

A new technology platform now offers foundries the possibility to work with a cold box part 1 that does not contain any hazardous substances subject to labeling requirements and that helps them to significantly reduce their phenol emissions.

Newest technology platform for cold box binders

Emissions form in the various phases of the foundry process. When using organic binders, pollutants are emitted that can be harmful for workers and the environment. During core production some of the solvent as well as volatile components like amines and residual monomers contained in part 1 of the cold box formulation evaporate or vaporise. In some cases, this involves volatile organic compounds (VOCs) that can also be highly odorous. VOCs have been comprehensively identified and classified by the European Union⁽¹⁾.

Components of a typical cold box formulation

In the cold box amine process, amines are used for the hardening of cores and moulds. When investigating emissions in the foundry process, the solvents with a low boiling point that are used in part 1 and/or part 2 must be taken into account above all. These are aromatic solvents, in particular, that are

produced via the fractional distillation of crude oil, and organosilicate solvents. Such solvents are used to reduce the viscosity to a level suitable for processing and to optimise the various core characteristics.

To produce a typical phenolic resin, a polymer is synthesised from phenol and formaldehyde that can still contain residual monomers such as phenol and formaldehyde as a result of an incomplete reaction.

Also, certain additives that are used for the optimisation of the binder performance (moisture resistance, processing time, etc.) can prove to be toxic for workers.

Occupational exposure limits and volatility of hazardous substances

There are numerous products with special compositions on the market that are less harmful or dangerous according to the information provided by the manufacturers. However, how are the

risks of a binder evaluated? In Europe, all hazardous substances are classified in accordance with the *GHS/CLP Regulation* and must be declared in the safety data sheet.

On the basis of various studies, the European Union has specified a certain occupational exposure limit (OEL) for each identified hazardous substance. This refers to the acceptable upper limit (concentration within a given time frame) up to which a worker may be exposed to the particular chemical in the workplace. The lower the OEL, the more hazardous the chemical is classed as.

The volatility of a chemical is another parameter that influences the health of a worker. Volatility can be assessed on the basis of the vapour pressure. The higher the vapour pressure, the easier it is for the chemical to vaporise and the higher its concentration is in the workplace air.

For occupational health and safety, it is therefore always better to use chemicals with the highest OEL - or ideally chemicals that require no OEL - and the lowest vapour pressure.

Odour detection threshold is not reliable

To evaluate the risks of a chemical, the odour detection threshold is also often used as a parameter. Odour helps us to detect the presence of molecules in the air. However, the same odour can be an irritant to one person while another may perceive it as being pleasant. This is completely dependent on the specific circumstances and the individual acclimatisation to the odour. The odour detection threshold is thus a subjective parameter that does not provide reliable information about the risk or safety of a chemical.

Of course, the odour can constitute a selection criterion for the selection of binders; however, it should not be the only evaluation benchmark. A strong odour can also indicate that the area is insufficiently ventilated or that the extraction system is not efficient enough, for example. A stronger-smelling product must never be exchanged offhandedly for an odourless binder without considering the OEL and the vapour pressure of the alternative products. For instance, if the supposedly harmless (odourless) product has the lowest OEL and the highest vapour pressure, the changeover would constitute a much greater hazard for the worker.

Emissions during casting

Developments in recent years show that emissions during core production can be avoided or at least localised and removed in an appropriate manner. The majority of pollutants in foundries occur during casting. Their formation occurs in three phases - due to the high temperatures, a large part of the solvent, which is contained in the core and mould, the phenol and the formaldehyde as well as the further residual monomers vaporise. In the second phase, the polyurethane chains combust as a reaction to the oxygen in the mould, the



Fig.1 Occupational exposure limits and vapour pressure

Systems	Pictograms	Hazardous substance as per chapter 3 of the safety data sheet
Aromatics		Phenol, aromatics, (formaldehyde), additives
Biodiesel		Phenol (formaldehyde), additives
TEOS		Phenol, TEOS, (formaldehyde), additives
High-efficiency		Phenol, additives
	NO pictograms	NO hazard class

Table 1 ECOCURE BLUE does not contain any substances and/or concentrations subject to labeling requirements in part 1 of the formulation

cores and the surfaces are exposed to the air. This is known as complete combustion. As soon as the oxygen content is too low, what is known as 'pyrolysis' begins, i.e. the thermal decomposition of organic compounds or other reaction partners. Depending on the temperature gradients and gas pressures in the various areas of the core, the organic substances contained in the binder are combusted, gasified, cracked and condensed again. During this, what are known as 'free radicals' form that can be reformulated into new forms. This leads to the forming of pyrolysis products such as BTX (benzene, toluene and xylene) as well as CO, NO_x or other HAPs (hazardous air pollutants). Factors such as temperature, the ratio of oxygen content to the percentage of organic compounds in cores and moulds, etc. play an important role in pyrolysis. Alongside the composition of the binder, application-specific parameters such as core and mould geometry, the ratio of sand to metal, the casting temperature or the ingate system, greatly influence the release of pollutants.

ASK Chemicals has thoroughly investigated these emissions in recent decades. For this purpose, what is known as the 'Hoodstack device' has been used (alongside other procedures), which was developed by Ashland. Tests with the Hoodstack provide information on the extent to which the binder composition influences the composition of the emissions. Hoodstack analysis enables the recording of the VOCs, carbon monoxide (CO), carbon dioxide (CO₂), nitrogenous gases (NO, NO₂, NO_x) and sulfurous emissions (e.g. SO₂). Lead substances - e.g. benzene, toluene, xylenes, phenol and formaldehyde - can be recorded via absorption on appropriate media and quantified via subsequent chemical analysis. Hoodstack analysis allows emissions from the casting, cooling and demoulding process to be monitored, depending on the configuration of the core and/or mould package.

ASK Chemicals was able to demonstrate that the main emissions are monomers, BTX and NO_x. Monomers form within split seconds after casting via vaporisation. BTX and NO_x form in the further course of the casting phase.

Building upon this newly obtained knowledge, the company introduced a new generation of binders in 2008 with the 'ECOCURE™ High Efficiency' cold box binder that was continuously developed and supplemented in 2014 by the solventless cold box system

'ECOCURE SL'. An extremely effective measure, albeit a slightly surprising realisation, is that the reduction of the organic material in the core and mould proves to be one of the most effective ways of minimising emissions in every stage of the foundry process and particularly during casting. A main focal point at ASK Chemicals is the development of solutions that enable the achievement of the same performance level with a reduced use of binders.

ECOCURE™ BLUE - the first cold box binder without substances subject to labeling requirements in part 1

The starting point for the development of the latest technology platform from ASK Chemicals was the knowledge surrounding the following three specific emission sources:

- Evaporation of volatile compounds during core production (mixing, shooting, storing, etc.)
- Evaporation of the residual phenol and formaldehyde monomers and solvents with a higher boiling point during the first split seconds of casting.
- Emission of BTX (and other products of decomposition) during the casting phase due to the pyrolysis of the carbon backbone of the polyurethane polymers.

Solutions for the first two emission sources have also been in intensive development for a number of decades. Numerous suppliers are now already offering cold box binder systems that dispense with VOCs entirely. In simple terms, we can say that the majority of cold box systems on the market that do not contain any aromatic and/or TEOS solvents can be sold as being free from VOCs in accordance with European law.

The development of the HE and SL systems by ASK Chemicals aims specifically at a reduction of the third emission source. The reduction of the added amounts of binder is equivalent to a lower organic load and thus leads to reduced emissions during pyrolysis.

The targeted reduction in monomer content (especially free phenol) was for a long time neglected in the course of the aforementioned modifications. This is unsurprising as the development of such solutions is considerably more complex and involves significantly more research effort. This also includes the need to consider new production procedures and modifications to existing production systems.

The result of such an intensive

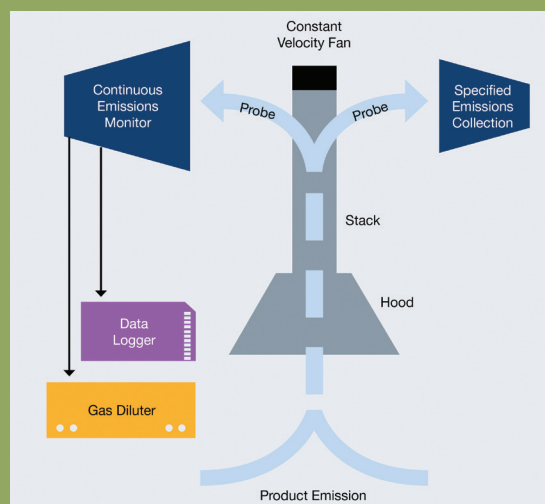


Fig.2 Schematic depiction of the Hoodstack set-up

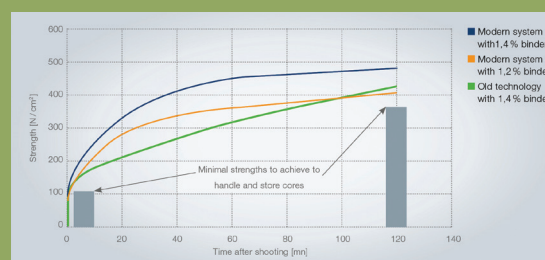


Fig.3 High-efficiency or solventless cold box binders enable a reduction in the binder agent while providing higher initial and final strengths

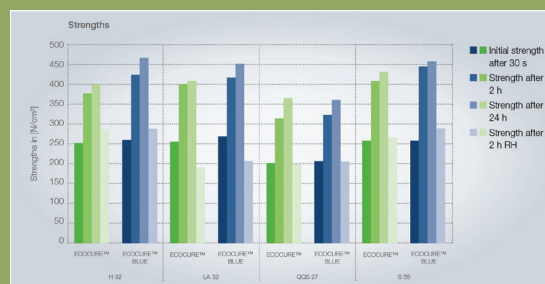


Fig.4 Comparison of the bending strength of ECOCURE BLUE and ECOCURE 30 HE 1 LF with various sand qualities from Western Europe. All tests were performed with 0.7 per cent per part with the catalyst 706 (DMPA)

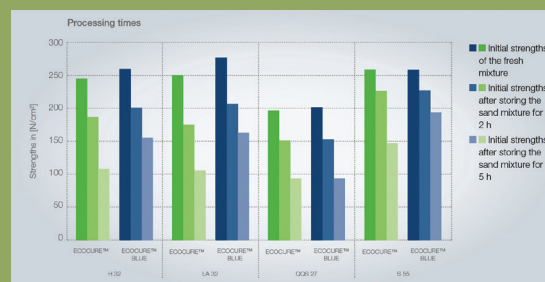


Fig.5 Comparison of the processing time of ECOCURE BLUE and ECOCURE 30 HE 1 LF with various sand qualities from Western Europe. All tests were performed with 0.7 per cent per part with the catalyst 706 (DMPA)

development is the new cold box technology ECOCURE™ BLUE, which is based on a phenol resin in which the concentration of substances subject to labeling requirements was substantially undershot or where such substances were omitted completely. Labeling with a hazard symbol is therefore not necessary. Substances and concentrations subject to labeling requirements refers to the substances and concentrations that have to be declared in chapter 3 of the safety data sheet as per the new European CLP Regulation.

ECOCURE BLUE does not contain any components that have to be declared due to their OEL (with the exception of DBE in Germany) or that exceed the concentration limit for hazardous substances. Only part 2 of the cold box formulation is still based on isocyanate, which must be declared.

Products that are based on the 'ECOCURE BLUE' platform combine the advantages of the 'ECOCURE high-efficiency' binders, which are known on the market, with the advantages of the 'ECOCURE BLUE' technology, and so enable the foundry to optimise the emissions along the entire value added chain.

The foundry therefore receives a product that does not contain any substances subject to labeling requirements in the part 1 component and that additionally has the technically superior performance of the high-efficiency technology. Its reactivity and the ability to specifically optimise initial strengths - a deciding factor in the selection of the binder system - are what distinguish high-efficiency technology.

Performance comparison

The development of cast parts constantly presents new challenges for foundries and raw material suppliers. Core geometries are becoming increasingly more complex. Thin-walled casting is playing an increasingly larger role - particularly in the automotive field. Solutions for increased productivity to ensure the competitiveness of foundries are becoming ever more important in all areas. Thus, extremely short cycle times are a significant requirement in core production. Furthermore, environmental considerations are one of the key parameters in the selection of the appropriate cold box technology for European foundries in particular.

A new binder that lives up to all of these requirements or even exceeds them must distinguish itself via exemplary mechanical strengths and an excellent reactivity for short cycle times, as well as very good casting results and with as minimal an influence on the environment, health and occupational safety as possible.

The first product of the new technology platform ECOCURE BLUE 30 HE1/ECOCURE BLUE 60 HE 1 achieves the good technical performance of ECOCURE 30 HE 1 LF/ECOCURE 60 HE 1 LF (2nd

generation high-efficiency system), which is said to be the best non-aromatic system on the market and is used in nearly all European countries for iron applications.

Various cold box systems available on the market were examined via the Hoodstack analysis regarding the emissions that formed during the casting process.

The analysis of the VOCs during casting, cooling and demoulding reveals a clear reduction when using this new technology platform compared to aromatic or TEOS systems.

The analysis particularly focused on the phenol and BTX emissions that form at the start of casting via pyrolysis.

When examining the results, it was possible to once again confirm that the most efficient method of minimising BTX emissions is the reduction of the added amounts of binder. This can be identified in the measurement values of the ECOCURE HE system, which on average emits fewer emissions than comparable systems.

Moreover, with the ECOCURE BLUE platform the phenol emissions - and therefore also the proportion of free phenol content - are significantly reduced. After comprehensive tests, ASK Chemicals undertakes that foundries employing the 'ECOCURE BLUE HE' systems can reduce the phenol emissions during casting by up to 80 per cent.

Initial experiments in foundries have shown that particularly the phenol content in waste sand can be reduced by at least 20 per cent, sometimes even up to 50 per cent - depending in the procedure and the quantity of the new core sand used - via the use of this new technology platform.

Conclusion

For the first time ever, this new technology platform offers foundries the possibility to work with a cold box part 1 that does not contain any hazardous substances subject to labeling requirements and that helps them to significantly reduce their phenol emissions. Initial experiments also show a reduction in the phenol content in waste sand, which can have positive effects on the class of landfill and the corresponding costs.

That ecology and economy, which do not have to be mutually exclusive, is demonstrated by the new ECOCURE BLUE HE systems, which are in no way inferior to

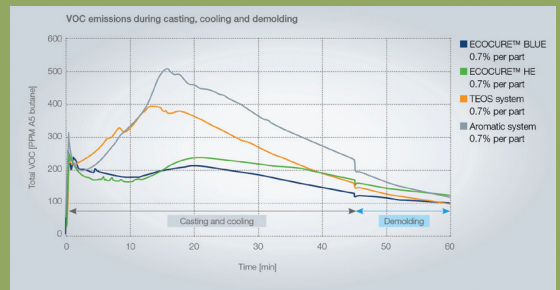


Fig.6 VOC emissions during casting, cooling and demoulding (using Hoodstack method)

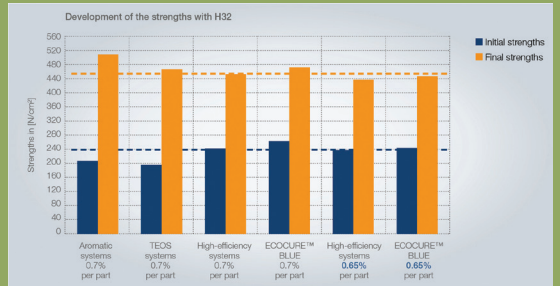


Fig.7 As a result of higher strengths, the binder quantity can be reduced with ECOCURE HE and ECOCURE HE BLUE

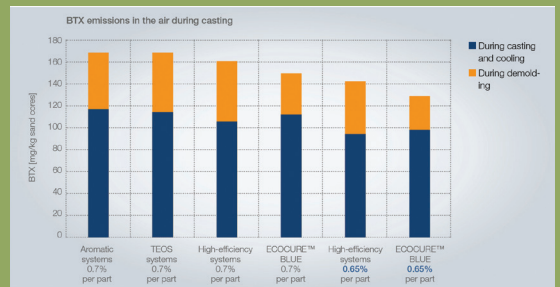


Fig.8 The BTX emissions from the pyrolysis of the polyurethane can be significantly reduced with ECOCURE BLUE and ECOCURE HE via the reduction in binder quantities

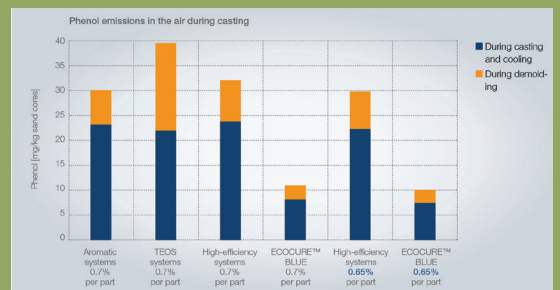


Fig.9 The technology platform ECOCURE BLUE can reduce phenol emissions during casting by 80 per cent

the current best cold box binders available on the market regarding reactivity, strengths and casting results. This technology was developed for iron and steel casting and is not only recommended for the production of hydraulic components, turbochargers, brake disks and engine blocks, but also for other application areas.

The new technology platform ECOCURE BLUE can be used with all common sand qualities (quartz, special sands and reclaimed sands) and is compatible with numerous sand additives (organic, inorganic or hybrid additives).

All catalysts currently available on the market can be used. Naturally, the new technology platform is very compatible with water-based and alcohol-based coatings.

Reference

1. Solvents Emissions Directive 1999/13/EC.

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