THE IDENTIFICATION OF PYROLYSIS PRODUCTS OF THE ALPHASET BINDER WITH GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Pyrolysis-gas chromatography-mass spectrometry (PyGC/MS) was used to identify the major organic products created by pyrolysis of the ALPHASET binder components: hardener/catalyst, resin and cured resin. During the casting process, the cores and moulds are subjected to intense heat from the molten metal. As a result the organic components undergo thermal decomposition and produce a number of complex organic compounds. In this study, the organics were tentatively identified by GC/MS after pyrolysis of the components at 700, 900 and 1100 $^{\circ}$C.

Key words: foundry sand, chromatography/mass spectrometry, binder, alkaline phenolic resin, ALPHASET technology

INTRODUCTION

The annual world production of 100 million tonnes of castings is a powerful factor of economic development the world. At the same time requirements for manufactured castings grow. Castings are becoming more complex, and the desire to reduce their weight causes the walls of castings to get thinner. They therefore require better technologies for producing molds and cores, and the introduction of new alloys to meet these requirements. Casting processes generate a number of different compounds, often harmful, particularly when the binders based on synthetic resins are used. Research has shown that in the gases emitted from the foundry, there are over 40 compounds present on the HAP list (Hazardous Air Pollutants defined here in as the 188 compounds that are categorized in Title III: Hazardous Air Pollutants of the 1990 Clean Air Act Amendments). One of the major sources of VOC and HAP is the pyrolysis of resins used in the core and molding sands (i.e. organic resins, carbon additives) during casting.

To meet the demands for environmental protection, it is necessary to reduce the consumption of organic substances, which can be achieved either by replacing organic binders with inorganic ones or the use of more reactive organic binders, which allows to use them in smaller quantities.

Currently, in the range of molding sands with organic binders molding sands with furan resins hardened with sulfonic acids (sulfonic acid cured furan no-bake) occupy the main position. They are characterized by very good

technological properties and can be applied to both ferrous and non-ferrous metals (e.g. aluminum alloys). Because of the large sulfur content derived from the use of hardeners, these sands cannot be used in the production of ductile iron or vermicular castings [1 - 3].

Another very important disadvantage of this technology is free furfuryl alcohol content, which was qualified as poison if its concentration exceeds 25 % [4]. These molding sands are also characterized by relatively high emissions during thermal decomposition under the influence of the liquid metal. Special attention is given the presence of compounds of the group BTEX and PAH [5 - 7]. The products of binder thermal decomposition largely condense in the depth of the mold on the grains of sand and escape to the atmosphere during casting (when the matrix is with addition of reclaim) and casting cooling mold and knocking out.

Therefore we are looking for a suitable molding technology, which could replace the molding sands with furan resin hardened with sulfonic acids, and would be more environmentally friendly. It seems that such technology is No Bake Curing Process with Added Esters (process ALPHASET).

PROCESS ALPHASET

Process No Bake Curing with Added Esters (alkaline phenolic resin ester hardened) (ALPHASET) is used for small or medium batch production. It may be used for all alloys types. The absence of nitrogen and sulphur in the compounding reagents is a benefit for steel casting and spheroidal iron casting.

ALPHASET binders require the addition of an ester component to enable polymerisation of the system to take place. A highly alkaline phenolic resin generally containing up to 25 % potassium hydroxide is used as a

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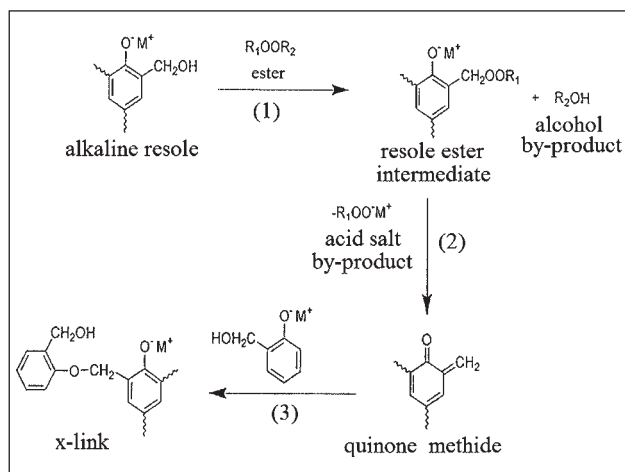
Figure 1 The crosslinking mechanism of the ALPHASET reaction showing (1) the formation of a resole ester via an ester exchange followed by (2) the formation of a reactive quione methide intermediate and (3) the reaction between the quinone methide and a phenoxide ion to form a phenyl-benzyl ether x-link [11]

binder. In sand conditioning 1,5 - 2 % of the highly alkaline phenolic resole (based on sand) is first blended into the sand, followed by about 20 % of an aliphatic ester (based on resin). The reactions between the specific esters or mixtures of these with the potassium hydroxide-containing resin leads to curing and solidification.. Depending on the type of ester used, the stripping time may be adjusted to 5 - 30 min. The polymerization process of the binder runs in two stages. The first step comprising partial polymerization takes place at room temperature. Full polymerization occurs only at a higher temperature by heat from the liquid metal [8 - 10].

ALPHASET mechanism: [11] The ester curing agent interacts with the hydroxymethyl group of a resole, via an ester exchange mechanism to form a resole ester (Figure 1):

Alkaline phenolic resin + Ester co-reactant → Suspected unstable intermediate → Splits to form: Polymerized phenolic resin alkaline salts and Alcohol

A secondary reaction is thought to occur when the partially polymerized resin contacts heat during the pouring operation, yielding an extremely rigid structure.

MATERIALS FOR INVESTIGATIONS AND METHODOLOGY

The object of the research was the binder used in the technology ALPHAET coming from one of the European manufacturers of binders used in foundry. It consisted of phenol-formaldehyde resole in an alkaline solution and the catalyst. The resin contained (mass %), sodium hydroxide (≤ 5 - < 10), potassium hydroxide (≤ 5 - < 10), methyl alcohol (≤ 3 - < 10), phenol < 1 %, and formaldehyde ($\leq 0,1$ - $< 0,2$). In contrast, the catalyst was a mixture of esters. The curing process of the resin was performed at room temperature. The main objective of this study was to identify major pyrolysis products of the catalyst, resin and the cured resin used in the ALPHASET technology depending on the decomposition temperature. Thermal decomposition of samples was carried out in the pyrolyzer at 700, 900 and 1 100 °C. The measuring system consisted of a pyrolyzer (Py) Pyroprobe 5000 (CDS Analytical Inc.), gas chromatograph (GC) equipped with a Thermo Scientific 15 meter chromatography column having a diameter of 0,25 mm RTX 5MS (Restek) coupled with mass spectrometry (MS) Thermo Scientific. Sample weight was 1 mg, heating rate of the sample 10 °C/sec., pyrolysis time < 1 sec. He (99,9999) was used as the carrier gas in the column. The obtained mass spectra were compared with the mass spectra given in the NIST MS Search 2,0 Libera (Chemm. SW, Version 2,0, Fairfield, CA, USA).

RESULTS AND DISCUSSION

Table 1 lists the identified compounds formed during the thermal decomposition of the samples tested at 700, 900, and 1 100 °C, together with the corresponding molar masses and CAS numbers (names of all compounds are consistent with the recommendations of the International Union of Pure and Applied Chemistry). In contrast, Figures 2 a, b, c contain selected chromatograms for each sample

(catalyst/hardener, resin, cured resin).

Catalyst/hardener: at 700, 900 and 1 100 °C virtually the identified compounds were: 1,2-diacetylglycerol ($C_7H_{12}O_5$), butyrolactone ($C_4H_6O_2$) and propylene carbonate ($C_4H_6O_3$) , their share was close to 100 %. They were probably compounds which was used as catalyst/curing agent. Additional at 900 °C identified probably a very small amount of 2-propen-1-ol (C_3H_6O) and benzene (C_6H_6).

Resin: As a result of pyrolysis of the resin the main component of the generated gas is carbon dioxide (CO_2). The share of this compound increases with temperature pyrolysis and 900 °C its share is about 78 %. The involvement of other compounds in this range of temperature, namely the decomposition temperature such as benzene (C_6H_6), phenol (C_6H_6O), phenol 3-methyl (C_7H_8O), benzene 1-ethyl-3-methyl (C_9H_{12}) phenol 2,6-dimethyl ($C_8H_{10}O$) is on the level of few percent (Fig. 2).

Cured resin: In the pyrolysis temperature of 700 °C the main component of emitted gases was 6-octadecenoic acid ($C_{18}H_{34}O_2$), which accounted for more than 30 %, and phenol 3-methyl (C_7H_8O) and phenol, 2,3-dimethyl ($C_8H_{10}O$) which accounted for more than 35 %. Acetic acid is due to reaction of potassium salt of phenol-formaldehyde resin ester and glycerol 1,2-diacetate. This is the initial stage of the curing of the binder (Fig. 1).The increase in decomposition temperature to 900 °C caused an increase in the share of carbon dioxide over 50 %, and derivatives of phenol: phenol, phenol 2-methyl , phenol 3-methyl and 1, 2, 3 -propanotriol, which constituted the second half of the emitted gases (Figure 2 chromatograms with peaks 9, 10, 14, 15).

Table 1 **Results of gas generated during thermal decomposition of the: hardener/catalyst, resin and cured resin**

| Peak no	Compounds	Hardener/Catalyst			Resin			Binder			MW
		700 °C	900 °C	1 100 °C	700 °C	900 °C	1 100 °C	700 °C	900 °C	1 100 °C	
1	Carbon dioxide/CO_2	0,0009		0,0006	0,2712	0,7836	0,8567	0,0901	0,5409		44
3	2-Propen-1-ol/C_3H_6O		0,0011								58
4	Acetic acid/ $C_2H_4O_2$							0,0090			60
5	Acetone/C_6H_6O							0,0905			58
6	Benzene/ C_6H_6		0,0002			0,0071	0.0569			0,0223	78
7	Benzene, 1,3-dimethyl-/C_8H_{10}							0,0495			106
8	Cyclobutanemethanl/$C_5H_{10}O$								0,0095		86
9	1,2,3-Propanetriol/ $C_3H_8O_3$										92
10	Phenol/C_6H_6O				0,0005	0,0752		0,0933	0,2408		94
11	Cyclopropylmethyl alcohol / C_4H_8O									0,9732	72
14	Phenol, 2-methyl-/C_7H_8O										108
15	Phenol, 3-methyl-/C_7H_8O					0.0504		0,1853	0,2408		108
16	Phenol, 2,3-dimethyl-/ $C_8H_{10}O$							0,1688			122
17	Benzene, 1-ethyl-3-methyl-/C_9H_{12}				0,0002	0,0349	0,0280				120
18	Benzene, 1,2,3-trimethyl-/C_9H_{12}						0,0462				120
19	Phenol, 2,6-dimethyl-/$C_8H_{10}O$					0,0488					122
20	Benzyl methyl ketone/ $C_9H_{10}O$									0,0045	134
23	1,2-Diacetylglycerol/ $C_7H_{12}O_5$	0,6688	0,3849	0,6249							176
27	6-Octadecenoic acid/$C_{18}H_{34}O_2$				0,7281			0,3135			282
28	Butyrolactone/$C_4H_6O_2$	0,2045	0,2865	0,2138							86
29	Propylene carbonate/$C_4H_6O_3$	0,1258	0,3273	0,1607							102
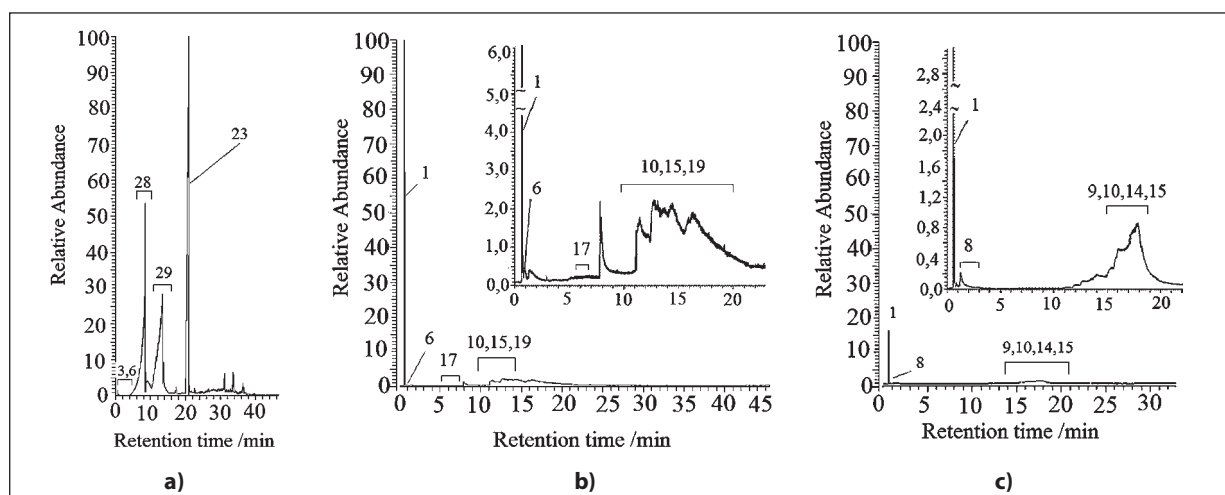
Figure 2 a - c): The chromatograms of pyrolysis products of: a) catalyst/hardener; b) resin c) cured resin (pyrolysis temperature of 900 °C)

SUMMARY AND CONCLUSIONS

Studies of thermal decomposition products of the binder components used in the ALPHASET technology and cured resin (alkaline phenolic ester hardened) (ALPHASET) over a broad temperature range under inert atmosphere showed that:

• ester hardener used is very stable at high temperature – changes is only above 900 °C;

• the basic resin decomposition product over a range of temperature (700 - 1 100 °C) was carbon dioxide, which share increased as the temperature of pyrolysis;

• the main component of the gases generated during the pyrolysis of the cured resin (binder) at 700 °C was 6 - Octadecenoic acid (about 30 %). With the rise in temperature to 900 °C 6 - Octadecenoic acid no longer occurs, while increasing the share of carbon dioxide, and the derivatives of phenol are present.

Although the pyrolysis was conducted under inert atmosphere (He), oxygen-containing compounds occurred in the products, e.g. carbon dioxide. This behavior may be associated with the fact that oxygen-containing groups such as ether bridges are still present in the resite structure and partly induce the greater degradation [9].

Acknowledgements

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