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Research of Emission of Commercial Binders Used in ALPHASET Technology - Estimated Quantitative Analysis

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Abstract

The results of investigations of three commercial binders applied in the Alphaset technology marked as: Sample E , Sample T and Sample S are presented in the hereby paper. These samples were subjected to the pyrolysis process at a temperature of 900°C (inert atmosphere, He 99.9999). The gas chromatograph coupled with the mass spectrometer and pyrolizer (Py-GC/MS) were used in the study.
The identification of gases emitted during the thermal decomposition was performed on the basis of the mass spectral library. The obtained results indicate a certain diversification of emitted gases. Among the pyrolysis products the following harmful substances were identified: furfuryl alcohol, formaldehyde, phenol and also substances from the BTEX (benzene, toluene and ethylobezneze and xylenes) PAHs (Polycyclic Aromatic Hydrocarbons) and VOC groups (Volatile Organic Compounds). Therefore, from the environment protection point of view performing systematic investigations concerning the harmfulness of binders applied in the moulding and core sands technology, is essential.

Keywords: Environment protection, Foundry engineering, ALPHASET technology, Py-GC/MS, BTEX emission

1. Introduction

The foundry industry indicates lately a growing tendency in amounts of castings produced in Poland and in the world. The world production of castings equaled more than 104 million tones, in the year 2015. The participation of Poland constituted approximately 1% (1 062 000 ton) [1]. A production increase is usually increasing the environment hazard and worsening work conditions. To prevent these problems new raw materials are looked for, new technologies are developed and the actually used ones are modified. Within the foundry engineering field, which constitutes significant hazards for the environment and for employees, intensive efforts are also undertaken. The main hazards should be mentioned here: contact with hot metals, noises and vibrations, crystalline silica, radiation, dusts of metals and their oxides, chemical substances influencing the breathing system and skin. The exposition to chemical substances is specially high in case of moulding and core sands. Therefore within this scope of the foundry engineering intensive works on limiting the negative influence on the environment - especially the emission of hazardous air pollutants (HAPs) - are carried out. Emissions of these compounds originates mainly from the pyrolysis of organic substances, e.g. carbonaceous additives, organic binders, which occurs at the mould pouring with liquid metal, during its cooling and at castings knocking out. Investigations of harmfulness of materials applied in the casting production constitute the important element in selecting technologies and raw materials of the lowest possible hazardous influence on the environment and on employees. Investigations concern, among others, additives substituting coal dusts, developments of resins of a small content of furfuryl alcohol [2], developments of hardeners of a reduced sulphur content (or even sulphurless), substituting currently used solvents (characterised by a significant PAHs emission) by biodiesel based solvents not containing naphtalene (in the polyuretane moulding sands technology) [3], and limiting emissions from moulding sands produced in the ALPHASET technology [4]. Moulding sands with binders based on hydrated sodium silicate hardened by physical factors constitute a significant competition for the currently applied technologies, especially the ones with chemically hardened binders. It is important to assure that these solutions, more beneficial for the environment, will not cause worsening of the technological properties of moulding sands. As it was shown by the current investigations [5-7] moulding sands produced in the ALPHASET technology, based on phenol-formaldehyde resol type resins, are characterised by significantly lower harmfulness than furan resin based moulding sands. Phenol-formaldehyde resins applied in the ALPHASET technology do not contain nitrogen and sulphur. Due to that, this technology can be used for producing steel castings and spheroidal castings. It is also essential that the ALPHASET technology can be applied for producing thin-walled castings as well as high-dimensional castings of complicated shapes. [8]. In practice, every company producing foundry materials offers binders for the moulding sands, ALPHASET type. The Huttenes – Albertus Company offers Sinotherm 8255 resin cured by the J 120 activator, the Prec-Odlew Company offers Estrofen resin cured by PR series catalysts, ASK Chemicals Company produces Avenol NB 700 resin and catalyst 4040, while the Hexion UK Limited Company produces Momentive TPA 70 resin and ACE 1035 catalyst.

The preliminary results, regardless of a very similar chemical composition of the mentioned above binders for the ALPHASET technology, indicated certain differences in the composition and concentration of gases emitted within the given temperature ranges. This became the impulse for more accurate investigations - concerning the negative influence on the environment - of the commercial binders offered in the domestic market.

The results of investigations of three commercial binders, applied in the ALPHASET technology, marked as: Sample E, Sample T and Sample S, subjected to pyrolises at a temperature of 900°C, in the inert atmosphere (He 99.9999), are presented in the hereby paper.

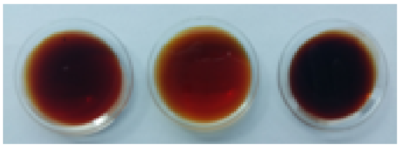
These investigations constitute the part of the research concerning the negative influence of the casting production process on the environment and work conditions, which is realised in the Faculty of Foundry Engineering for many years [9-11].

2. Materials used for investigations

Three kinds of binders (originated from various producers) applied in the ALPHASET technology, marked as:

- Sample E,
- Sample T,
- Sample S

were subjected to tests.



sample E, sample T, sample S

Fig. 1. Samples of the investigated, cured resins

Samples for tests (Fig.1) were prepared by mixing resins with hardeners in proportions recommended by individual producers. Then, after 24 hours, the cured resin was ground into a powder, which was dried for 2 hours at a temperature: 40-50^{o}C.

Binders applied in this technology consist of alkaline phenol-formaldehyde resin, resol type (pH = 14), soluble in water with addition of KOH/NaOH and of hardener/catalyst in a form of a mixture of water soluble esters [12,13].

The hardening reaction is as follows:

alkaline phenol resin + ester hardener (catalyst) + alcohol = polymerised phenol resin + sodium salt (potassium)

3. Methodology of investigations

In the studies, the following instrumentation was used: the pyrolizer (Py) Pyroprobe 500 by CDS Analytical Inc., the gas chromatograph (GC) by Thermo Scientific with a 30 m chromatographic column, 0.25 mm in diameter, type RTX 5M (Restek), coupled with the mass spectrometer (MS) Focus ISQ by Thermo Scientific. The gas products were identified based on the mass spectral library NIST MS Search 2.0 Libera [14].

Tables 1 show the detailed parameters of the study: the pyrolizer (Py), the gas chromatograph (GC) and the mass spectrometer (MS) .

Table 1.
List of basic parameters of measurements

Pyrolysis parameters	
Pyrolysis temperature	900°C,
Pyrolysis time (flash)	< 1 s
Type of applied atmosphere	Helium (He 99.99999)
Type of sample	solid sample: 1 mg
Type of applied probe	Platinum spiral probe

Table 1. Continued

GC parameters	
Column type	Rxi-5MS (Restek)
Column length	30 m
Column diameter	0.25 mm
Gas flow	30 ml/min
Column temperature program	40°C (5 min), 5°C/min to 200°C, 2°C/min to 250°C, 10°C/min to 300°C
Carrier gas	He (99.9999)

MS parameters	
Transfer line temperature	250°C
Ion source temperature	250°C
Electron energy	EI, 70 eV
Emission current	50 µA
Scope of analyzed masses	30–600 amu

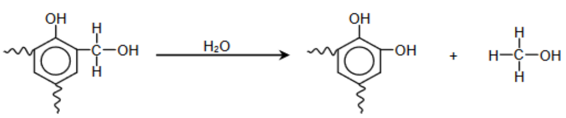
4. Investigation results and their discussion

Substances identified in the emitted gases (together with their retention times) from 3 samples of cured resins applied in the ALPHASET technology, are listed in Table 2. In addition - for easier identification - numbers of CAS (Chemical Abstract Service), molecular weights, are given in this Table. Surface areas of individual peaks were determined. On the bases of the surface area of the given peak and the molecular weight of the corresponding substance the approximate quantitative analysis of the gases emitted in the pyrolysis process, was performed. The comparison of three commercial binders, applied in the ALPHASET technology, produced by various European producers, indicated certain differences in the composition of gases emitted in the pyrolysis process performed at a temperature of 900°C. Substances containing nitrogen (propano-2-amine and 1-methoxy-2-propylamine) were found in gases emitted from Sample E and S. On the other hand, in gases emitted by Sample T methyl alcohol was found. The presence of nitrogen is probably a result of adding urea to phenol-formaldehyde resin for its stabilization, which degradated at 200-400°C, and releasing ammonia [15,16].

$$H_2N\text{-}CO\text{-}NH_2 + \text{heat} \rightarrow NH_4NCO \rightarrow NH_3 + HNCO$$

R.S. Dungan [14] states that ethylamine was found in pyrolysis products of phenol-formaldehyde resin. Amine-based compounds are common catalysts in phenolic resin systems.

The presence of methanol in the resin solution could be due to earlier reactions involving hydrolysis of unreacted methoxy groups (CH_3 O-) within the polymer adduct .



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or simply by hydrolysis of free formaldehyde with the production of CO_2 :

$$3\ H_2C{=}O + H_2O \longrightarrow 2\ H_3COH + O{=}C{=}O$$

The presence of such compounds as: acetaldehyde (peak 5), methyl acetate (peak 7) and acetone (peak 6) is the result of the decomposition of esters applied as hardeners in this technology, among others: dioctan of ethylene glycol, dioctan of butylene glycol, trioctan of glycerol and propylene carbonate (from which acetone originates) [18].

The next large group of substances emitted at retention times longer than 4 minutes are benzene and its methyl and ethyl derivatives. Moreover, as long as benzene occurs in all samples, its derivatives are diversified in individual binders.

At the retention time longer than 17 minutes phenol is evolving (peak 16) from each sample, too. However, it constitutes a diversified fraction in the whole volume of gases emitted from various binders, as its methyl- dimethyl- and trimethyl- derivatives and ethyl- derivatives. Small fractions of 1-benzofuran and 7-methylbenzofuran are present in Sample E. Methyl derivatives of phenol constitute large fractions - even to 10% - in the whole emission of gases (the highest in binder E).

Starting from the retention time of 19 minutes components of the mixture of esters - applied as hardeners - are emitting (peaks: 19, 29, 33 and 34). Their fraction in the whole emission is very large, from 50 to 80%. The highest fraction constitutes glycerol 1,2-diacetate, which is present in all binders. Dimethyl glutarate (peak 29) is present (above 21%) only in gases emitted from binder S.

Chromatograms obtained for individual samples of cured resins are presented in Figures 2 - 4.

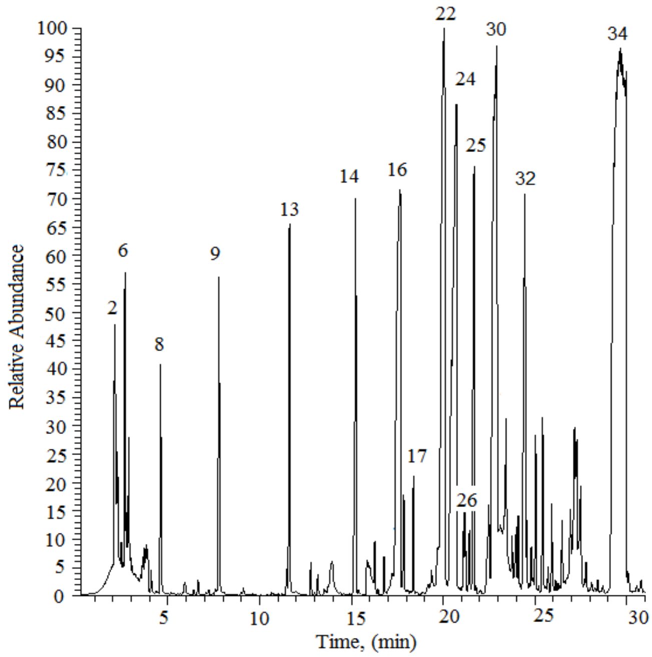

Fig. 2. Chromatogram obtained for Sample E at a temperature of 900 °C

Table 2.
Overall list of substances identified in gases emitted from commercial cured resins for the ALPHASET technology subjected to pyrolysis at 900°C (inert atmosphere); RT - retention time (min.)

Peak No.	CAS No.	Compound name	MW	Sample E 900 °C		Sample T 900 °C		Sample S 900 °C	
				RT [min]	Fraction [%]	RT [min]	Fraction [%]	RT [min]	Fraction [%]
1.	124-38-9	Carbon Dioxide /CO_2	44			2.11	0.88		
2.	75-31-0	Propano-2-amine C_3H_9N	59	2.12	1.16				
3.	37143-54-7	1-methoxy-2-propylamine /$C_4H_{11}NO$	89					2.15	1.7
4.	67-56-1	Methylalcohol /CH_4O	32			2.21	0.34		
5.	75-07-0	Acetaldehyde / C_2H_4O	44					2.30	0.19
6.	67-64-1	Acetone / C_3H_6O	58	2.66	0.65			2.72	0.24
7.	79-20-9	Methyl acetate / $C_3H_6O_2$	74			2.79	0.7		
8.	71-43-2	Benzene / C_6H_6	78	4.61	0.76	4.60	0.43	4.62	0.33
9.	108-88-3	Methylbenzene / Toluene C_7H_8	92	7.78	1.46	7.77	1.14	7.76	0.77
10.	100-41-4	Ethylbenzene / C_8H_{10}	106					11.55	1.32
11.	108-38-3	1,3-dimethylbenzene / m-Xylene / C_8H_{10}	106			11.64	2.88		
12.	100-66-3	Anisole / C_7H_8O	108			14.86	0.53		
13.	95-47-6	1,2-dimethylbenzene / o-Xylene / C_8H_{10}	106	11.63	1.92				
14.	95-63-6	1,2,4-trimethylbenzene,C_9H_{12}	120	15.24	2.54			15.11	1.87
15.	620-14-4	1-ethyl-3-methylbenzene / C_9H_{12}	120			15.25	4.28		
16.	108-95-2	Hydroxybenzene /Phenol C_6H_6O	94	17.63	6.12	17.51	1.07	17.77	2.58
17.	271-89-6	1-benzofuran / C_8H_6O	118	17.83	0.44				
18.	1758-88-9	2-ethyl-1,4-dimethylbenzene / $C_{10}H_{14}$	134			18.38	1.44		
19.	123-25-1	Diethyl succinate / / diethyl ester / $C_8H_{14}O_4$	174					19.63	1.0
20.	108-39-4	m-Cresol/C_7H_8O	108					20.13	3.7
21.	576-26-1	2,6-Dimethylphenol / $C_8H_{10}O$	122					21.69	1.9
22.	95-48-7	2-methylphenol / C_7H_8O	108	20.73	8.67	19.80	7.11		
23.	93-51-6	Creosol / $C_8H_{10}O_2$	138			20.55	0.8		
24.	106-44-5	4-methylphenol / C_7H_8O	108	20.49	9.17				
25.	17059-52-8	7-methylbenzofuran / C_9H_8O	132	21.13	0.90				
26.	95-87-4	2,5-dimethylphenol / $C_8H_{10}O$	122	21.69	2.77	21.62	2.90		
27.	90-00-6	2-Ethylphenol / $C_8H_{10}O$	122			22.80	9.22		
28.	2416-94-6	2,3,6-Trimethylphenol / $C_9H_{12}O$	122			24.42	4.46	24.43	0.87
29.	1119-40-0	Dimethyl glutarate / dimethyl ester / $C_7H_{12}O_4$	160					22.90	21.00
30.	105-67-9	2,4-dimethylphenol / $C_8H_{10}O$	122	22.92	11.10				
31.	123-07-9	4-ethylphenol / $C_8H_{10}O$	122	23.43	1.01				
32.	527-60-6	2,4,6-trimethylphenol / $C_9H_{12}O$	136	24.47	4.53				
33.	627-93-0	Dimethyl adipate / dimethyl ester / $C_8H_{14}O_4$	174			25.94	4.74	26.09	31.25
34.	102-62-5	Glycerol 1,2-diacetate / $C_7H_{12}O_5$	176	29.78	46.71	29.67	57.31	29.49	31.16

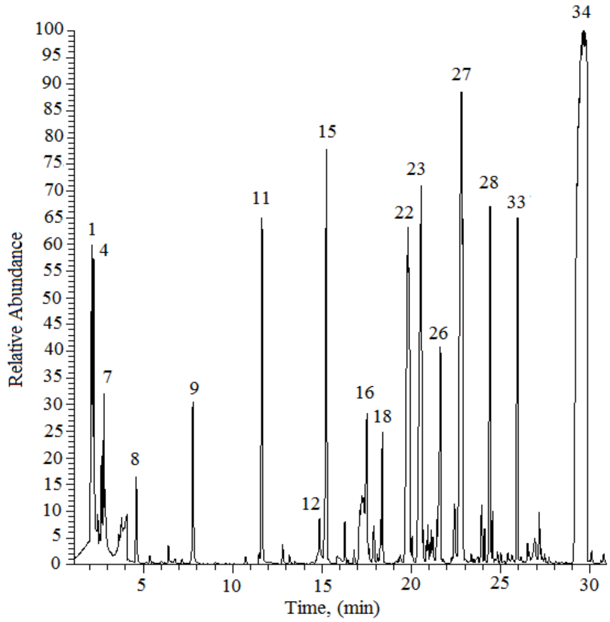

Fig. 3. Chromatogram obtained for Sample T at a temperature of 900 °C

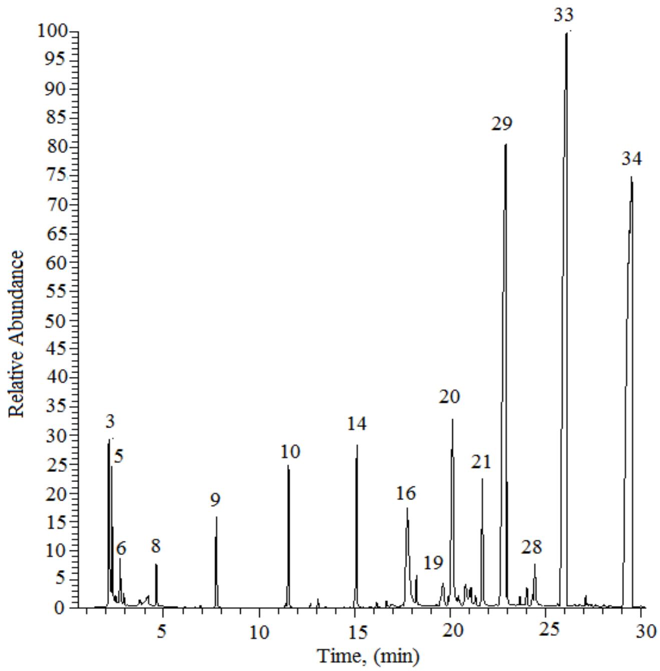

Fig. 4. Chromatogram obtained for Sample S at a temperature of 900 °C

5. Conclusions

The written below conclusions are obtained on the basis of the pyrolysis results (performed in the inert atmosphere) of three commercial cured resins (applied in the ALPHASET technology), originated from various producers.

1. Components of hardener/catalyst which were not utilised in the resin hardening process constituted the significant fraction (even to 50%) of the emitted gases. In addition, decomposition products of some components of hardeners were also occurring (e.g. acetone). There could be two reasons of such situation: either too much of the hardener amount - in relation to the resin amount - was used, or the resin hardening process was not finished.
2. Substances containing nitrogen were found in the emitted gases, which indicates that probably the stabiliser, e.g. urea or amine were added to phenol-formaldehyde resin.
3. Main substances which are emitted during pyrolysis are benzene and its methyl- and ethyl- derivatives (at retention times exceeding 4 minutes) and phenol and its methyl- and ethyl- derivatives (at retention times being more than 17 minutes).
4. On the basis of the analysis of gases emitted in the pyrolysis process of binders - originated from three producers - it occurs that the main composition of these binders was very similar, however resin stabilising additions were different and the hardener compositions (mixture of various esters) were also different.
5. However, it should be taken into consideration that investigations performed in the inert atmosphere, are not fully resembling conditions occurring in the mould during the casting production. Quite often these conditions are significantly different. It is well known, that in the reducing or oxidising atmosphere substances different from the ones formed in the inert atmosphere will be found.

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