

M. HOLTZER*[#], R. DAŃKO*, S. ŻYMANKOWSKA-KUMON*, M. KUBECKI**, A. BOBROWSKI***ASSESSMENT OF THE HARMFULNESS OF MOULDING SANDS WITH ALKYD RESIN SUBJECTED TO THE HIGH TEMPERATURE INFLUENCE**

Out of moulding sands used in the foundry industry, sands with organic binders deserve a special attention. These binders are based on synthetic resins, which ensure obtaining the proper technological properties and sound castings, however, they negatively influence the environment. These resins in their initial state these resins are not very dangerous for people and for the environment, thus under an influence of high temperatures they generate very harmful products, being the result of their thermal decomposition. Depending on the kind of the applied resin, under an influence of a temperature such compounds as: furfuryl alcohol, formaldehyde, phenol, BTEX group (benzene, toluene, ethylbenzene, xylene), and also polycyclic aromatic hydrocarbons (PAHs) can be formed and released.

The aim of the study was the development of the method, selection of analytical methods and the determination of optimal conditions of formation compounds from the BTEX and PAHs group. Investigations were carried out in the specially designed set up for the thermal decomposition of organic substances in a temperature range: 500 – 1 300°C at the laboratory scale. The object for testing was alkyd resin applied as a binding material for moulding sands. The qualitative and quantitative analyses of compounds were performed by means of the gas chromatography coupled with the mass spectrometry (GC/MS).

Keywords: moulding sand, binding, BTEX, thermal analysis, GC/MS

1. Introduction

A foundry practice belongs to an industry branch of an increased professional risk. During the whole casting production process employees are endangered by hazardous, harmful and uncomfortable factors related, among others, to the emission of hazardous substances. One of the reasons of this emission are binders (e.g. synthetic resins) and hardeners undergoing thermal decompositions at high temperatures. This is related to formation of several organic compounds, more or less harmful. Depending on the kind of resin applied (phenol-formaldehyde, urethane, furfuryl-urea, alkyd) - under an influence of temperatures - such substances as: furfuryl alcohol, formaldehyde, phenol, compounds from the BTEX group (benzene, toluene, ethylbenzene, xylenes) and also polycyclic aromatic hydrocarbons (PAHs), can be formed and released [1-8]. These substances are mainly generated during a mould pouring with liquid metal (e.g. liquid ferrous alloys are of temperatures: 1 350 – 1 550°C) [9-11].

More and more strict regulations, concerning the environment protection as well as the growing social pressure, cause that foundry plants are searching for new, more environment friendly moulding sands and core technologies or modifications of currently used ones, to limit the harmful substances and pungent smells emission during moulding sands preparation, pouring, cooling and castings knocking out. These elements decide significantly on the foundry sector image. Simultaneously it forces the foundry materials producers to

develop such binders, which will meet these requirements. Changes in binding materials for moulding and core sands will concern mainly limiting the negative environment influence, increasing yield and improvements of technological properties [12-16].

Inorganic harmful substances are mainly emitted during melting and casting cleaning processes. Organic dangerous substances constitute up to 96% of all dangerous substances emitted from a typical cast iron foundry. Organic substances are emitted from operations of making moulds and cores, during mixing, when organic binders are used. To this group belong also catalysts e.g. triethylamine, protective coatings on the alcohol base, model separators [17-19]. However, the highest amount of dangerous organic substances is emitted during pouring, cooling and knocking out moulds of bentonite sands, additions of lustrous carbon carriers or moulding sands with organic binders. Under an influence of a liquid metal high temperature, at not sufficient oxygen amount the total decomposition of organic components occurs and as the result several new compounds are formed. Out of substances generated due to high temperatures influencing binding materials used for moulding sands the specially hazardous group constitute PAHs and BTEX. Therefore investigations aimed at in depth learning of conditions of their formation, which should allow - in the future - such control of the foundry process parameters which would minimize the amount of hazardous substances, were undertaken [20, 21].

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2. Methodology of investigations

The subject of investigations were binders based on alkyd resins used for moulding sands, hardened by a hardener based on isocyanates, originated from various producers. Investigations were performed in two stages: laboratory scale investigations and pilot plant scale investigations.

2.1. Laboratory scale investigations

The laboratory stand for the thermal decomposition of organic binders encompassed: resistory furnace of a temperature range up to 1 300°C, tubular reactor and column with an adsorbent [21-23]. When substances from the BTEX group were analysed active carbon was the adsorbent, and when from the PAHs group - XAD-2 resin was the adsorbent. The equipment element responsible for the adsorption of newly formed substances consisted of two columns with the adsorbent: the first (main) and the second (control). In addition, the columns were equipped with two filtration layers: preliminary – quartz wool and the main – MILLIPORE filter (symbol AQFA) of quartz fibres. The reason of such solution was a significant amount of dusts liberated from tested samples during their decomposition, which was causing their excessive deposition on the adsorbent. The sample of the tested resin (marked A), hardener and hardened resin (in proportions recommended by the producer - hardener: resin = 0.25 : 1) of a mass app. 10 mg, was placed in the ceramic boat, which was introduced into the reaction tube heated to the determined temperature: 500, 700, 900, 1 100 and 1 300°C. Before the appropriate measurement and during it, the reactor was flashed with high purity argon (Ar 99.999) with a rate: 3 dm³/h. Such procedure corresponded to the situation, which occurred during the mould pouring with liquid casting alloy in the moulding sand layer directly adjacent to the casting.

2.1.1 Determination of substances from the BTEX and PAHs group

Substances from the BTEX group were extracted from adsorption columns by means of diethyl ether. The current control of the BTEX extraction process was performed by introducing on the column with the adsorbent - before the desorption by diethyl ether - the internal standard: deuterated benzene (C₆D₆). The control standard contained deuterated toluene (C₆D₅CD₃). Diethyl ether extracts obtained for individual samples were analysed by the gas chromatography technique coupled with the mass spectrometry (GC/MS). The identification of substances was carried out by means of the TRACE GC Ultra chromatograph, equipped with the chromatographic column RTX 5MS (ResteK) (30 m long and 0.25 mm internal diameter) and the mass spectrometer: FINNIGAN MAT 95 XP. The mass spectrometer operated within 30-450 amu (atomic mass unit) at the photomultiplier voltage 1.8 kV. Quantitative determination of BTEX formed during the thermal decomposition of the tested samples was performed on the bases of pure substances (benzene, toluene, ethylbenzene and xylenes), for which series of calibration samples were prepared [22].

The extraction of substances from the PAHs group from the adsorption columns was done by means of dichloromethane. The current control of the PAHs extraction process was performed by introducing on the column with adsorbent - before the desorption process by dichloromethane - the internal standard – with five deuterium – labelled PAHs. Extracts obtained for individual samples were analysed by the gas chromatography technique coupled with the mass spectrometry (GC/MS). The identification of substances emitted when the determined temperature was influencing the tested sample was carried out on the bases of chromatograms obtained for standard solutions and retention times determined for individual compounds as well as of the strongest ionic peaks [23]. The identification of 2-methylnaphtalene, PAHs and BTEX was performed on the bases of comparing retention times of these compounds contained in extracts with retention times of compounds contained in the standard mixture.

The mass spectra base of the NIST (*National Institute of Standards and Technology*), being the software element of the mass spectrometer, was used for the identification of the remaining substances. However, this base allows comparing of spectra with the determined probability only and does not allow to confirm fully the presence of the given substance in the analysed solution. Therefore the quantitative analysis was performed for such substances which presence in the samples was confirmed on the bases of the relevant standards.

2.2. Semi-industrial Tests

Investigations of the gases emission in the test foundry plant were performed according to the original method developed in the Faculty of Foundry Engineering, AGH UST [23-25].

A sample of the investigated moulding sand on the matrix of the standard high-silica sand of a roll shape of dimensions ϕ 50 x 50 mm, weight about 150 g, compacted by a moulder's rammer stroke, is poured with liquid cast iron of a temperature of 1 350°C. The liquid metal mass was 9 kg. Gases emitting from the sample - after pouring it with liquid metal were led by means of a steel pipe via the drying system and the capsule with active carbon (during the BTEX measurement) or with polyurethane foam (during the PAHs measurement) into a tightly sealed container with the liquid. The gases pushed out the liquid from this container and the weight of this displaced liquid was measured as a time function. The whole mould (weight 24 kg) was made of green sand. Two layers of active carbon separated from each other were placed in the glass tube. The first layer (A) containing 700 mg of active carbon constituted the main adsorption place, while the second layer (B) containing 200 mg of active carbon was of a control character, providing information on an eventual 'breakthrough' of the first adsorption layer. The active carbon layer with adsorbed organic substances is extracted in carbon disulphide. The analysis was carried out by the gas chromatography method with the application of the flame-ionising detector (FID) [26].

At the determination of compounds from the PAHs group a part of hydrocarbons was condensing on the formed dust particles and together with them was deposited on the filter placed in the capsule before the polyurethane foam. Therefore for determining the total amount of generated PAHs

the polyurethane foam as well as the dust on the filter were analysed. Both, the filter and foam, were extracted by toluene for 16 hours in the Soxhlet apparatus, and then separated from the matrix in hexane. The further operations were the same as in case of samples obtained in the laboratory.

Three binders based on alkyd resin hardened by isocyanate, originated from various producers, marked respectively A, B and C were applied in investigations in the pilot plant scale. The total amount of emitted gases, kinetics of their emission as well as content of individual substances from the BTEX and PAHs group were determined:

- Binder A: loss on ignition – 1.35%, composition: resin - 1 part by mass, hardener – 0.25 part by mass;
- Binder B: loss on ignition - 1.43%, composition: resin – 1.3 part by mass, hardener – 0.3 part by mass;
- Binder C: loss on ignition – 1.12%, composition: resin – 1.3 part by mass, hardener – 0.3 part by mass.

3. Results and discussions

3.1. Investigations in the laboratory scale

The quantitative analyses results of the PAHs generated during the decomposition of alkyd resin (R), hardener (H) and hardened alkyd resin (R + H) in dependence on the decomposition temperature are given in Table 1.

At a temperature of 700°C PAHs of a lower boiling point start forming (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene – boiling point of these compounds is below 400°C). Only benzo(a)pyrene, which was found already at a temperature of 700°C,

had a higher boiling points of (495°C). The remaining PAHs, of higher boiling point (chrysen, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)anthracene), occurred when the decomposition was performed at a temperature of 900°C (their source was practically only the resin), while those of the highest boiling point (500°C and higher) (indeno(1,2,3-c,d), dibenzo(a,h)anthracene, benzo(g,h,i)perylene) emitted only at a temperature of app. 1100°C.

The main source of the PAHs emission was the resin, independently on a thermal decomposition temperature. However, after the resin hardening an amount of the PAHs group components was significantly lower.

This is probably caused by bonding the resin components, (which at high temperatures generated PAHs components) by hardener components (mainly polyisocyanate). These new bonds were still subjected to a thermal decomposition, but did not form such large amounts of PAHs. Moreover, the highest PAHs amounts originated from the resin decomposition were formed at a temperature of 1300°C (37.6 mg/g resin), while those from the hardened resin decomposition at a temperature of 1100°C (14.75 mg/g hardened resin). Large amounts of substances from the PAHs group were formed at a temperature of 1100°C also at the hardener decomposition (11.1 mg/g hardener). In case of the resin an increase of the decomposition temperature caused an increase of the generated PAHs, while in case of the hardener and hardened resin an increase of the PAHs amount occurred up to a temperature of 1100°C, while during a further heating the amount of these substances was decreasing. Naphthalene, acenaphthylene and anthracene were the main PAHs substances emitted from the resin. From the hardener mainly naphthalene and fluorene were emitted, while from the hardened resin: naphthalene, acenaphthylene and fluorene.

TABLE 1
Concentration of polycyclic aromatic hydrocarbons formed during the decomposition of alkyd resin (R), hardener (H) and hardened resin (R+H) in relation to 1 gram of a sample (investigations carried out in the argon atmosphere)

PAHs	700°C			900°C			1100°C			1300°C		
	mg/g											
	R	H	R+H	R	H	R+H	R	H	R+H	R	H	R+H
naphthalene	0.06	0	0.03	5.96	0.2	0.02	6.71	3.79	3.87	6.08	1.4	1.1
acenaphthylene	0.01	0	0	4.87	0	0	4.98	0	2.95	11.84	0	0.77
acenaphthene	0.01	0.04	0.01	0.34	0.02	0	0.23	0.01	0.09	0.12	0.28	0.03
fluorene	0.06	0.19	0.03	1.25	0.43	0	0.87	2.41	1.21	0.49	2.82	0.33
phenanthrene	0.01	0	0.01	1.98	0.03	0.01	2.14	1.21	0.8	3.26	0.64	0.07
anthracene	0.04	0	0	3.64	0.17	0	2.88	1.99	0.97	2.4	0	0.08
fluoranthene	0.02	0	0	0.52	0	0	1.08	0.53	0.83	2.47	0.76	0.25
pyrene	0	0	0	0.68	0	0	1.31	0.21	0.68	2.99	0.64	0.17
benz(a)anthracene	0	0	0	0.64	0	0	0.57	0.64	0.96	1.22	0.21	0.09
chrysen	0	0	0	0.36	0	0	0.51	0.18	0.42	0.75	0.05	0
benzo(b)fluoranthene	0	0	0	0.31	0	0	0.71	0.06	0.4	1.2	0	0
benzo(k)fluoranthene	0	0	0	0.25	0	0	0.54	0.1	0.36	0.81	0	0
benzo(a)pyrene	0.06	0	0	0.12	0	0	1.24	0	1.03	2.1	0	0
indeno(1,2,3-cd)pyrene	0	0	0	0	0	0	0.33	0	0.15	1	0	0
dibenzo(ah)anthracene	0	0	0	0.07	0	0	0.08	0	0.03	0.09	0	0
benzo(ghi)perylene	0	0	0	0	0	0	0.22	0	0.03	0.74	0	0
TOTAL	0.3 ± 0.06	0.2 ± 0.04	0.1 ± 0.02	21 ± 4.2	0.8 ± 0.16	0.03 ± 0.06	24.4 ± 4.88	11.1 ± 2.22	14.75 ± 2.95	37.6 ± 7.52	6.8 ± 1.36	2.9 ± 0.58

TABLE 2

BTEX content in gases emitted during the thermal decomposition - under laboratory conditions - of alkyd resin (R), hardener (H) and hardened resin (R + H)). Results in mg/1 g of the binder A tested sample. Tests performed in the argon atmosphere („-“ means a result below 1 ppm.)

Substances	Temperature														
	500°C			700°C			900°C			1100°C			1300°C		
	R	H	R+H	R	H	R+H	R	H	R+H	R	H	R+H	R	H	R+H
Benzene	1.2	0.1	0.6	4.1	2.7	4.3	105.6	7.2	32.5	91.8	44.6	63.2	5.9	32.2	24.3
Toluene	0.8	0.9	0.6	1	5.7	2.8	21.7	9.1	12.9	0.7	1.2	2.5	-	0.2	0.4
Ethylbenzene	2.3	-	0.1	2.1	-	0.1	0.4	-	0.4	0.2	-	0.1	0.2	-	0.1
o-xylene	0.1	-	-	0.1	-	-	0.2	-	0.1	-	-	-	-	-	-
m, p-xylene	5.5	0.	0.1	5.7	1	0.4	2.3	1.2	4.3	0.7	0.8	0.8	0.7	0.7	0.4
o, m, p-xylene	5.6	0.3	0.1	5.8	1	0.4	2.5	1.2	4.4	0.7	0.8	0.8	0.7	0.7	0.4
TOTAL	15.5	1.6	1.5	17.9	10.4	8.0	132.7	18.7	54.6	94.1	47.4	67.4	7.5	33.8	25.6
	±	±	±	±	±	±	±	±	±	±	±	±	±	±	±
	3.1	0.32	0.30	3.58	2.08	0.16	26.54	3.74	10.92	18.82	9.48	13.48	1.5	6.76	5.12

The results of quantitative analyses of substances from the BTEX group formed during the alkyd resin (R), hardener (H) and hardened resin (R + H) decomposition, in dependence of the decomposition temperature, are given in Table 2.

At temperatures 500 – 700°C xylene, originated from the resin, was mainly emitted. At a temperature of 700°C comparable amounts of benzene (from a resin) and toluene (from a hardener) were emitted. Only at 900°C a violent emission of benzene and toluene from the resin occurred, which was also seen at the hardened resin decomposition.

The BTEX emission from the resin is at the maximum at this temperature. A further increase of the decomposition temperature to 1 300°C caused a decrease of the BTEX emission from the resin. In case of the hardener and hardened resin the maximum of the BTEX group compounds emission occurred at 1 100°C and also here benzene was the main component of gases. Concentration of toluene, in case of all tested samples achieves maximum at a temperature of 900°C and the main source of its emission is also the resin. Ethylbenzene is emitted mainly from the resin at a temperature of 500°C, but its amounts were one order of magnitude smaller than of toluene. It can be assumed that the limiting temperature, at which the concentration of substances from the BTEX group achieves maximum, was 900°C, except for benzene generated from the thermal decomposition of the hardener, which maximum concentration was at 1 100° C.

3.2. Investigations in a pilot plant scale

Three alkyd binders were investigated in a pilot plant scale. In two of them (marked A and B) the same polyisocyanate hardener was used, while in the third one (marked C) another hardener - however also polyisocyanate - was applied. The diagram showing the amount of the generated gases in time is presented in Fig. 1, while the kinetics of their emission in Fig. 2.

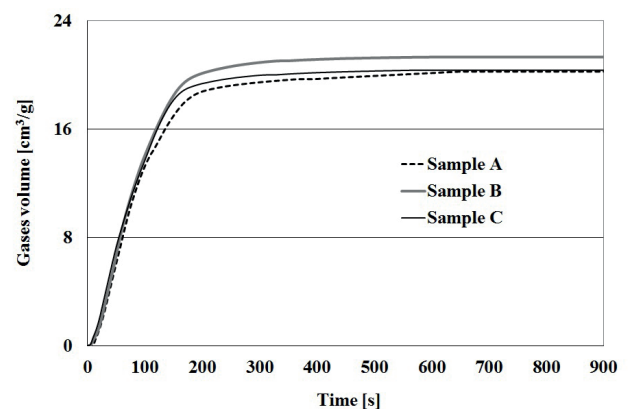


Fig. 1. Volume of gases emitted from moulding sands

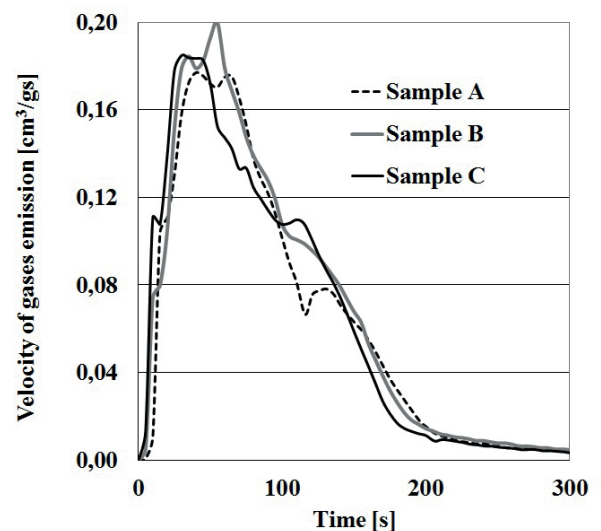


Fig. 2. Emission rate of gases from moulding sands

3.2.1 Determination of the BTEX content

Quantitative data concerning substances emitted from the BTEX group, in relation to 1 kg of a moulding sand, are listed in Table 3.

The moulding sand with resin C was characterized by the largest volume of emitted gases (2.0 dm³/kg), by approximately 25% larger than moulding sand with resin A and B (about 15 dm³/kg moulding sand). Resin C has the highest maximum rate of emission. The main component generated from the BTEX group - in case of all moulding sands - was benzene.

The highest amount of benzene (600 mg/kg moulding sand) was generated by the moulding sand with resin C.

3.2.2 Determination of the PAHs group substances

The total concentration results of all 16 substances from the PAHs group, emitted from the investigated binders are given in Table 4. The highest emission of the PAHs substances indicated the moulding sand with resin A (total amount of PAHs was above 3000 µg/kg moulding sand), while the lowest the moulding sand with resin C (total amount of PAHs was above 300 µg/kg moulding sands). The majority of these substances was adsorbed on the polyurethane foam.

The main substances from the PAHs group emitted from investigated moulding sands were: naphthalene, fluorene, phenanthrene, anthracene and fluoranthene (for the sand with resin A), naphthalene, acenaphthylene, anthracene, fluoranthene and pyrene (for the sand with resin B) and fluorene,

phenanthrene, anthracene and fluoranthene (for the sand with resin C). Such substances as: phenanthrene, anthracene, fluoranthene and pyrene condensed mainly on dusts which was deposited on the filter, while naphthalene and acenaphthylene were nearly totally adsorbed on the polyurethane foam.

4. Conclusions

On the bases of investigations performed in the laboratory and pilot plant scale concerning thermal decompositions of binders (alkyd resins) used in moulding sands, the following statements can be formulated.

- Kinds and amounts of the formed substances from the PAHs group depend significantly on a temperature. At temperatures close to 700°C PAHs of a lower boiling point start forming, while at 900 and 1100°C compounds of a higher boiling point (e.g. chrysene, indene(1,2,3), c,d pyrene, dibenzo(a,h)anthracene). The main source of these compounds are alkyd resins. The hardened resin emits less PAHs than not hardened one. Therefore, from the environment protection point of view it is important to make hardener additions sufficient for complete hardening of the resin.
- In the case of the hardener and hardened resin the maximum emission of compounds from the BTEX group occurs at a temperature of 1100°C, and the main component of gases is benzene. The concentration of toluene, in all tested samples, achieves maximum at 900°C and in this case also the resin is the main source. It can be assumed

TABLE 3

Results of gas analyses from the BTEX group generated in tests in a pilot plant scale

Sample	Gases Volume, dm ³ /kg moulding sand	Gases emission, mg/kg moulding sand				Maximum rate of emission, dV/dt cm ³ /g·s
		Benzene	Toluene	Ethylbenzene	Xylenes	
A	17.61	448.548	19.712	0.405	23.417	0.177
B	15.799	442.697	12.462	1.37	6.410	0.184
C	20.367	605.91	29.45	2.75	13.69	0.199

TABLE 4

Analytical results of the total PAHs content, emitted from moulding sands made with fractions of individual binders (in relation to 1 kg of a moulding sand)

Sample	Filter	Foam	TOTAL
	µg/kg moulding sand		
A	376,68 ± 76,61	2873,01 ± 574,6	3249,69 ± 651,21
B	449,86 ± 87,29	637,86 ± 127,57	1087,72 ± 214,86
C	138,27 ± 27,65	193,58 ± 38,72	331,85 ± 66,37

that the limiting temperature, at which the concentration of the BTEX substances emitted from the hardened resin achieves maximum, is a temperature of 900°C.

- In investigations performed in a pilot plant scale significant differences in the amounts of the PAHs group compounds emitted from individual moulding sands were found. The highest emission indicated the moulding sand with resin A and the smallest the moulding sand with resin C (10-times lower emission).
- The main from the PAHs group emitted from the tested sands were: naphthalene, fluorene, phenanthrene, anthracene and fluoranthene (for the sand with resin A), naphthalene, acenaphthylene, anthracene, fluoranthene and pyrene (for the sand with resin B) and fluorene, phenanthrene, anthracene and fluoranthene (for the sand with resin C). Such as: phenanthrene, anthracene, fluoranthene and pyrene condensed mainly on dusts which were depositing on the filter, while naphthalene and acenaphthylene were nearly totally adsorbed on the polyurethane foam.
- Diversification in between tested sands was also seen within the emission of compounds from the BTEX group, however not so large as for PAHs. The main component in case of all sands was benzene. Its highest amount was generated by the sand with resin C (approximately 1/3 more than by the sands with resins A and B).
- The sand with resin C was characterised by the largest volume of emitted gases, by approximately 25% larger than the sand with resin B.

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