Introduction

In recent years, the cold box process has become increasingly popular in the Indian foundry industry. Many foundries already use this coremaking process, or are interested in doing so. Many questions arise in connection with the use or planning of this process, and will be considered in the following remarks.

1. Chemical Characterization of Cold Box Resins and Activators

In the classic polyurethane-based cold box process, the binder represents a two-component system chemically composed of a polyol and a polyisocyanate.

The "polyol" representing one of the components is a phenol-formaldehyde resin exhibiting benzyl ether character. These resins display the general formula:

\[
\begin{align*}
\text{OH} & \quad \text{CH}_2\text{OCH}_2 \quad \text{OH} \\
\text{X} & \quad \text{CH}_2\text{OCH}_2 & \quad \text{CH}_2 & \quad \text{OH} & \quad \text{X}
\end{align*}
\]

in which the sum of \(m\) and \(n\) is at least two, and the ratio \(m:n\) is at least 1:1 (\(x = -\text{H} \) or \(-\text{CH}_2\text{OH}\)).
The polyisocyanate is an oligomeric product of 2,4'- and 4,4'-diphenylmethanediisocyanate, and exhibits the following structure:

![Structure of polyisocyanate](image)

Both the phenolic resin component and the isocyanate are generally used in the form of solutions in organic solvents.

However, the difference in polarity of the polyisocyanate and phenolic resin limits the choice of appropriate solvents that are compatible with both components. This "compatibility" is nonetheless necessary to achieve complete reaction and curing of the binder.

Polar solvents are, for example, very appropriate for phenolic resins, but less so for polyisocyanates. The situation is exactly the reverse when nonpolar solvents are used.

The preferred nonpolar solvents are high-boiling aromatic hydrocarbons (generally in the form of mixtures) exhibiting a boiling range above 150°C at atmospheric pressure. Esters with sufficiently high boiling points are used as polar solvents.

Despite all the advantages polyurethane binders offer to the foundry industry, the aromatic solvents hitherto considered indispensable in them have created serious disadvantages due to emissions in production of core and mold components, and particularly after pouring off. At the high temperatures prevailing during the casting operation, the binder components are subjected to a pyrolysis process involving creation of new, stable compounds. In the presence of aromatic hydrocarbons, this pyrolysis process generates benzene, toluene, and xylenes, which exhibit particularly great thermal stability.
The development of the new cold box binder systems at HÜTTENES-ALBERTUS followed a completely different path.

Instead of the previously favored high-boiling aromatic hydrocarbons, plant-based solvents (methyl esters of vegetable oils) were used for the resins and activators.

Aside from the ecological advantages of these odorless, environmentally friendly, non-polluting and CO₂-neutral natural products, the new solvents meet all physical requirements for polyurethane binder systems. They are high boiling, sufficiently low in viscosity, odorless, and are classified as innocuous at the workplace. They are furthermore nonflammable, a property that considerably simplifies transportation and storage of the resin and activator solutions prepared from them.

1.1 Catalysts

The gases required for curing are members of the family of tertiary amines. These tertiary amines vary with respect to their vaporization points:

DMEA Vaporization point 36 - 38 C  
DMIA Vaporization point 65 - 68 C  
TEA   Vaporization point 87 - 89 C

2. Molding Matrices

2.1 Sands

The sand molding matrix is of special significance in the cold box process. In this method, the question of sand is equally as important as in the other mold and coremaking processes used in the foundry. The economy of the process and quality of the castings to be produced depend to a critical extent on the sand being used.

In principle, all refractory matrices used in the foundry industry can be employed for the cold box process. These essentially represent silica sand, chromite sand and zircon sand.
2.1.1 Silica Sands

Silica sand represents the bulk of the sand grades used for the cold box process, although no statistical data on the exact distribution of the sand matrices exist. European silica sands nearly exclusively date from the Tertiary and Cretaceous periods, and represent the products of weathering of quartz-rich prehistoric rocks in sedimentary deposits. Silica sands are considered of high quality when they contain only minor amounts of accompanying minerals. Such accompanying minerals largely represent the following products:

Feldspar, mica, glauconite, alkaline metal oxides and carbonaceous minerals.

It is known that these impurities depress the sintering point of silica sand to a greater or lesser extent. In the cold box process, the presence of alkaline metal oxides and carbonaceous minerals furthermore affects sand workability and the required level of catalyst.

Foundry-quality silica sands are basically conditioned by:

Washing, desludging, grading and drying.

Aside from the above criteria, the grain shape and surface character are of significance in a foundry silica sand.

The grain shape is differentiated according to the following types:

Round                Rounded grains (edges rounded)
The grain surface could be classified as follows:

Angular

Splintered

Smooth, with microstructure

Smooth, no microstructure

Rough

Conchoidal to highly fissured
As in all mold and coremaking processes, the particle size of the sand has a major effect on the bending and tensile strength of the core produced using the cold box method. The fact must also be considered that the required binder level is directly related to the particle size.

Graph 1 illustrates the bending strength levels as a function of the AFS number.

Silica sand H 31, AFS 41  H = Haltern sand quarry
Silica sand F 32, AFS 60  F = Frechen sand quarry
The screen analyses of the silica sands used for the bending strength test are shown below.

Graph 2 shows the particle size distribution of an H 31 sand with AFS 41.

Further data on H 31 sand:
Mean particle size  0.37 mm  
\(\text{pH} \quad 7.1\)  
Fines  0.2 %  
LOI  0.1 %
Graph 3 shows the particle size distribution of an F 32 sand.

Further data on F 32 sand:

Mean particle size   0.22 mm
pH               6.8
Fines           0.7 %
LOI             0.1 %
The dependence of the bending strength on the AFS number is clearly apparent in Graph 1. It would be necessary to add a greater amount of binder to achieve an identical level of bending strength using the finer (F 32) silica sand. At this point, it should be noted that the casting surface quality and the economy of castings production similarly depend on the particle size of the silica sand being used. The foundry professional can make the choice between a coarser particle size, coupled with a savings in binder, and a finer particle size with a higher packing density, offering a smoother casting surface.

Following this detailed discussion on the use of silica sand as a basic raw material in the foundry (specifically in the coremaking shop in this case), two other types of sand that are used in the cold box coremaking shop - zircon and chromite sand - should also be considered.

2.1.2 Chromite Sand

The starting material for chromite or chrome ore sand, as this material is often termed in practice, is chrome ore. As in the case of silica sand, this material is appropriately conditioned for use in the foundry.

Use of chrome ore sand in the cold box process is always necessary when casting defects such as finning occur in gray cast iron. Finning is one of the group of defects caused by sand expansion, and because of the pertinent coefficients of thermal expansion is encountered particularly frequently when silica sand is used (cf. Table 1, Page 10).

2.1.3 Zircon Sand

This represents a zirconium oxide silicate, in mineralogy termed "zircon". Although zirconium is relatively widely distributed in the earth's crust, there are only few workable zircon sand deposits. The zircon sand used in the foundry industry mainly comes from Australia. Both zircon sand and chrome ore sand are used to fight the casting defect of finning.
The following must be considered when chrome ore sand or zircon sand are processed in a cold box mixture:

♦ They reduce the flow of the molding sand mixture.

♦ Due to the reduced flow mentioned above, an increase in the shooting pressure is required to achieve an identical level of core compaction.

♦ This results in a reduced corebox service life.

♦ They also reduce the bench life of the molding sand mix.

♦ If mixtures of chrome ore sand and silica sand are used, the flow is similarly reduced and in some cases where long shooting paths are involved accompanied by demixing (also applies to mixtures of zircon sand and silica sand).

Comparison of the three types of sand considered above

<table>
<thead>
<tr>
<th></th>
<th>Quartzite</th>
<th>Chromite</th>
<th>Zircon Silicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical composition</td>
<td>SiO₂</td>
<td>FeO Cr₂O₃</td>
<td>ZrO₂ SiO₂</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>2.65</td>
<td>4.4 - 4.6</td>
<td>4.6 - 4.7</td>
</tr>
<tr>
<td>Bulk density (vibrated), g/cm³</td>
<td>1.52 - 2.00</td>
<td>2.9 - 3.1</td>
<td>3.01</td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>1723</td>
<td>2180</td>
<td>1900 - 1995</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (0 to 1000 C) in mm/(mm K)</td>
<td>0.065</td>
<td>0.019</td>
<td>0.0013</td>
</tr>
</tbody>
</table>
3. Mixing

The subject of this talk is "Working With the Cold Box Process in the Coremaking Department of a Foundry".

However, working with the cold box process requires more than just the Gasharz (Resin), Aktivator, catalyst and refractory matrix components discussed above. Mixers, core shooters, coreboxes, gassing apparatus and similar equipment are also necessary. The mixing principles that dominate the German foundry industry will be described below.

The purpose of blending a molding sand mix is to coat the refractory matrix components with the gas-curing resin and activator. The following facts illustrate the enormous effort involved in this task. Silica sand H 32, AFS 46, exhibits a theoretical specific surface area of 77 cm$^2$/g. This means that 50 kg of this silica sand possesses a theoretical specific surface area of 3850 m$^2$. This corresponds to the area of a hall with sides 62.0 x 62.0 meters long. In a very brief time, this 3850 m$^2$ area must now be coated with a quantity of only 360 mL resin and 360 mL activator in a mixer.

3.1 Agitator-Type Mixers

3.1.1 Operation of an Agitator-Type Mixer

The motor-driven agitator or mixing beam propels the mixture, which is forced outward against the walls of the vessel by the rotary motion of the agitator. The continuous movement forces layers of the mixture upward along the walls of the vessel until the mixture falls back towards the center into the bulk of the material. Figure 1 illustrates this operation.
Figure 1

The mixing capacity depends on the following parameters:

- Rotational speed (rpm) of the agitator
- Peripheral velocity at the tip of the agitator
- Ratio of diameter to height of mixing vessel
- Mixing equipment design
- State of wear of mixing equipment

3.2 Vibratory Mixers

3.2.1 Operation of a Vibratory Mixing Vessel

The mixing vessel (Wall A) is set into oscillating motion (B) by the horizontal rotation of an eccentric that is instrumental in producing the vibratory movement. The resultant friction between the mixing vessel (1) and mixture (7) causes rotary movement (C) of the mixture. Part (b) of Figure 2 shows a momentary situation. This clearly demonstrates that the inertia of the mixture (7) always causes it to contact only a small area x (c in Figure 2) of the vessel wall. Compressive forces D (c in Figure 2) originate at this rapidly oscillating
interface, and are directed toward the interior of the mixture. These cause "liquefaction" of the mixture and furthermore produce agitation of the mixture within itself (d in Figure 2). Figure 3 shows the various mixing equipment system designs.

Figure 2 (schematically) illustrates the mode of action of the vibratory mixing vessel.

Figure 3 (1. Mixing unit; 2. Vibration shovel; 3. Vibration pipe to speed up)

The mixing system (a in Figure 3) features multiple blade-shaped baffles whose outer edges are angled against the direction of flow of the mixture. These blades (2 in Figure 3)
are rigidly attached to the mixing vessel, and depending on their numbers cut corresponding numbers of layers out of the mixture to be rolled over one another and carried upward in the interior of the mixer in rapid sequence. This achieves a highly intensive mixing effect.

The efficacy of the mixer depends on the

- Diameter of the mixing vessel
- Angle of incidence
- Width of transport blades
- Frequency of the vibratory motor
- Diameter of the oscillation cycle

4. Transportation

In the present sense, transportation only refers to conveyance of the molding sand from the mixer to the core shooter. In series-production foundries such as an automotive foundry, such transportation is accomplished using automatic floor conveyers. However, foundries certainly still exist even in Germany where this transportation is accomplished by manual means. The transportation time should be as brief as possible. There is a great danger that sand workability problems will arise, since the molding sand is also stored in the hopper of the core shooter (cf. Section 5).

5. Core Shooters, Gassing Equipment

These points will only be discussed to the extent that this is indispensable. More precise information is available from the pertinent manufacturers.

From the point of view of the binder manufacturer, it is important that the core shooters be matched to the size of the cores to be produced with them. The reason for this requirement may be explained as follows.
Shooting of a 1 kg core on a 25 L core shooter should be avoided. If this were to happen, the result would be that the core shooter - with a molding sand supply of 200 kg - would only exhaust this supply in approximately three hours. In case of outdoor temperatures in excess of 30 C, storage of the molding sand for a three-hour period could lead to problems in core fabrication (cf. Section 4).

As a rule of thumb, the reaction rate doubles with every 10 C increase in the temperature.

A further point to be observed when installing core shooters and gassing equipment is to also provide for a dehumidifier (chill dryer). As already known, the activator of the cold box system reacts with the moisture in the air, forming a polyurea and CO₂. The polyurea does not form stable binder links between the individual sand grains, i.e. the core does not achieve its required strength. Moreover, the polyurea is not thermally stable, and decomposes to yield nitrogen when exposed to the heat of casting.

6. Pattern Equipment for Core Production

6.1 Coreboxes

Coreboxes for the cold box process may be manufactured from various materials including:

- Wood
- Wood/plastic
- Aluminum/plastic
- Grey Iron
- Steel

The selection of a construction material depends on the number of cores to be produced in the corebox. Combinations of wood and plastic, or better of aluminum and plastic (Slide 1) can definitely be used as corebox materials in a jobbing foundry with lot sizes of 20 to 1000 cores. In selecting the plastics for use in corebox construction, it should be noted that the plastic must be resistant to the components used in the cold box process. When the lot
sizes mentioned above are exceeded, it is advisable to perform a cost analysis for the pattern equipment.

After selection of the materials to be used, the second most important consideration in core production is the design of the corebox.

Slide 1 shows a core with quite simple geometry. Cores of this or a similar shape are always produced in vertically parted coreboxes.

A cylindrical injection port may be seen in the upper part of the corebox. This should be as large as possible and as small as necessary. A port that is as large as possible permits the molding sand to be shot into the corebox with the lowest possible pressure. Further advantages of a large injection port are:

- Increased corebox service life (lower wear)
- Less cleaning expense
Reduced binder buildup below the injection port
Improved, faster permeation of the catalyst (large area)
Reduced catalyst consumption
The port should also be as small as necessary to avoid the following disadvantage:
The large injection port section must be separated from the core if it cannot be used as a coreprint.
Slide 2 shows a somewhat larger core.
Dimensions: Length 500 mm, height 300 mm,
Width 400 mm, core weight 20 kg
The upper section of the core is shown with the injection port section and the attached core. The unusual feature of this core is its height, resulting in the large number of vents in the upper section of the corebox. At this point we are not referring to gassing inlets, but to vents.

**Basic rule:**
Every corebox fills with molding sand from the bottom to the top, i.e. the air present in the corebox and that introduced with the shot is forced upward by the column of sand that builds up, and must thus escape from the corebox through the vents at the top.

This is the reason for the large number of vents in the upper section of the corebox. However, we must also consider the fact that we are working with the cold box process and thus must permeate the quantity of molding sand in the corebox with a gaseous catalyst. This means that if there are too many vents in the upper section of the corebox, the catalyst will escape through these and no cure will take place in the lower section of the core being made. For this reason, a compromise between good core compaction in the upper section of the core and catalyst consumption must be reached for each and every type of core.

Slide 3 now shows the lower section of a corebox.
The arrangement of gassing inlets shown here is necessary. If these inlets were not arranged in this manner, permeation of the molding sand by the catalyst could not be assured, and the core would not cure in the indicated positions due to the back pressure developed in the upper section of the core.

Thus, an optimal arrangement of inlets must also be found to permit the fastest possible cure of the core, since the advantage of the cold box process lies in the fact that large numbers of cores can be produced in a brief period.

Slide 4 illustrates another possibility. This corebox contains three impressions, permitting three cores to be manufactured with one shot.
7. Coatings

7.1 Classification of mould and core coatings

Minerals: e.g. Aluminium silicate
Zircon silicate
Graphite

Carrier liquid: Water
iso – Propanol

Delivery from: Powder
Paste
Slurry (Ready for Use)

The table below shows a general view over the Coating products from HÜTTENES – ALBERTUS and their principle applications.

<table>
<thead>
<tr>
<th>Product Group</th>
<th>Main refractory materials</th>
<th>Carrier</th>
<th>Main Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirkofluid</td>
<td>Zircon</td>
<td>Alcohol</td>
<td>Steel</td>
</tr>
<tr>
<td>Zirkopal</td>
<td>Zircon</td>
<td>Water</td>
<td>Steel</td>
</tr>
<tr>
<td>Arkofluid</td>
<td>Al-Silicates</td>
<td>Alcohol</td>
<td>Heavy grey iron</td>
</tr>
<tr>
<td>Koalid</td>
<td>Lamellar Al-Silicate</td>
<td>Alcohol</td>
<td>Grey iron Aluminium and non ferrous automobile castings</td>
</tr>
<tr>
<td>Arkopal</td>
<td>Various (lamellar) Al-Silicates</td>
<td>Water</td>
<td>Heavy grey iron /grey iron Aluminium and non ferrous automobile castings</td>
</tr>
<tr>
<td>Disopast</td>
<td>Various Refractory Materials</td>
<td>Water</td>
<td>Gas permeable coatings for the full mould and lost foam processes</td>
</tr>
</tbody>
</table>
References

Mould and Coremaking with “No bake Systems”.
Klaus Loechte, "Diplomarbeit" Planning of the Coreshop University–GH Duisburg 1987-88