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**The Resole - CO₂ Process**

**Carbophen® Binders**

### Introduction

Changes and transitions sometimes take place over the course of years, and thus the transition from heat curing methods to gas curing processes is still incomplete. Many foundries are progressing toward the cold box method, sometimes coming from the sodium silicate -CO₂ process and coming to a halt with the resole-CO₂ method.

### Process Components

The two required components are the following:

- **Resole**
  - Phenolic resin condensed under alkaline conditions
  - Viscosity: 300 - 700 mPa·s
  - pH: 14
  - Storage life: Nine months at 15 – 20 °C
  - Monomer levels: Free phenol < 1 %
    - Free formaldehyde < 0.1 %

- **Carbon dioxide**
  - Present in the atmosphere at a level of approx. 0.03 %
  - In this process, gaseous carbon dioxide (CO₂) is used to cure the molding sand mix in the sealed corebox.

### Process Chemistry

The process is based on use of a water-soluble phenolic resin condensed under alkaline conditions – a phenolic resole – containing an oxygen anion. This resin is the sole binder component added to the sand. The crosslinking reaction is induced by passing CO₂ into the sealed corebox. It should be noted that the CO₂ represents a true reaction component. The crosslinking reaction would require several hours for completion if CO₂ were not introduced into the corebox. For the foundry person, it is important to know that the resin contains no nitrogen, sulfur or phosphorous.
Modern coremaking sand conditioning systems are equipped with storage tanks for the required components. These materials, as in this case a phenolic resin condensed under alkaline conditions with a pH of 14, are frequently transferred to the locations where they are required through lengthy piping systems. Materials that are recommended or not recommended for the piping systems used to transfer the above material are listed in the following table:

<table>
<thead>
<tr>
<th>Recommended</th>
<th>Not Recommended</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>Aluminum</td>
</tr>
<tr>
<td>Steel</td>
<td>Zinc (including galvanized lines)</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Copper</td>
</tr>
<tr>
<td>High-density polyethylene</td>
<td></td>
</tr>
<tr>
<td>Glass fiber-reinforced plastics (FRP)</td>
<td></td>
</tr>
</tbody>
</table>

**Molding Matrices**

All molding matrices used in the foundry industry – silica, zircon, chromite and chamotte sands – are suitable for the process. However, these must be washed, dried and graded. The moisture level of the molding matrix must be lower than 0.1 %.

If the molding matrix is to be modified or recycled sand used, is it advisable to conduct a practical trial in advance.

In a graduation project (Diplomarbeit) monitored by HA, Mr. W. Piel investigated the use of mechanically recycled sand from various coremaking processes. A selection of the results from this work will be published in this paper. Up to 20 % mechanically recycled sand could be used in a “mono-process” system, i.e. new sand plus recycled sand from the resole-CO$_2$ process. In a “dual-process” system, up to 20 % of a mechanically recycled sand from a hot box process could be used, which also applied to mechanically recycled sand from the methyl formiate process. Recycled sand from the cold box and shell molding processes could be added to the molding sand mix at levels of up to 10 PBW (parts by weight). Depending on the core geometry, addition levels in excess of those mentioned above may certainly be possible in isolated cases, but generally lead to a loss in strength. The following principles should always be observed when the molding matrix is modified:

- The finer the sand, the higher the resin addition rate
- The more angular the grain structure, the higher the resin addition rate
- The “rounder” the grain structure, the lower the resin addition rate
- The more alkaline the sand, the higher the CO$_2$ demand
- The more acidic the sand, the shorter the bench life
Molding Sand Conditioning

All commercially available mixing equipment can be used for molding sand conditioning. Great care must be taken during conditioning to ensure that the operation affords a homogeneous mix. If such a homogeneous mix cannot be prepared within a reasonable period of time, the mix absorbs CO₂ from the ambient air, resulting in a decreased sand bench life and an increase in the molding sand temperature due to the lengthy mixing period. It should be noted at this point that only one metering pump is required for this process.

Core Shooters and Automatic Curing Systems

All core shooters presently on the market are suitable for use with molding sand mixes prepared using the resole-CO₂ process. Any commercially available gassing unit set up for CO₂ gassing can be used to cure the molding sand mix in the sealed corebox. During the gassing operation, the carbon dioxide should have a temperature of 45 °C at the gassing plate, since this increases the rate of reaction.

Molding Sand Storage

In most foundries, the molding sand is stored in open containers – closed hoppers would be better – located above the core shooter. When stored in this manner, the molding sand mix develops a more or less thick surface crust of cured molding sand after a certain period of time. The thickness of the crust is closely related to the temperature of the environment and the percentage of CO₂ in the ambient air/factory atmosphere. Exhaled air contains approx. 350 ppm CO₂, and levels ranging between 2500 – 5000 ppm CO₂ have been determined in coremaking shops. The more reactive the Carbophen® binder, the faster the rate of crust formation. High reactivity is necessary to achieve elevated levels of immediate bending strength, but also leads to faster crust formation. The latter reaction also proceeds inside the shot cylinder of the core shooter, since the molding sand is permeated with air every time a core is shot.

Figure 1

Figure 2
The shooting head of the core shooter should be cleaned after every shift. *Figures 1 and 2* illustrate the variations in behavior experienced with molding sand containing two different Carbophen® binders when the shooting head is opened at the end of a shift. *Figure 1* shows the behavior using an older type of binder, and *Figure 2* the behavior of sand containing a newly developed binder.

**Molding Sand Properties and Applications**

The following bar chart shows the bending strength levels in N/cm² of cores made with various Carbophen® binders.

![Bending strength chart](chart1.png)

*Chart 1*

The bending strength bars were fabricated under the following conditions.

100 PBW  H33 Silica sand, mean particle size (MK) 0.27 mm, AFS 52
3.0 PBW  Carbophen®
Blowing pressure  6 bar
Gassing time with CO₂  15 s
Corebox temperature  20 °C
Ambient temperature  20 °C
Relative humidity  48 %

*Chart 1* clearly shows the stages in strength development from the initial strength to the levels after the cores have been stored for various periods of time. The new product developments offer core storage periods of up to 20 days, as may be seen in *Chart 1*. The present initial strength level is also twice as high as in older systems. Moreover, the new system was also enhanced with respect to its flowability. This means that a level of molding sand flowability comparable to that in the cold box process has been achieved. In conjunction with the improved initial strength, this property enables fabrication of delicate
cores that could not be produced in the past. The enhanced flowability makes it possible to reliably produce cores that have otherwise experienced problems with compaction.

*Figure 3* shows two cores. The core marked with an “R” exhibits compaction problems, whereas the core on the left, fabricated using the new product development, no longer suffers from this problem.

*Figure 4* shows a section of a core that had exhibited serious compaction problems in the past. These problems could be eliminated by use of the new product development, affording increased productivity and reducing the numbers of defective cores.

**Coreboxes**

Practically all existing coreboxes can be used for the resole-CO₂ process. It should be noted that the carbon dioxide represents a true reaction component, and must therefore persist in the corebox for a certain period of time. This means that when Carbophen® bonded cores are fabricated in a corebox built for the cold box process, it may be necessary to modify some of the gassing vents to ensure optimal curing conditions.

**Emissions During Core Production**

Only carbon dioxide is emitted during core production. Therefore, no major investments are required for the design of the pertinent work station and for environmental protection. No scrubber is required for treatment of the exhaust air from the coremaking shop.
Refractory Coatings

The binder links are damaged when a refractory coating is applied to the cores. This damage is observed regardless of whether the coating vehicle is water or alcohol. Due to the high alkalinity of the system, the damage to the core and loss of bending strength is greater when the coating vehicle is water than if it is alcohol. However, it should also be noted at this point that refractory coatings for cores bonded with alkaline resoles have been developed, and result in a great reduction or even complete elimination of the damage to the binder links.

Emissions During the Casting Operation

As already described in the case of core production, the emissions liberated during the casting operation may be considered minor. As in the case of any other organic binder system, tiny traces of benzene are emitted, and carbon monoxide is liberated in addition.

Casting Defects

Casting defects such as finning have not been observed when this binder system is used. Nitrogen defects and graphite degeneration caused by sulfur do not occur. However, one disadvantage does exist, and may not be disregarded at this point. As in the case of all alkaline phenolic resoles, Carbophen® binders tend to permit deformation of the core when it is located near a thermal ("hot") center.

Summary

Following a full decade of experience with Carbophen® binders, it may meanwhile be stated that this system offers a desirable option in every respect:

- Only a single component is metered
- No scrubber is required
- The resin contains no nitrogen, sulfur or phosphorous
- No glossy carbon is formed
- No finning tendency exists
- Low BTX emissions
- Low odor nuisance outside the foundry

Suggestions and requests from customers have encouraged this development work, and we are confident that we will achieve our common goals with such continued cooperation.