a 69 % decrease in the odour level. Since a comparable solvent-free binder system (sand mixed with heated polymer and isocyanate, shot and cured with an amine) “only” offers a 76 % reduction in the odour, only limited possibilities exist to further reduce the odour level by way of solvent substitution [2].

A further noticeable improvement can only be achieved by modification of the basic polyurethane molecule. This principle was realized in the author’s company by development of new resins with modified structures (see the simplified structural schemes in Figure 10).

![Figure 10: Modification of the resin structure carried out by substitution of moiety X by moiety Y](image)

The monomer levels (free phenol and formaldehyde) could be markedly reduced by this modification. Whereas the standard systems exhibit monomer levels of 4.5 – 5 % (the level may not exceed 5 % because the product must otherwise be marked with skull and crossbones), the new generation of cold box resins features a lower monomer level ranging from 2.0 % to 2.5 %.

Phenolic, gas-curing resins exhibiting low levels of free phenol influence the pollutant emissions, and have a positive effect on the technological properties of the cold box system.

In the author’s company, this new “8000” generation was subjected to a series of tests to determine the technological and environmentally relevant parameters, with the results described below.

**Strength Properties**

The bending strength levels were determined analogously to the method in VDG Technical Leaflet P73.
The immediate strength level is a very important parameter for PU (polyurethane)-based binder systems. This determines the possible level of automation in machine operation, since the use of robots and grippers requires high-strength cores, particularly when these are intricate as in the case of water jackets and oil return channels in engine castings. As shown in Figure 11, modification of the resin structure in the gas-curing binder – the solvent composition is identical in both cases – led to a noticeable increase in the immediate strength level. This higher level is retained even after a lengthy sand mix bench life.

Figure 12 shows the bending strength after coating with a mould wash, and the effect of storage at high humidity on the strength levels. The new resin systems feature improved behaviour in this case as well.
Reactivity

The reactivity of a cold box system refers to the demand of tertiary amine or the gassing time required to cure a certain amount of moulding sand. The standardized VDG test method P73 may be used as a basis for determining this parameter. Bending strength test bars were produced in a core shooter using a mould measuring 22.4 x 22.4 x 185 mm. Instead of the specified 0.5 ml of amine, only one fiftieth of this amount was metered in. The length of the cured bending strength test bar was determined at gassing times ranging from 10 to 60 seconds. The length of the test bar is a parameter related to the reactivity of the cold box system. The new systems exhibited higher reactivity, and thus permit the use of shorter cycle times and/or a reduction of the added amine quantity.

![Graph showing comparative reactivity of two binder systems.](image)

**Figure 13:** Comparative reactivity of two binder systems. The bending strength bar of the 8000 system is completely cured starting at 40 sec gassing time (mm von insgesamt 185 mm Länge: Cured mm of total 185 mm length, "": sec, Begasungszeit: Gassing time, Katalysatormenge 0,01 ml DMIA: catalyst amount: 0.01 ml dimethylisopropylamine, GT: parts by weight, decimal commas)

Sticking Tendency

This property was tested using a core box developed at Hüttenes-Albertus (Figure 14). Moulding sand at a pressure of four bars is shot on a replaceable plate (no external parting agent being applied) from a height of 50 mm until the core sticks to the plate and cracks when an attempt is made to lift it (Figure 15). As a rule, a resin build up or sticking of sand grains on the plate may then be expected (Figure 16). The number of shots required before the core breaks or sticks is a measure of the sticking tendency of a system.

The use of replaceable plates permits simulation of various metal and PU materials. The curved shape offers the possibility of testing the flowability of the sand mix (at a shooting pressure of two bars) and the reactivity of a binder system (at reduced amine addition levels).
Figure 14: Core box for testing of the sticking tendency and flowability of gas-curing sand mixes.

Figure 15: Adhesion of the core to the plate and core cracking indicates sticking.

Figure 16: Sand grains remain bonded to the plate; the core is defective.

Figure 17: The old RME (solvent: methyl esters of plant-based fatty acids) system sticks to a steel plate after 267 shots, a very good result. Mix: 100 PBW (parts by weight) H32 sand, 0.8 PBW gas-curing resin, 0.8 PBW activator.

Figure 18: The solvent of the 8000 system is similarly based on RME; 260 shots is a very good result. Mix: 100 PBW (parts by weight) H32 sand, 0.8 PBW gas-curing resin, 0.8 PBW activator.
The test showed no difference in the good separation properties between a resin with normal structure and the new system, in both cases using RME as a solvent (Figures 17 and 18).

**Gas Behaviour**

It is of great importance to be familiar with the gas behaviour of binder systems including and excluding the effects of additives and mould coatings in development and/or improvement of new products. The reason for this is that the magnitude of the gas pressure and the point in time at which gas is evolved are key factors influencing the occurrence of gas defects in the casting.

Traditional methods used to determine the quantities of evolved gas can only yield limited information, since these cannot take account of the effects of materials that inhibit gas permeability, such as additives and mould coatings. A comparative analytical method was advanced and refined by the author’s company (Figure 19). This immersion method is closely related to practice, and the gas pressure that develops in the core is measured. Some of the relevant data on this analytical method are listed below.

- **Core length**: 220 mm
- **Core diameter**: 30 mm
- **Immersion depth of core**: 185 mm
- **Inner diameter of probe**: 4 mm
- **Melt temperature**: Aluminium (850 - 870 °C); iron (1400 - 1450 °C)

![Figure 19: A core made from the sand system to be tested (binder, additives and mould coating) is immersed in a melt, in this case aluminium. The measurement period is approx. 120 sec.](image-url)
Measurement of a system with the new resin structure containing ethyl silicate as a solvent showed no difference in gas evolution compared to that of a system based on an unmodified binder also using an ethyl silicate solvent (Figure 20). The magnitude and time of the first peak are nearly identical.

**Condensate Formation**

In modern NE/L (nonferrous/light metals) gravity mould casting, the moulds are sometimes held at various temperatures in different areas in order to achieve local modifications of the crystal structure. Particularly in cooler zones, pyrolysis products from degradation of cold box binders deposit as condensates. Build-up of condensates in the mould can then quickly lead to dimensional inaccuracies in the casting. In order to prevent such defects, the mould must be cleaned at frequent intervals, leading to a fall in productivity. In iron casting, condensates in the vicinity of exhaust system are a particular problem. These can occasionally auto ignite, or they negatively affect the odour emissions. Condensates from cold box binders mainly consist of organic compounds.

The COGAS® tester is presently available to determine the condensate-forming capacity of a test system, and automatically immerses a test piece into an aluminium melt. The gases evolved during the pyrolysis are passed through a cold trap to condense them (Figure 21). The increase in weight of the collecting tube indicates the quantity of evolved condensate.
Figure 21: Illustration of the COGAS® tester [3]

Investigation of the condensate-forming capacity with the COGAS® tester shows that the modification has a negative effect on this property. The new modification evolves 18.6 % more condensate than an unmodified cold box system. The reasons for this are presently still unknown. Efforts are presently being made to find a plausible explanation for this phenomenon.

**Thermal Stability**

A test method for determination of the susceptibility to erosion and veining or finning tendencies was developed in the course of doctoral research in cooperation with Special Section (Fachbereich) 8 of Duisburg University and foundries located in North Rhein-Westphalia. This method (Figures 23 and 24), that not only tests for veining in a cylinder...
core sample, but also permits assessment in an actual casting, represents a very useful comparative instrument for improving the thermal resistance of PU-based binder systems in the author’s company. The method similarly allows determination of the effects of additives and mould coatings.

A GJL 200, that is particularly susceptible to finning, is used as a casting alloy. The casting temperature varies from 1450 °C to 1500 °C, depending on the actual casting being tested. After the casting operation, the castings are sawed down the middle and assessed as described below:

The mean of the total length of fins in all holes of the cylinder sample, expressed in millimetres, is a measure of the veining tendency of a sand mix. The same assessment is also made in the actual casting. The erosion tendency, expressed in units of cubic millimetres (mm$^3$), is determined in the erosion nose (Figure 24) and in the actual casting.

Modification of the resin systems leads to a noticeable improvement in the thermal behaviour. Less veining develops than in the case of the old generation (Figure 25). The erosion
and penetration tendency is markedly suppressed (Figure 26). These results could be repeatedly verified in practice.

Figure 25: Comparison of veining tendency. The cores are uncoated. Sand mix: 100 PBW (parts by weight) H32 sand, 0.8 PBW gas-curing resin, 0.8 PBW activator (GH and Gasharz: gas-curing resin, Akt. and Aktivator: activator)

Figure 26: Comparison of erosion and penetration tendency

Pollutant Emissions
The monomer level represents the sum of the levels of free phenol and free formaldehyde, phenol being the major component.

The free phenol can not only be emitted into the air during conditioning of the sand mix, in shooting cores and when the cores are dried after being coated with a water-borne wash, but also to a considerable extent during the casting operation and when the flasks are emptied. The new, modified cold box resins with their low levels of free phenol offer a marked reduction of the phenol emissions after the mould is poured off. This belief has been verified by measurements in practice.

The existing status in a GJS foundry using a normal RME system (solvent: methyl esters of plant-based fatty acids) was first determined. The core making shop was then switched to the modified system. The previously used solvents were left unchanged. The pollutant emissions were again measured eight weeks after the switchover to the new system. Not only was there a marked decrease in the phenol emissions on the casting line and at shakeout, but it was also possible to further reduce the BTX levels (Figures 27 and 28).
Summary

The increase in complexity in the design and manufacture of castings over the past years has inevitably led to continuous improvement of the technological properties of the core binders used for them. For example, it was necessary to adapt the chemical curing process to match the shortened fabrication times in addition to enhancing the strength properties. Achievement of this enhancement in the technical properties was and remains linked to the requirement to improve the environmental behaviour of the binders. This has led to a revolution in the way modern organic binders are advanced, as in the case of the cold box process.

In recent years, such improvements have mainly focused on modification or substitution of solvents. Thus, replacement of aromatic hydrocarbons by methyl ester-type aliphatic compounds led to increased productivity due to the greater reactivity and lower sticking tendency of the resultant binder systems. A further advantage centred on the marked reduction in pollutant emissions during core making and after pouring off the mould. A second successful example is the use of silicic acid ester-type solvents. In light metals casting, this modification has improved the collapse as well as reducing the tendency to form condensates in gravity mould operations. The environmentally relevant strength of these new binder systems centres on the radical decrease in odour emissions after pouring off the mould.

In the above modifications, the phenolic polyols and Polyisocyanat responsible for polyurethane formation were left essentially unchanged. However, modification of the phenolic molecule offers a possibility to radically decrease the monomer levels (free phenol and formaldehyde). This renders it possible to reduce pollutant emissions after pouring off the mould even further. Another advantage of this novel concept is the increased thermal stability and thus the reduction in sand expansion-related casting defects. The above properties are united in the 8000-series cold box system.

References

[3] COGAS® tester brochure