PANELIST'S REMARKS

CONTROL TECHNOLOGY FOR FURFURYL ALCOHOL - BASED SYSTEMS: THE FURAN NO-BAKE PROCESS

Daniel S. P. Eftax, Ph.D
Manager, Product Development - Foundry
Quaker Oats Company
Chicago, Illinois

INTRODUCTION

The recent NIOSH report on foundries presented the available technology to control exposure to potential physical and chemicals agents (1). Three chemically bonded sand processes were covered: phenolic shell molding, furan hot box coremaking, and phenolic urethane cold box coremaking. In addition, case histories on each of the above processes were presented.

In this presentation the no-bake chemically bonded sand process will be covered, that is, the process by which cores and molds are produced at room temperatures. I will identify controls and precautions that are recommended to improve the quality of the workplace environment when utilizing furan foundry binder systems, i.e., binders based on furfuryl alcohol. The comments will be specific for the furan no-bake process since the major outlet for furfuryl alcohol is the no-bake process.

In certain respects, the controls recommended for the furan no-bake process may be applicable to other furan processes that are utilized in the foundry: hot box, cold box, and warm box.

SYSTEM COMPONENTS

Binders

The composition of a furan no-bake binder varies depending on the performance required in a particular foundry. Furfuryl alcohol content may vary from 45% up to nearly 100%, and may be present as a monomer or in a prepolymerized form, or blends thereof. Other ingredients may include urea, formaldehyde, urea-formaldehyde polymers, phenolic materials, water, and possible other additives. In addition, small amounts of silanes (0.1 to 0.3%) are added to ensure high tensile strength under conditions of high humidity. Formulations include nitrogen-free, formaldehyde-free, water-free types, as well as binders with varying proportions of any or all of the additives mentioned above. The main constituent is furfuryl alcohol. The binder is placed on the sand after the catalyst has been added to the sand and mixed.

Catalysts

Furan no-bake catalysts are generally proprietary mixtures of acids and solvents, and, at times, color-coding dyes. The two main types of acid are: phosphoric acid and aromatic sulfonic acids (benzene-, toluene-). Common solvents are water and/or methanol. The catalyst is always placed on the sand first, followed by the binder.

PRECAUTIONARY MEASURES/CONTROLS AND PERSONAL PROTECTION

The following are recommendations to minimize the potential for, and exposure to, hazards associated with furan no-bake systems. Recommendations for the mixing, molding, and coremaking areas are presented first, followed by pouring, cooling and shakeout.

Mixing, Molding and Coremaking

Potential hazards involve air contaminants and skin and eye contact. The air contaminants of industrial hygiene concern and their OSHA permissible exposure limits (PEL) are:

Furfuryl alcohol (50 ppm);
Formaldehyde (for furan binders that are formulated with formaldehyde) (3 ppm);
Toluene (from free toluene in the toluenesulfonic acid catalyst)(200 ppm);
Benzene (may arise from the use of benzene sulfonic acid catalyst)(10 ppm).

1. Do not directly mix binder and catalyst. The reaction is violent unless sand is present to absorb a significant amount of released heat.

2. Use protective equipment when handling the binders, catalysts, and mixed sand (gloves, aprons, long-sleeved shirts, safety glasses). In general, furan binders are slightly irritating to the skin, slightly toxic dermally, and severely irritating to eyes. The catalysts are potentially more hazardous to skin and eyes than the binders. The mixed sand is a much less potential hazard than the binders and catalysts since it is about 98% sand, and sand is regarded as inert.

   A series of Ames tests on furfuryl alcohol and representative furan binders indicated that they were not mutagenic or carcinogenic (2).

3. Use high purity rounded silica sands (AFS GFN 55±10;3 or 4 screen). Rounded sands generally require much lower levels of binder and catalyst than subangular or angular sands; lowest levels of binder and catalyst are thus attained.

4. Use sand at 21-32°C (70-90°F)(new and/or reclaimed). Higher sand temperatures result in larger amounts of volatiles being emitted and lower levels of catalyst being used. Lower sand temperatures have an opposite effect: lower amounts of volatiles and higher levels of catalyst. Each foundry arrives at its own optimum

compromise with respect to sand temperature, depending on ventilation controls and process requirements.

5. Use functional exhaust fans on the mixer and in the work areas, with air circulation away from the employees' stations. Fans will control gases (from the binder system) and silica dust (from the sand or mixer). The use of continuous-type sand mixers minimizes employee contact with binder and catalyst.

6. Use binders that are free or contain less than 0.5% free formaldehyde; use catalysts that do not contain volatile solvents. Furfuryl alcohol is a high boiling liquid with a low vapor pressure; when catalyzed it polymerizes to a non-volatile solid. Furan binders are reactive and do not contain volatile or non-reactive solvents.

Pouring, Cooling and Shakeout

Organic binders are composed primarily of carbon, hydrogen, and oxygen, which, under optimum conditions of combustion, should decompose into carbon dioxide and water. However, these optimum conditions are not present in a foundry mold filled with molten metal in the presence of such things as core washes, adhesives, and exothermics. The following two recommendations are considered important in improving the quality of the air at pouring:

1. Use the lowest possible levels of binder and catalyst. Low percentages of binder result in decreased amounts of decomposition products on pouring and lower levels of potential volatile material in the reclaimed sand. In addition to improved air quality at pouring, low binder consumption provides the added benefit of greater economy.

2. Provide adequate ventilation. Air quality at the pouring station can be substantially improved by any ventilation arrangement that will effectively prevent the decomposition gases from entering the breathing zone of the personnel in the pouring area.

Test Data for Decomposition Products--
A long series of volatile decomposition tests by various organizations has concluded that the major volatile decomposition product of foundry binder systems that is of any serious concern is carbon monoxide (CO) (4). Binder systems evaluated in these studies included hot box, shell, silicates, all the various no bakes, and also green sand. The other major volatiles, carbon dioxide and water, were not of serious concern environmentally.

Laboratory experiments showed that the type of decomposition products emitted during pouring depends on the specific binder and catalyst used. Furan no-bakes that are nitrogen-free decomposed into carbon dioxide, carbon monoxide, hydrocarbons, and traces of formaldehyde. Binders that contain urea emitted minimal amounts of nitrogen-containing compounds (ammonia, hydrogen cyanide) in addition to the above gases. Sulphur-containing catalysts (sulphonic or sulphuric acids) predictably decomposed into sulphur-containing gases, e.g., sulphur dioxide, and hydrogen sulfide. The fate of phosphoric acid has not been fully documented; ammonium phosphate is believed to be an intermediate with binders containing urea. It is reasonable to assume that phosphoric acid eventually shows up as 'phosphate'.

The amount of volatiles depends on the sand-to-metal ratio and the level of the binder system used: lower sand-to-metal ratios and/or heavier metal sections and higher levels of binder system result in larger quantities of volatiles being evolved.

When the laboratory test concentrations and the toxicities of individual gases are compared to one another, carbon monoxide stands out as a possible problem in poorly ventilated foundries. Many operating variables can affect the type and amount of volatiles, but if the carbon monoxide level is maintained within the acceptable standard (50 ppm, 55 mg/m^3), all other trace gases will most likely be either below the OSHA permissible exposure limits or below the detectable limit (4).

Recently, there has been some publicity regarding benzo(a) pyrene (BAP), a suspected carcinogen that is found in coke oven emissions, char broiled meats, in automobile exhausts, in cigarette smoke, in metal pouring of green sand molds, etc. (5). The question was raised whether BAP could possibly form during the decomposition of a furan no-bake binder. The testing that has been conducted to date indicates that BAP is not a problem with furan no bakes; this confirms the results obtained by an independent research institute that examined, besides furan no bakes, other types of foundry binder systems.

FOUNDRY MEASUREMENTS

Mixing Area

Since October, 1976 under foundry operating conditions, the Quaker Oats Company has made measurements for furfuryl alcohol, formaldehyde, toluene, and benzene vapor levels in about 40 foundries pouring from 5 to over 100 tons of ferrous metal per day; with a strip time of 2-30 minutes; using continuous mixers of 45-363 kg/min (100-800 lb/min); at sand temperatures of 18-55°C (65-130°F); at pouring temperatures of 1290-1620°C (2350-2950°F); using a variety of sands: 100% new, 100% reclaimed, in various mixtures.

All the foundries tested to date have shown levels of less than 50 ppm of furfuryl alcohol; about half of the breathing zone measurements were less than 5 ppm. Formaldehyde levels averaged about 1 ppm for those furan binders formulated with formaldehyde. Toluene and benzene measurements were about 1 ppm.

Independent sampling in European foundries has confirmed our values since all of their results showed less than 50 ppm of furfuryl alcohol (6, 7, 8). This also holds true for OSHA measurements in several U.S. foundries (9, 10).

Pouring Area

In the pouring areas of foundries, carbon monoxide and sulfur dioxide (for systems using sulfonic acids) were found to be the major gases of interest. Furfuryl alcohol levels were generally below 1 ppm.

Generally, breathing zone levels below standards were recorded for carbon monoxide and sulfur dioxide in adequately ventilated pouring areas. The carbon monoxide levels varied, depending on the time and place of measurement. As expected, higher values were obtained immediately following pouring. In those foundries that used a sulfonic catalyst for curing the core or mold, sulfur dioxide levels averaged around 1 ppm (OSHA PEL = 5 ppm).

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NIOSH Project Officer: Dennis O'Brien
Project Manager: Robert C. Scholz

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