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Identification Odor Compounds Emitted During the Heating of Molding Sands

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Abstract

The paper presents the results of analyzes of gases emitted during exposure to high temperature foundry molding sands, where binders are organic resins. As a research tool has been used special gas chromatograph designed to identify odorous compounds including the group of alkanes.

Keywords: Foundry binders, Odor, Molding sand, Core, Thermal decomposition, Gas chromatography

1. Introduction

Currently used in the production of foundry molding and core binders contain ever less dangerous to humans and the environment of organic compounds. As a result, decrease the amount of harmful or toxic compounds emitted into the environment during the production of castings.

It should be noted that, in the emitted gases that are released by the action of high temperature on the weight of the molding materials, and also may include substances that do not occur in the composition of the starting binder. Such compounds may also be issued at lower temperatures, for example during cooling casting or stamping, becoming a source of gaseous effluents and foul smells [3].

Greenhouse gas resulting from the thermal decomposition of chemical compounds contained in the casting molds are often the source of foul smells plaguing local residents, and therefore binders based on organic compounds are increasingly being replaced by much less harmful to people and the environment inorganic substances.

Due to their favorable physical and chemical properties are still among the most commonly used organic binders are furan

and phenolic resins. All furan resins comprise the furfuryl alcohol as a monomer or polymer. These may be introduced by other chemical compounds such as urea, formaldehyde, phenol and derivatives thereof, depending on the desired properties of the resin, which results in both of varied composition, although similar in reception odor emitted gases. For the proper mechanical strength of the masses should be made thereto curing agents which are generally sulfonic acids or esters [4].

2. Emissions at ambient temperature

From the published studies [4] it shows that due to the low vapor pressure at ambient temperature during the preparation of moulds and cores with the participation of resins chemosetting emission of toxic compounds and odoriferous, such as phenol, formaldehyde or furfuryl alcohol is low or absent.

3. Emission of the compounds released from molding sand by the action of heat

Pouring casting and core hot metal causes that the organic compounds act as binders, molding materials or coatings are degraded thermally.

The chemical composition of the substance is determined if the emitted gases contain organic and / or inorganic. As analyzes in the process of thermal decomposition commonly used in foundry resins most often they can be released water vapor, CO, CO₂, NH₃, HCN, SO₂, H₂S, PH₃, phenol formaldehyde, benzene, toluene, ethylbenzene, xylene, isocyanates, polycyclic hydrocarbons aromatic (PAHs), dioxins and furans and other [1, 2, 4, 5, 11, 13, 19].

The composition and amount emitted gases depends on the percentage of components organic substances and water, and the temperature. The resulting gases in the largest quantities are: water vapor, carbon monoxide and dioxide, nitrogen oxides, and in much smaller quantities as different organic substances, including fragrances giving them a distinctive scent, often perceived as unpleasant.

Besides the above-mentioned water vapor, carbon oxides and nitrogen depending on the type used for the preparation of the molding and core binders releasing compounds have the characteristic of those resins used in foundry [4, 14]:

Table 1.
Emission of compounds during the decomposition of different binders used sand molds and core [4]

Compound	Emission [g/kg binder]	
	min.	max.
ammonia	0.04	10.931
Hydrogen sulfide	0.009	1.462
nitrogen oxides	0.012	0.372
Sulphur dioxide	0.036	15.107
benzene	0.648	11.209
formaldehyde	0.01	0.257
hydrogen cyanide	0.029	1.184
m-xylene	0.094	2.227
naphthalene	0.005	0.04
o-xylene	0.03	0.729
phenol	0.024	3.904
toluene	0.121	8.825
aromatic amines	0.049	1.275

Comprehensive analysis of the composition of the gases emitted during the process of casting show the presence of approx. 330 different compounds [6, 20], part of which has a peculiar odor.

Listed below are examples of the results of analysis of gases evolved during a casting molds produced using various organic binders [2]. They have been identified in these compounds having the prescribed exposure limit values (MAC) for the job.

Table 2.

The results analysis of gases released during casting molds [2]

Com- pound	MAC [mg/m ³]	Mouldin g with pheno lic resin [mg/m ³]	Mould ing with a phenol formaldehy de resin [mg/m ³]	Mouldin g with resin Nova nol 165 [mg/m ³]
ethane + ethene	-	< 0.01	< 0.01	< 0.01
propane + propene	1800–2000	< 0.01	< 0.01	< 0.01
i-butane	50	0.01	< 0.01	0.00
n-butane	1900	0.00	0.00	0.15
i-pentane	100	0.01	0.01	0.01
n-pentane	3000	0.09	0.09	0.03
2,2 di- metylo - butane	400	0.00	0.00	0.00
2,metylope ntane	400	0.00	0.00	0.35
3-metylo- pentane	400	0.00	0.00	0.00
n-hexan	72	0.00	0.00	0.00
CO ₂	9000	18.30	24.03	7.53
nitrogen+ oxygen [ppm]	-	57.66	64.96	80.28
methane	-	0.27	4.71	0.08
Carbon monoxide	23	30.43	18.43	16.39
Hydro gen	-	1.12	0.35	0.39

For the foregoing analysis, it shows that above organic compounds present in the gases emitted in very low concentrations by several orders of magnitude lower than their MAC value. Their occurrence in these amounts does not pose a health hazard, but some of them can give them a smell, especially in combination with other odorous compounds.

The results of analyzes of the compounds from the group of BTEX in the flue pyrolysis released from molding sand by the action of heat indicate that these are issued in the largest quantities, benzene and toluene, ethylbenzene and xylenes are present in much smaller quantities [7, 11].

4. Research

In order to identify organic flavor compounds which are released from the molding material during operation on the high temperature gas samples. Olfactometric qualitative analysis are released gases were conducted by gas chromatography [15] using a portable equipment zNose® 4300 dedicated to the detection of flavor compounds from the group of alkanes (ie. "e-nose") [8, 16, 17].

For the analysis of odoriferous compounds of degradation products selected molding sands prepared with the participation of seven resins: Supereko (Prec-Odlew sp. z o.o), Kaltharz X850

(Huettenes Albertus Chemische Werke), Kaltharz XA 20 (Huettenes Albertus Chemische Werke), Furanol FR-75 (Prec-Odlew sp. z o.o), Novanol 165 (ASK Chemicals), Modofen (Ciech S.A.) and FRN 100 (SQ Polska) commonly used in foundries.

4.1. Measuring station

For the examination of aromatic compounds contained in gases emitted from the above molding material as a result of thermal decomposition furnace was used to test levels of an volume of gases arising during heating molding. This is a quartz tube furnace with an electrically heated in a controlled manner with regard to 1100 ° C, with the stabilization of the target temperature.

Samples of the rate of 1 kg were prepared in a laboratory in accordance with commonly used recipes. For heated to a 1000°C furnace tube was introduced 1 g fresh molding sand containing the tested binders, and passed odorless and non-reactive carbon dioxide at low pressure in order to push the separated gases into a glass flask, where it was collected for testing. Pyrolysis binders took place in conditions of limited supply of air, as is the case in casting molds.

Gas collected in the flasks were analyzed by gas chromatograph specialized zNose® 4300 intended for the selective analysis of fragrance.

4.2. Olfactometric analysis

To identify compounds emitted in the gassing and core sand mold was used a portable gas chromatograph selective zNose® 4300. This device is for the detection, analysis and identification of more than 700 organic compounds described and their associated scents. These are compounds belonging to the group of alkanes having carbon chain C6-C22 present in concentrations of ppm and ppb contained in a specialized database Chemical Library (Kovate Indices 700)

Since the apparatus identifies only the aroma compounds from the group of alkanes, and therefore gas in the test samples are listed only those compounds occurring in them.

They are summarized below and characterized in terms of odor nuisance and health (if any) compounds in quantities of more than 200 cts, wherein cts is a quantitative measure of chemicals associated with their odors.

Analysis shows that three of the identified compounds are emitted during the thermal decomposition of all the resins tested, three more are common to the four resins, and another one for the other three

Table 3 summarizes the results of the analysis of gases released during thermal decomposition molding involving these binders, for occurring in those aromatic compounds from alkanes.

Present in the analyzed samples of individual compounds belonging to the alkanes are characterized by smells of phenolic-wax-smoky. The smell of resultant, people experience the present state of knowledge it is not possible to predict the results of the

analysis, because it is not fully understood mechanism mixing of fragrances [8].

5. Conclusions

Since the measuring apparatus identifies compounds based on indexes Kovatsca and assigns the compounds of similar index values different odors, so as a result of multiple analyzes of samples and comparisons diagnosed compounds that appearing in the largest quantities (concentrations) are the most likely impact on the subjective perception of smell accident.

The samples analyzed gases in relatively large quantities were found fifteen aromatic compounds from alkanes wherein identified:

- in seven samples of phenol (smell of phenol); 2-furfuryl-entantioat (the smell of burning sulfur); benzoic acid (smell of formaldehyde, urine); cresol (odor of phenol, medical)
- in four samples: skatole (smell of faeces, mothballs), lauryl alcohol (the smell of wax, fat); syringol (odor of phenol, smoke); perhydrofarnezyloacetone (smell of fat).

These compounds are present in the samples at levels significantly higher compared to other compounds in the mixture. To date, they are not precisely known and explained the mechanisms governing the recognition of odors being a mixture of aromatic compounds. It is understood [8, 9] that the feeling of the resultant gas mixture responsible smell are those that have a low threshold of olfactory and those that are present in greatest concentration. However, based on the identified individual odors of the compounds can not uniquely determine the odor mixtures thereof [10].

In many cases, perceived odor of a single compound is dependent on its concentration, for example skatole in high concentrations has a repulsive odor of feces, while low has a pleasant floral scent and is used for perfumery.

Based on its own work and observations in the vast majority of the compounds tested their concentration occurring in the relative amounts of less than 200 cts their smell is imperceptible or very poor, while undoubtedly is related to the size of their olfactory threshold, which for most compounds is uncertain.

Attention is clear that, in the case of compounds which are known thresholds olfactory and certain size MAC detection threshold is much lower (4 times in the case of cresol and 50-fold in the presence of phenol) than the allowable concentration in the environment or working environment.

The gases emitted in the process of thermal decomposition of the organic binders tested include the trace amounts of aromatic compounds suitable for the characteristic odor, which is dominated in all cases phenolic-smoky smells, doped with odor of urine in the case of a resin comprising urea. These organic compounds give the resultant odor of described as unpleasant and oppressive.

It should be emphasized that during the pyrolytic decomposition of molding sands containing organic binders in the largest quantities released water vapor, carbon oxides, nitrogen, and identified organic fragrances in the present quantities do not have harmful effects for health, although some of them are referred to as harmful or dangerous substances. In most these substances, also do not have thresholds olfactory.

The practical use of research results may help to reduce odor nuisance gases that are released during pyrolysis molding binders,

eg. by minimizing or eliminating some of the ingredients used in resins.

Table 3.

Results of the analysis of the gases from the pyrolysis of a variety of foundry binders

Resins	Odor compound	Odor	Odor threshold [mg/m ³]	MAC [mg/m ³]	COMMENTS
KALTHARZ X850	phenol	phenolic	0.156	7.81	Listed fragrances are present in all tested resins, other compounds, specific to particular types of binders is given with them
FURANOL FR75	2-furfurylethanol-tioat	burning			
FRN 100	benzoic acid	formaldehyde			
NOVANOL 165	cresol	phenolic			
SUPEREKO					
KALTHARZ XA20					
KALTHARZ X850	styrene	gasoline	1.38	50	In the sample are a predominant amount of aromatic compounds: benzoic acid, skatole, lauryl alcohol
	skatole	faeces	0.0031		
	lauryl alcohol	wax			
	p-hydroxy ethylbenzene	phenolic	0.4 - 2.6		
	octadecanol	olive			
FURANOL FR75	skatole	faeces	0.0031		In the sample are a predominant amount of aromatic compounds: benzoic acid, lauric alcohol
	lauryl alcohol	wax			
	perhydrofarnazylo-acetone	fat			
	syringol	smoky			
FRN 100	methylpentane	mint			In the sample are a predominant amount of aromatic compounds: benzoic acid, lauric alcohol, syringolu
	styrene	gasoline	1.38	50	
	p-cresol	phenolic			
	lauryl alcohol	wax			
	syringol	smoky			
MODOFEN OD	skatole	faeces	0.0031		In the sample are a predominant amount of aromatic compounds: benzoic acid, lauric alcohol, perhydrofarnazylo-acetone
	lauryl alcohol	wax			
	perhydrofarnazylo-acetone	fat	0.4 - 2.6		
	p-hydroxy ethylbenzene	phenolic			
	syringol	smoky			
NOVANOL 165	p-cresol	phenolic	1.2	5	Very small concentrations of all compounds
SUPEREKO	p-cresol	phenolic	1.2	5	Small concentrations of all compounds
	cedrenol	wood			
KALTHARZ XA20	o-cresol	phenolic			In the sample are a predominant amount of aromatic compounds: furfuryl alcohol, phenylacet-aldehyde, cresol
	furfuryl alcohol	burning		30	
	phenylacetaldehyde	hawthorn			
	p-cresol	phenolic	1.2	5	
	stearyl alcohol	olive			

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