Reduction of Foundry Odor Emissions by Use of New Generations of Organic Binders

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Features such as high strength levels at low addition rates, high productivity and economy, good thermal stability and good collapse properties in nonferrous-light metals (NE/L) casting are presently considered requirements for series production and are taken for granted in modern coremaking processes. Furthermore, modern foundry binders are judged according to specific ecological requisites. In the future, only binders that offer low odor emissions, low smoke and condensate deposits, as well as low pollutant emissions during the coremaking process and after pouroff will be successful in the European market.

In addition to their process engineering strengths, modern cold box systems offer great potential for improvement of their environmental properties. Developments in the past years demonstrate the environmentally relevant performance of the cold box process (Figure 1). Replacement of the solvents used in the resins and activators alone leads to a marked improvement in the pollutant balance (First and Second Generations in Figure 1). The benefits offered by use of methyl esters of fatty acids as solvents have already been described at various meetings and in diverse publications [1,2,3].

| First Generation: | Replacement of aromatic solvents by methyl esters of rapeseed fatty acids with consequent reduction of pollutant (BTX = benzene, toluene and xylene) emissions during coremaking and after pouroff |
| Second Generation: | Use of modified methyl esters of fatty acids with the goal of reducing smoking during drying of cores and after pouroff compared to first-generation levels |
| Third Generation: | Reduction of the level of free phenol in the resin component with the goal of improving the disposability of used sand and further decreasing pollutant emissions |
| Fourth Generation: | Use of silicate-based solvents with the goal of reducing odor emissions, smoking and condensate deposits after pouroff |

Figure 1: Chronology of environmentally relevant evolution of new cold box generations

Aside from the problem of reducing pollutant emissions during production of castings, foundries are nowadays increasingly confronted with further types of emissions. The present geographic proximity of some plants to residential areas, and the increased environmental consciousness of the population have led to sensitization of nearby residents to the nuisance factors of noise and particularly odors. To preserve the social acceptance of the foundry, the foundry operator must become active in the question of odor emissions. Two approaches to this exist:

1. Secondary measures – in the past, use of post-process exhaust treatment systems such as biological filters and thermal afterburners has shown that it is possible to improve the quality of foundry exhausts. However, such measures are cost-intensive and in some cases offer only inadequate efficiency.
2. Primary measures – in the last three years, the foundry chemicals industry has intensively dealt with the problem of odors, and presented solutions in the form of primary measures. New generations of binder systems offering reduced emissions after pouroff have been developed.

1. Odor Emissions and Problem Solutions

1.1. Sources of Foundry Odor Emissions

Various sources of odor emissions are located in the foundry. The main sources are described below in order of decreasing intensity.

1.1.1. Coremaking Shop

In coremaking, the process being used is the key factor in creation of odors. In the waterglass-CO₂ and resole-CO₂ processes, coremaking is essentially odor-free, whereas the odor nuisance in the case of the polyurethane cold box method can be slight to very severe depending on the tertiary amine being used and the composition of the solvent.
Use of alcohol-based refractory coatings additionally increases the odor nuisance and environmental impact. The environmentally more benign water-borne refractory coatings widely used today require oven drying. Portions of the solvents contained in the binder vaporize during the drying operation and cause odors. The intensity of the odors depends to a great extent on the boiling points and vapor pressures of the solvents used as well as on the surface area of the heated sand and accordingly on the core geometry.

1.1.2. **Melting Shop**

Particularly in gray iron foundries, cupola furnaces are mainly used to smelt iron. The raw materials they use emit levels of odors that are far from negligible. Odors are also emitted when electric furnaces are used. The raw materials may also be considered primary sources of emissions in this case.

1.1.3. **Molding Line**

The main emission flow originates at the molding line after the pouring operation and during the cooling phase. The intensity in this case is similarly process-dependent (Figure 3).

In a mold of bentonite-bonded sand with the pertinent cores, portions of the odors are emitted by the glossy carbon donors contained in the molding sand. However, the highest emissions originate from the chemically bonded cores. The total odor emission level in this case depends on the weight ratio of mold to core sand, the thermal exposure, and the process used in core production. Although the level of odor emissions in resole-CO$_2$ systems is negligible during core production, the odor burden following pouroff is markedly higher than that experienced with cores from most other familiar coremaking processes.

1.2. **Odor Emission Measurement Method**

In order to simulate the behavior of molds/cores made using various mold and core fabrication processes following pouroff, a practice-related test method for measurement of odor emissions (Figure 2) was developed in cooperation with the IfG (Institut für Giesserei or Foundry Institute) in the scope of an EU-sponsored research project.

![Figure 2: Schematic of pyrolysis experiment principle](image)

In this arrangement, the test piece – made from sand bonded with the binder to be tested – is inserted in the middle of the pouring vessel, which is then hermetically sealed. This creates a purging channel through which a flow of gas is passed at a specific rate. This is used to entrain gaseous components liberated from the test piece and transport these to sampling devices used for analyses such as olfactometry [4]. The odor potential and its development over time are expressed in OU/m$^3$ (Odor Units per cubic meter of aspirated air).

1.3. **Reduction of Odor Emissions in the Polyurethane Cold Box Process**

The IfG test method as adapted for the foundry not only affords practice-related results for the odor potential of many chemically bonded molding sands, but is also an important instrument for continued development of more environmentally friendly binders (Figure 3).
1.3.1. Effect of Solvents

The effect of the solvents on the pollutant balance could already be illustrated in references [1,2] in the case of the new first and second-generation cold box systems. A consideration of the difference in odor potential between a commercially available cold box system containing aromatic hydrocarbons as solvents and the same system without solvents (Figure 3) makes it clear that solvents similarly represent a key factor influencing odor emissions. A consideration of the total emissions in a process should distinguish between pollutant and odor emissions. Although the new first-generation systems offer a considerable reduction in pollutants (BTX) compared to the levels in classical cold box systems, the odor emissions in the two process variants are nearly equally high/bad (Figure 4).

This make it clear that the solution to the odor emission problem in the polyurethane cold box process lies in the search for suitable solvents with low odor potential, preferably those exhibiting an inorganic character similar to the components in the low-odor waterglass process (cf. Figure 3). Solvents with such properties are found in the silicate ester group, and have already been used in foundries for years in production of investment casting compounds (Figure 5). It is known that alkene and alkyne-group hydrocarbon compounds are primarily responsible for odor emissions. On the other hand, ethyl silicates undergo partial transformation to an amorphous SiO$_2$ compound due to their silicate character when
exposed to thermal stress. Such SiO₂ compounds are odorless, and offer a number of additional technical advantages.

1.3.2. Effect of Additives

Additives are used to prevent certain sand expansion defects in the field of iron casting. These are generally based on wood flour impregnated with a cold box resin, and as a rule are added to the sand mix at a far higher rate than the binder component. The level of resin used for impregnation of such additives is generally higher than 10 % based on the aggregate contained in the additive. These facts explain why such additives in the molding matrix exert an enormous effect on the level of odor nuisance (Figure 6).

The effect of organic additives is illustrated in Figure 7 using the example of Feranex added at a rate of 2.5 %. The bar on the left represents the cumulative total odor emissions from three measurements of sand made with a first-generation binder and containing a commercially available additive. The bar on the right shows the intensity of the odor produced by a fourth-generation system without additive. Finally, the middle bar shows that inclusion of 2.5 % of a common additive drastically impairs the good odor properties of the new system. In this case, the odor potential is only insignificantly lower than that of the old system. This is attributable to the presence of the impregnating resin used in the additive.
When a low-odor cold box resin is used to impregnate the additive, the difference to the normal cold box system becomes apparent (Figure 8). To some extent, the new cold box system exhibits quasi-inorganic character thanks to the silicon compounds it contains.

This property and its effect on the level of odor nuisance have pointed the way for development of inorganic additives.

Surprisingly, the newly developed inorganic additive led to a further reduction in the level of odor emissions. This may be explained in part by the adsorptive properties of several components of this additive.
2. Practical Experience With the New Cold Box System

2.1. Experience in the Iron Casting Field

2.1.1. Effect of the New Cold Box System on Molding Sand

A series production foundry with an annual casting volume of approx. 120 metric tons has been working with the new cold box system using ethyl silicate-based solvents since September, 2001. Before the new system was introduced, its effect on the molding sand properties was checked as shown in the flow chart illustrated below. In this work, molds were fabricated using the new cold box system, and half of these poured off with a gray iron melt at a temperature of 1440 °C. The thermally exposed sand and the remaining unused molds were then granulated to recover the sand.

The sands obtained in this manner were regarded as 100 % molding matrices, and molding sands produced from them. A comparison was also made with the molding sand used in practice, taken from the main molding unit. Except in the case of the “practice” sand, the molding matrices were mixed with eight parts by weight of Greek bentonite, and conditioned for ten minutes, or adjusted to a compaction rate of 40 %, in a laboratory sand muller (Figure 10). The main technological parameters of the sand were determined (Figure 11). No clear differences were apparent in the molding sand properties of the various samples. Only the water demand of the “practice” sand was elevated. This was attributable to the higher level of sediment in this sand (Figure 12).
After this test, molds were prepared from half of each conditioned sand and poured off at a temperature of 1440 °C. The sand-to-iron ratio was 1 : 3.4. The poured molds were allowed to cool for 24 hours, granulated, the sand mixed with the remaining half of the original sand, and the product then homogenized by conditioning for 10 min in a laboratory sand muller. The sand properties were again determined by exhaustive testing (Figures 13 and 14). In this experiment, conducted under extreme conditions – a molding sand was produced exclusively from core sand – it was found that the new binder system exerts no negative effect on the molding sand properties. No negative changes in the system sand were observed after this new cold box system had been used for six months under practice conditions at the Georg Fischer company in Mettmann.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Compactability (%)</th>
<th>Water (%)</th>
<th>Bulk density (g/cm³)</th>
<th>Compression strength (N/cm²)</th>
<th>Transverse strength (N/cm²)</th>
<th>Wet tensile strength (N/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poured off cold box</td>
<td>40</td>
<td>2.9</td>
<td>1.53</td>
<td>20.3</td>
<td>6.2</td>
<td>0.30</td>
</tr>
<tr>
<td>Core breakage</td>
<td>40</td>
<td>3.0</td>
<td>1.58</td>
<td>18.4</td>
<td>6.1</td>
<td>0.28</td>
</tr>
<tr>
<td>Silica sand</td>
<td>40</td>
<td>2.9</td>
<td>1.53</td>
<td>20.0</td>
<td>5.4</td>
<td>0.29</td>
</tr>
<tr>
<td>“Practice” molding sand</td>
<td>40</td>
<td>3.8</td>
<td>1.44</td>
<td>18.8</td>
<td>6.6</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Figure 12: Molding sand properties of tested sand systems after adjustment to 40 % compactability
In addition to the effect of the new cold box system on the technological properties of the system sand, the change in molding sand odor emissions produced by the new binder was determined. The existing situation prior to switching to the new cold box system was first established. In order to ensure that an equilibrium state had become established in the system sand, the comparison measurement was only carried out seven weeks after switching to the new cold box system. Figure 15 shows the results of the olfactometric tests by the IfG test method.
2.1.2. White Corebox Deposit

Deposits on the corebox opening flanges were observed after the switchover to the new cold box system. Analysis of the white deposit indicated it to be amorphous silica (Figure 15). Thermal decomposition of the cold box binder liberates gaseous SiO under reducing conditions; this immediately reacts with oxygen at the exterior surface of the corebox, forming environmentally innocuous, physically harmless amorphous silica.

2.1.3. On-Site Odor Emission Measurements

The odor burden was determined at the refractory coating drying oven and at the various chimneys of the main molding line before the switchover, and after introduction of the new cold box system (Figure 17). The results agree with the IfG olfactometric test results. A reduction of 76% of the total odor emissions from the molding line could be achieved using the new binder.
2.2. Experience in the NE/L (Nonferrous – Light Metals) Field

2.2.1. Reduction of Odor Emissions

Countercurrent spraying of enzymes into the exhaust gas flow was initially employed to reduce odor emissions in an aluminum casting foundry using sand molds and a cold box system with methyl esters of fatty acids as solvents in its coremaking shop. Although implementation of this secondary measure led to a 40% reduction in the odor emissions, complaints from the neighborhood could only be adequately satisfied by introduction of the fourth-generation cold box system. This afforded an 85% reduction in the odor intensity (Figure 18). Measurements in a foundry using permanent molds showed a similar degree of odor reduction when this novel cold box system was used.

2.2.2. Minimization of Smoke and Pollutant Emissions

Despite their technological and environmentally relevant superiority to classical systems containing aromatic hydrocarbons, cold box systems using methyl esters of fatty acids as solvents have not gained
acceptance in aluminum foundries using permanent molds because of the thick smoke formed during pouroff and particularly when the permanent mold is opened. The new cold box systems using tetraethyl silicate as a solvent offer an attractive alternative solution in such cases. In fact, use of these new systems not only leads to a reduction in smoke development (Figures 19 and 20), but also to a marked drop in the pollutants that are - in contrast to the situation in casting using sand molds - liberated untreated into the air in permanent mold casting. The explanation for the reduction in emissions lies in the structure of the solvent, one that contains a certain percentage of silicon compounds. Formation of pollutants during the decomposition process requires a specific supply of carbon. Figure 21 compares the BTX measurement results to those of a cold box system containing aromatic hydrocarbons.

\[ \text{Figure 19: Fourth-generation cold box system} \quad \text{Figure 20: Second-generation cold box system} \]

\[ \text{Figure 21: TLC (German MAK) determinations at a permanent mold using two different cold box systems} \]

2.2.3. Reduction of Condensate Deposits

In modern permanent mold casting, the molds are sometimes heated to different temperatures at various locations in order to produce local modification of the casting structure. Pyrolysis products from cold box binders particularly deposit at cooler locations to form condensate. This condensate buildup in the mold can then quickly lead to inaccurate casting dimensions. In order to prevent such defects, the mold must be frequently cleaned, causing a loss in productivity.

The condensates derived from the cold box binder mainly consist of organic compounds. The silicon compounds contained in the new solvent thermally decompose to yield amorphous silica, thus leading to reduced condensate formation. Figure 22 shows the expected condensate levels based on the binder addition rate when different solvents are used.
3. Improved Utilization of Used Foundry Sand

Many foundries already possess or plan to apply for DIN EN ISO 14001 certification. This environmental management system includes an obligation to reduce the pollution balance and sponsor utilization of foundry wastes. Waste materials in the foundry industry include residual sands that can be used in applications such as excavation work and road construction. The requirements for such uses include a phenol index of 0.1 – 1 mg/L eluate determined as specified by the German LAGA (Ländergemeinschaft Abfall or Interstate Waste Community).

Third-generation cold box systems were developed to improve the situation with respect to phenol emissions after pouroff and utilization of used sands in gray iron foundries.

In contrast to the first two binder generations, whose benefits are solely attributable to changes in the solvents used in them, the reactive, i.e. resin component was modified in development of this third generation. A marked reduction in the level of free phenol in the cold box resin could contribute to an improvement in the phenol index of the molding sand.

The problem of phenol enrichment in the system sand was particularly severe at a medium-sized gray iron foundry with a relatively low rate of fresh sand addition to the molding sand, cores mainly being fabricated from used sand recovered from the molds. The process data of this operation were:

- Average ratio of sand to iron: 5 : 1
- Type of molding line: Horizontal
- Type of castings: Automotive castings
- Casting metal: GJS

This operation had successfully used the new, first-generation cold box system for years. After the existing situation had been established by analyzing the level of phenol in the molding and recovered sands, and determining the benzene and phenol emissions after pouroff and during shakeout, a long-term investigation was initiated.

Over a period of about six weeks, core production was converted to use of the new cold box system with a low level of free phenol. In order to retain the advantages of the series binder in core production, and leave the benefits in casting unchanged, the new, third-generation cold box system continued to use the same methyl rapeseed fatty acid ester-based solvent as previously.
The relative lengthy changeover period was used to establish a balance in the system sand and recovered sand. All measurements originally carried out to determine the existing situation were then repeated after six weeks under identical production conditions and without change in the casting program. The phenol index in the molding and recovered sands had been cut nearly in half (Figure 23).

![Figure 23: Reduction of the phenol index in molding sand and recovered sand by use of a third-generation cold box system](image)

It should be emphasized at this point that the older system represented an early first-generation resin with a solvent consisting of methyl esters of plant-derived fatty acids. Its monomer level was below 5 %.

Even the newer cold box systems of the first and second generations offer a considerable reduction in the pollutant emissions following pouroff. The new system tested in this case affords an even greater improvement in the industrial hygiene conditions at the casting line and after shakeout (Figures 24 and 25). In particular, the phenol emissions could be markedly decreased in this case.

![Figure 24: Pollutant emissions at the casting line](image)
4. Summary

Aside from the problem of reducing pollutant emissions during production of castings, foundries are nowadays increasingly confronted with further types of emissions. The present geographic proximity of some plants to residential areas, and the increased environmental consciousness of the population have led to sensitization of nearby residents to the nuisance factors of noise and particularly odors. To preserve the social acceptance of the foundry, the foundry operator must become active in the question of odor emissions. In addition to a drastic reduction in the levels of odor emissions after pouroff, new cold box systems offer a number of technical advantages to the light metals and iron foundry operator.

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