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# VOC-optimized Binder Systems for the Reduction of Pollution During Core Shooting and Core Storage

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The technical and financial effort to reduce emissions has been increasing for years. This affects all material flows, as well as exhaust air systems, afterburning and disposal of contaminated material (wastewater, sands).
The focus on the risks posed by combustion products on the casting line is increasingly giving way to a holistic view of emissions across the entire production chain.
The disposal of used sand is a growing problem for many foundries due to more restrictive limit values, higher costs, and thus a limitation of the available landfill operations. New binder systems with a reduced free phenol content <1% like ECOCURE™ BLUE are an important building block for minimizing pollution in old sand and can, therefore, expand the scope for action again.
Furthermore, since February 2020, the formaldehyde emissions in the exhaust gas must not exceed a mass flow rate of 12.5 g/h or a mass concentration of 5 mg/m³. The limit value is now only a quarter of the original value. This is particularly important in drying ovens and connected exhaust peripherals. In addition to technical solutions, low-formaldehyde systems (LFS) have recently become available, which, through a combination of formaldehyde-reduced and -reducing materials (coating, binder, additive), have been shown to reduce this value below the limit.

## Definition and meaning of VOCs

The issue of VOCs (volatile organic compounds) has not progressed very far yet, particularly in foundries, but could become more important in the future, as it has already in other industrial fields, such as paints and varnishes where far-reaching regulations have been passed to limit the emissions caused by VOCs.
But what is a VOC and what is the exact definition? There are different interpretations here, but one that applies to Germany and Europe and that dates back to Directive 1999/13/EC is:
*A VOC is an organic compound that has a vapor pressure of 0.01 kPa or more at 293.15 K or has a corresponding volatility under the particular conditions of use.*
This means that especially volatile and moderately volatile components, such as aromatic solvents or amines, are included.
The 1999 Gothenburg Protocol and its 2012 revision is a kind of international law contract that contains the first foundations regarding VOCs, that does not go beyond a declaration of intent, but aims to ensure that the EU or its member states set a legal framework, that ensures compliance with the agreed goals.
The relevant governments are then obliged to do so by means of the so-called NERC directive (National Emission Reduction Commitments).
For example, the NERC Directive (EU) 2016/2284 states:
*In order to move towards achieving levels of air quality that do not give rise to significant negative impacts on and risks to human health and the environment, this Directive establishes the emission reduction commitments for the Member States' anthropogenic atmospheric emissions of sulfur dioxide ($SO_2$), nitrogen oxides ($NO_x$), **non-methane volatile organic compounds (NMVOC)**, ammonia ($NH_3$) and fine particulate matter ($PM_{2,5}$) and requires that national air pollution control programs be drawn up, adopted and implemented and that emissions of those pollutants and the other pollutants referred to in Annex I, as well as their impacts, be monitored and reported.*
Both the Gothenburg Protocol and the subsequent NERC directive communicated reduction targets compared to the emissions from 2005, which are as follows:

### National emissions reduction targets in relation to emissions in 2005

| | Sulfur dioxide | Nitrogen oxides | Ammonia | NMVOC | PM2.5 |
|---|---|---|---|---|---|
| **Rev. Gothenburg Protocol, to be achieved from 2020** | -29% | -39% | -5% | -13% | -26% |
| **New NERC directive to be achieved from 2020*** | -21% | -39% | -5% | -13% | -26% |
| **New NERC directive to be achieved from 2030*** | -58% | -65% | -29% | -28% | -43% |

*Negotiation result at the end of June 2016

Source: German Federal Environment Agency (UBA) 2016, own compilation

This means that VOC emissions should be reduced by a further 15% in this decade.

So far, the foundry industry has not been directly affected by the relevant regulations, such as those that already exist for the varnish and paint industry, e.g. the Chemical Directive to Limit the Emissions of Volatile Organic Compounds which restricts the marketing of solvent-based paints and varnishes.
But such directives are already indirectly relevant for some foundries, namely, those for which there are vehicle painters on the same site.
In addition to these industry-specific regulations, there are other generally applicable regulations on VOC emissions, such as the following:

- COUNCIL DIRECTIVE 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations: *https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:01999L0013-20101201&qid=1586162267311&from=EN latest consolidated version*

In 2010, along with other and new requirements related to VOC, was transferred substantially unchanged to the IED directive:

- DIRECTIVE 2010/75/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 24 November 2010 on industrial emissions (integrated pollution prevention and control):https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02010L0075-20110106&qid=1586163430798&from=EN
- CHAPTER V - SPECIAL PROVISIONS FOR INSTALLATIONS AND ACTIVITIES USING ORGANIC SOLVENTS

It was implemented in Germany by the 31st Federal Emission Control Ordinance:

- 31st Ordinance for the Implementation of the Federal Emission Control Act (Ordinance to limit the emissions of volatile organic compounds when using organic solvents in certain installations): *https://www.gesetze-im-internet.de/bimschv_31/31._BImSchV.pdf (in German)*

Furthermore, a process based on Article 13 of the IED Directive for creating BAT reference documents (best available technology) and the BAT conclusions is gaining momentum, which will lead to new requirements in the medium term. The simplified process looks like this:

- Determination of emission-relevant industries
- Benchmarking regarding emissions and technologies used
- Creation of the BAT reference documents
- Creation of final BAT conclusions as a basis for requirements
- Entry into national approval regulations (Germany: Federal Emission Control Act and Federal Emission Control Ordinance, Technical Instructions on Air Quality Control, approval notices)

Such a BAT document has existed for foundries since 2005. A revision of the state of the art is planned and should be started at the end of this year after delays. In preparation for a new BAT document and to document the contribution of the German foundry industry to the state of the art, the Federal Environment Agency (BUA) commissioned a corresponding study from the German Institute for Foundry Technology (IFG) in 2012, which reflects the state of the art at that time: *https://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/texte_80_2014_innovative_techniques_vol_1.pdf (in German)*
The topic of VOCs is only mentioned in this document with regard to the drying of water-based protective lacquers but is not mentioned, for example, in connection with core production and core storage.

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## Measures to reduce VOCs in foundries

In principle, many foundries have already optimized processes and technology to such an extent that VOC emissions are significantly less "noticeable" than in the past, which everyone subjectively becomes aware of as a reduction in the odor level in the corresponding work areas. Core shooters are housed, improved air exchange or even extraction has been implemented in the core storage and binder and catalyst quantities have been optimized.
Despite these measures, further improvements are possible in individual cases, namely, if a binder system can be used which firstly can be declared low in VOC due to the ingredients, and secondly is so reactive that it can be cured with as little catalyst as possible.

Highly and moderately volatile components such as solvents or amines are considered VOCs. Solvents are used in particular to thin the binder systems to a processable viscosity and to control product properties, while amines (so-called tertiary amines) are essential in order to catalyze a curing reaction in the cold box process.

Release agents can also make a significant contribution to VOC emissions during core production, especially if they contain volatile aliphatic solvents such as heptane. There are however appropriate products available on the market already, such as the solvent-free ECOPART™ CB H 18-350. The impact of release agents is therefore not considered in more detail in the following studies.

The general trend has long been towards those binder systems that contain fewer aromatic solvents, especially in cast iron and steel. Nevertheless, these aromatic solvents exist for a reason, especially in aluminum applications (gravity die casting), where the accumulation of condensates leads to undesired residues. However, aromatic or hybrid systems (aliphatic/aromatic) can also be convincing in iron casting, for example when it comes to reducing gas defects or smoke.

Alternatives to this are inorganic binders or those containing silicate solvents, so-called TEOS (tetraethyl orthosilicate) binders. While inorganic binders would certainly be the best choice, the process window is significantly different (series applications are currently mainly limited to Al die casting), and with TEOS binders you must take into account that in addition to the advantages of reduced condensate and smoke, disadvantages also arise: A demanding workplace limit of 12 mg/m³ must be taken into account (*https://www.baua.de/DE/Angebote/Rechtstexte-und-Technische-Regeln/Regelwerk/TRGS/pdf/900/900-tetraethylorthosilikat.pdf?__blob=-publicationFile&v=2* (In German)) and the increase in VOC emissions on the one hand due to the pure substance tetraethyl orthosilicate itself and on the other hand as a result of the normally higher amine consumption of such systems.

## Modern cold box systems in a VOC comparison

To quantify and evaluate the differences in VOC emissions between two "modern" binder systems, the ASK Chemicals Foundry Technology Center in Hilden carried out corresponding emission measurements during core production and core storage.
Two systems were compared, which are used, among other things, for engine casting in iron foundries. The two systems were ECOCURE™ BLUE, a phenol and formaldehyde reduced cold box system, and a cold box system based on TEOS.
The sand mixtures to be compared were as follows: 100% H32 new sand and 1.6% total binder content (part 1 & part 2), while the TEOS binder was used according to the system with a slightly adjusted ratio (0.9% part 1 / 0.7 % part 2).
At the beginning of the series of measurements, the sand mixtures were optimized for amine consumption, i.e. the lower limit for catalyst addition was investigated. The first serious differences were identified here: Using a core with a filigree inner contour area (Core weight: 8.3 kg), it was determined that the ECOCURE™ BLUE only needed in case of the 4.5 g of catalyst (DMPA) to harden into the inner area and to ensure reliable removal from the mold. In contrast, 8.0 g was needed with the TEOS binder system. The increased reactivity of ECOCURE™ BLUE does not affect the bench life, which is the same level for both systems.

TEOS Binder System

| Core box parameters | Value |
|---|---|
| Shooting pressure | 3 bar |
| Shooting time | 2 sec |
| Amine dosage | 8.0 g |
| Start pressure | 0 bar |
| Final pressure | 0.5 bar |
| Gassing pressure | 3 bar |
| Ramp time I | 10 sec |
| Ramp time II | 10 sec |
| Gassing time | 20 sec |

ECOCURE™ BLUE HE-1/HE-11

| Core box parameters | Value |
|---|---|
| Shooting pressure | 3 bar |
| Shooting time | 2 sec |
| Amine dosage | 4.5 g |
| Start pressure | 0 bar |
| Final pressure | 0.5 bar |
| Gassing pressure | 3 bar |
| Ramp time I | 10 sec |
| Ramp time II | 10 sec |
| Gassing time | 20 sec |

Sand mixture TEOS

| | | |
|---|---|---|
| 100% | New sand | H32 |
| 0.9% | Binder | TEOS binder part 1 |
| 0.7% | Binder | TEOS binder part 2 |

Sand mixture ECOCURE™ BLUE

| | | |
|---|---|---|
| 100% | New sand | H32 |
| 0.8% | Binder | ECOCURE™ BLUE part 1 |
| 0.8% | Binder | ECOCURE™ BLUE part 2 |

The experiments shown below were carried out with these optimized gassing parameters. In the first series of investigations, it was the intention to determine how high the VOC emissions are during the core manufacturing process. A common measurement method to detect and quantify organic compounds is the FID (Flame Ionization Detector) measurement. In this case, an online FID was used, which due to its flexible usability is particularly suitable for measuring emissions from different sources.

**Figure 1:** FID sensor in the exhaust duct of the core shooter

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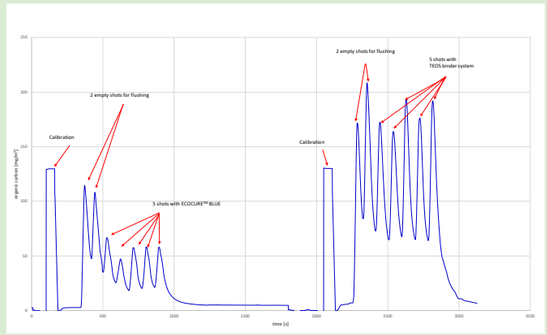
**Figure 2:** Online FID for the determination of total carbon content

**Figure 3:** Core shooter in the ASK Chemicals Foundry Technology Center in Hilden


The FID sensor was inserted into the exhaust duct and the series of measurements started after appropriate calibration. Two gassing cycles (amine only) were carried out to flush the gas supply lines and bring them up to temperature. Only then did the measurements take place with the appropriate sand-binder mixtures.
When evaluating the corresponding diagrams for the total carbon content, three aspects are particularly noticeable:

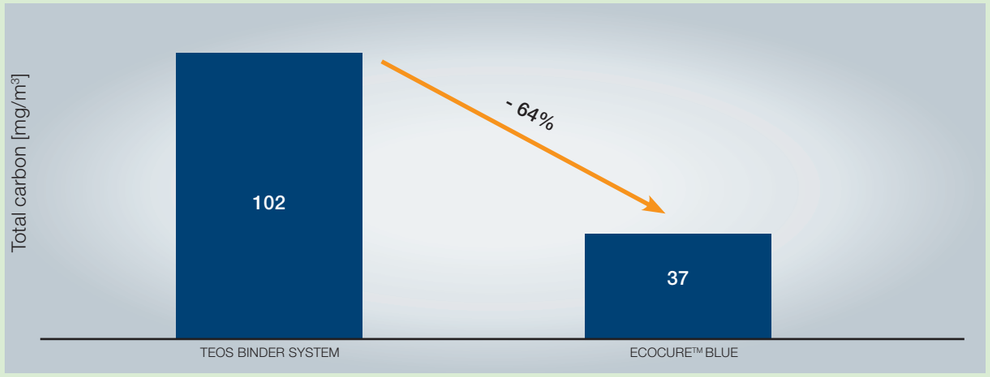
- The signal intensity of the "empty shots" reflects the 44% reduction in the amine requirement of the ECOCURE™ BLUE system very well
- The 5 shots with sand binder mixture each show a significantly lower intensity in the case of ECOCURE™ BLUE
- When comparing the rinse cycle to shot with sand binder mixture, it is noticeable that the intensity of the ECOCURE™ BLUE weakens, while that of the TEOS binder remains at the same level.

**Diagram 1:** Detailed evaluation of the total carbon content in the core shooting process




The determination of the average total carbon values during the period of measurement enables a quantitative comparison of the systems with regard to organic emissions during the core shooting process.

**Diagram 2:** Average organic emissions during the core shooting process - TEOS binder system vs. ECOCURE™ BLUE




The measured emissions of the ECOCURE™ BLUE systems are 64% lower than for the TEOS binder. This is not only due to the amine reduction, which, as mentioned above, was “only” approx. 44%, but above all to the fact that the ECOCURE™ BLUE can be viewed as a VOC-free binder system and that in core production essentially only the amine load contributed to noteworthy emissions.
This is also evident from the fact that when the sand binder mixture is shot, the FID intensity decreases, that is to say, the core encapsulates the amine. In the case of the TEOS binder system, this is not apparent, presumably because the TEOS "released" as a VOC covers this effect.

**But what about the storage of the cores? Are similar results to be expected, or could the contrast become even starker here?**

To answer the question, a measuring box was designed, in which a core can be placed for evaporation. A constant airflow, which is directed over the core, ensures that the resulting emissions at the outlet pipe of the box using an FID over a period of 80 minutes each could be recorded.

**Figure 4:** Measuring box with blower

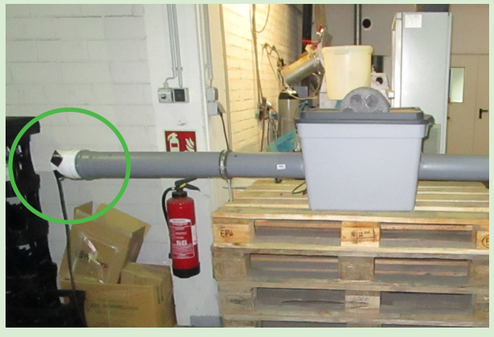


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**Figure 5:** Online FID for determination of the total carbon content during core storage

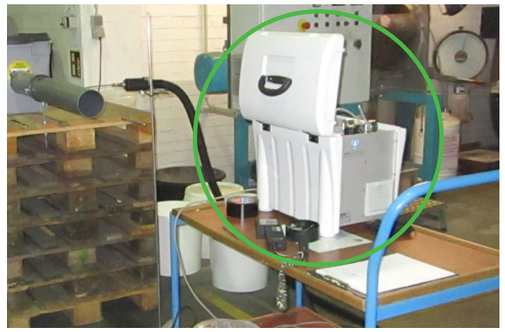


**Figure 6:** Position of the sensor in the outlet pipe

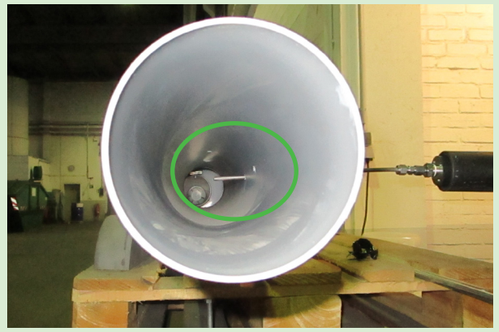
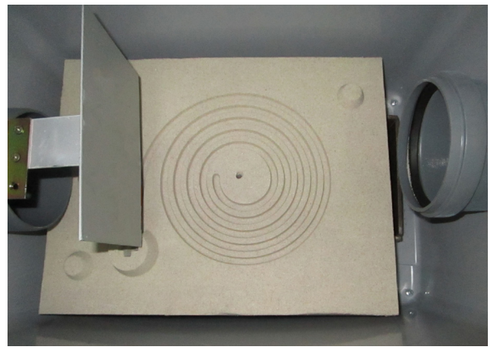
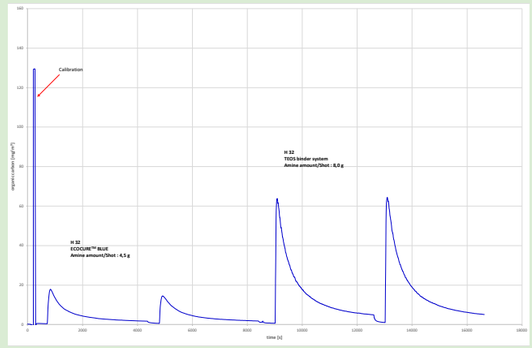


**Figure 7:** Test cores in the measuring box
Core weight: 8.32 kg



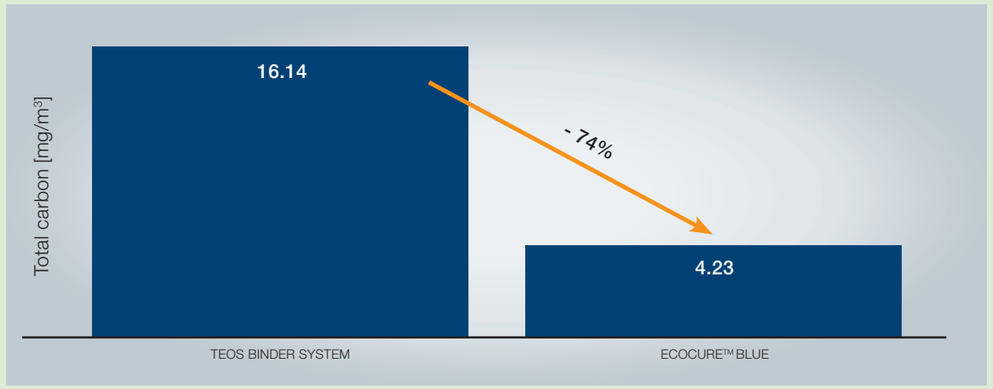
A freshly produced core from each binder system was continuously measured twice in succession. The result is shown in the diagram below and shows even much clearer differences between the systems.
The integration of the peak areas of the FID spectrum reflects the degree of evaporation during the core storage period and thus also gives an indication of the VOC emissions.

**Diagram 3:** Total carbon content during core storage




The comparison between the two binder systems shows that the TEOS binder system not only emits significantly larger amounts of organic components during core production, but also "evaporates" them over a longer period. The peak maxima are more than three times as high as those with ECOCURE™ BLUE manufactured cores.
In the case of the ECOCURE™ BLUE, the detected average of the total amount of organic compounds under controlled core storage was only about a quarter.

**Diagram 4:** Comparison of average organic emissions during core storage



## CONCLUSION

Emissions in foundries come from different sources. Many are easy to control, be it through the targeted selection of materials, through process optimization, or secondary measures such as housing, extraction, and processing. However, one mistake should be avoided, namely to ignore emissions that are not obvious. Everyone is aware - and this impression is reinforced by smoke and smell - that a large part of the emissions is caused by the combustion of products. However, what is underestimated are, for example, the imperceptible, volatile components that escape during core production and storage. Even if critical occupational exposure limits or odor thresholds may not yet be exceeded, options should be considered to minimize them to keep the exposure of people and the environment low. Finally, developments in other industries also suggest that VOC limits are being regulated more and more strictly.

VOC-reduced binder systems, such as ECOCURE™ BLUE, are one adjustment to achieve the optimum and to be equipped for future requirements and stricter VOC limits.

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