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Identification of Gas Products from Pyrolysis Process of Waxes Used in Lost-Wax Casting Technology

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Abstract

Foundry waxes currently used in lost-wax casting technology are composed of paraffin, stearin, and – to a lesser extent – ceresin, polyethylene wax, and other natural and synthetic waxes. Most of these compounds are non-toxic; however, they may release aromatic hydrocarbons as a result of exposure to high temperatures. Based on a chromatographic analysis (pyrolysis gas chromatography-mass spectrometry, Py-GC/MS), the compounds that are separated from the popular wax mixtures used in foundries were evaluated (as well as the impact they may have on foundry workers). For this purpose, the three main stages of the process (wax, burnout, and pouring) were analyzed, and the appropriate test temperature was chosen (similar to the actual conditions during the process).

Keywords:

lost-wax casting, foundry wax, gas chromatography, mass spectrometry

1. INTRODUCTION

Lost-wax casting is the process by which a duplicate metal sculpture (like silver, gold, brass, or bronze) is cast from an original sculpture. The steps used in casting small bronze sculptures are fairly standardized, though the process varies between foundries today. In modern industrial use, the process is called investment casting [1, 2]. Variations of the process include "lost mold," which recognizes that materials other than waxes can be used (such as tallow, resin, tar, and textile), and "waste wax process" or "waste mold casting," because the mold is destroyed to remove the cast item [3–5].

There is a very thin line between investment casting and lost-wax casting. We can differentiate the processes; if the investment casting is done by a wax pattern mold, then it is called lost-wax casting. In lost-wax casting, the wax patterns are manually prepared for each piece [3, 4], while in investment casting, metals are formed to produce high-quality casting components:

- Lost-wax casting is mainly used for small parts such as jewelry casting or even fashion accessories, while investment casting is highly used for the manufacture of complex or critical parts.
- In lost-wax casting, only one pattern can be used to make numerous patterns (even though the pattern is lost or melted), while through investment casting, one can produce an exact replica of the desired casting.
- In lost-wax casting, the manufacturer focuses on precise wax or mold design, while in investment casting, they focus on metals like nickel alloys, copper alloys, cobalt-based alloys, or super alloys [3].

Casts can be made of the wax model itself (the direct method) or of a wax copy of a model that need not be made of wax (the indirect method). Figure 1 shows the following steps for the indirect process [5–7].

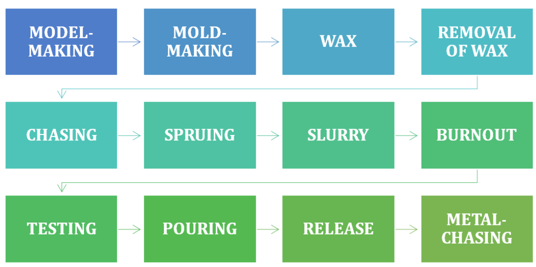

Fig. 1. Scheme of all steps in lost-wax casting technology

From these steps, the most important ecological steps are the wax, burnout, and pouring phases. The exposure to temperature is different.

In the "wax" step, molten wax is poured into a matrix-mold (made of the original model or sculpture from latex, polyurethane rubber, or silicone, for example). The substances that are used in lost-wax casting technology can be divided into three main groups: waxes, fatty acids, and wax substances.

Waxes are esters of higher fatty acid monocarboxylic and higher monohydric alcohols of even numbers of carbon atoms (from C_{16} to C_{36}). The model mixtures are not homogeneous [4, 7, 8]; these are mixtures with various chemical compositions, but they have one common feature – they consist of linearly placed particles containing between 20 to 70 CH groups. Taking into account the wax components in model mixtures, these particles very often contain ketone, oxide, and alcoholic substances together with the esters of higher fatty acids [9–11]. The temperature range of liquid wax is between 100-150°C (depending on the type of wax used).

The "burnout step" is intended to get rid of about 80% of the wax from the ceramic shell. The temperature range of this process is about 95–110°C. The last "pouring step" is related to cleaning the ceramic shell and removing all traces of moisture and the rest of the wax model. The temperature range of this process is between 870–1040°C.

All of these steps generate a lot of odors and chemical substances (mainly from the wax model), so the main purpose of this research is to analyze the types of these compounds by the pyrolysis gas chromatography-mass spectrometry method (Py-GC/MS).

2. MATERIALS AND RESEARCH METHODOLOGY

Two types of wax mixtures used in lost-wax casting technology were selected for the study. All of the basic parameters of the samples are presented in Table 1. The "W1" sample (not a popular wax mixture in foundries) generates many odors and has a smaller kinematic viscosity (dynamic). The solidification point of "W1" is lower than the "W2" sample (which is the most popular lost-wax casting technology). However, the "W1" wax mixture is about 12% cheaper, and it is characterized by better shape reproduction in the case of thick-walled and massive simple castings (a slight shrinkage of the wax when pouring it into the mold).

At a temperature of 150°C, the samples were pyrolyzed in a tube furnace in an inert atmosphere (argon). The emitted compounds were adsorbed on active carbon; after this process, they were extracted by means of diethyl ether. At a temperature of 1000°C, the samples were mainly analyzed by the pyrolysis gas chromatography (Py-GC/MS) method, which is based on transforming a solid sample (2–5 mg) into gas by heating it in an atmosphere of inert gas (helium) in a "Py" Pyroprobe 5000 pyrolyzer (CDS Analytical Inc.), which is accompanied by thermal decomposition. It has a platinum ribbon or coil, which enables the heating of a sample to any temperature within a range of 250–1100°C [12].

The obtained mixture of compounds is separated on a chromatographic column (Restek Rxi-5Sil fused silica) in a "GC" chromatograph (Focus GC, Thermo Scientific). A temperature program was applied: an initial temperature of 40°C was held for 5 min; ramped up by 5°C/min up to 150°C and held for 5 min; then, up to 250°C with a heating rate of 10°C/min and maintained for 5 min (helium carrier gas at 1 ml/min; sample split ratio – 1:20). The separated compounds are analyzed in an "MS" mass spectrometer (ISQ Thermo Scientific) in the full-range mass number/charge number (m/z). Electron ionization (70 eV) at a temperature of 250°C was then applied [12–14].

3. RESULTS

The compounds found after the pyrolytic decomposition of the samples of the wax mixtures are summarized in Table 2. A comparison of the measured mass spectra to the National Institute of Standards Technology database (NIST MS Search 2.0) and its own patterns (e.g., aromatic hydrocarbons like benzene, toluene, etc.) gave the possible types for the released compounds.

As a result of a temperature of 150°C (Fig. 2), only about 30% of the compounds were identified in the pyrolytic products as compared to the tests at 1000°C. Both samples contained similar compounds with a predominance for the W1 sample, which additionally have fatty acids (myristic acid, lignoceric acid, and isopropyl myristate – the ester of isopropyl alcohol and myristic acid for Sample W2). Both samples mainly contained fatty acids and some organic compounds based on the benzene ring and α-pinene of the terpene class (Tab. 2), which are the primary constituents of turpentine (a solvent for waxes).

At 1000°C, the chromatographic spectrum (Fig. 3) is much more complex and contains many different compounds, with a predominance for the W1 sample (mainly simple hydrocarbons). In the gaseous products for retention times within a range of 1 to 24 minutes, Sample W1 recorded many intense peaks coming from low molecular weight hydrocarbons. These compounds can be divided into the following groups: aromatic hydrocarbons with a benzene ring, carboxylic acids (e.g., acetic and butyric acid – wax solvents), ketones (e.g., diacetyl – simple ketones are, in general, not highly toxic), and alcohols (also wax solvents). Typical compounds of wax mixtures are glycerol (another name – glycerin) and azulene. Chloroform was probably also used as a solvent. For retention times within the range of 24 to 50 minutes, many intense peaks coming from high molecular weight hydrocarbons were recorded, mainly fatty acids (similar to 150°C). As compared to W2, wax mixture W1 generates about 40% more compounds, which is its disadvantage.

According to the steps of the lost-wax casting technology, more dangerous for human health is the "pouring step", where the temperature of the process is about 1000°C. An accumulation of toxic compounds occurs within this range.

Table 1
Properties of wax mixtures

Sample/Parameters	Solidification point, °C	Dropping point, °C	Kinematic viscosity at 100°C, mm^2/s	Penetration at 25°C	Acid number, mg KOH/g
W1	79.25	83.14	8.43	11	57.25
W2	84.34	87.12	9.95	12	48.38

Table 2
Results of Py-GC/MS investigations for selected temperature points

Peak No.	Name of compound	No. CAS	Molecular weight, u	Retention time R_T, min			
				W1		W2	
				150°C	1000°C	150°C	1000°C
1	Carbon dioxide	124–38–9	44	–	4.57	–	–
2	Acetic acid	64–19–7	60	–	8.12	–	–
3	Propan-2-ol	67–63–0	60	–	10.12	–	–
4	Cyclobutanone	1191–95–3	70	–	13.12	–	–
5	Methyl acetate	79–20–9	74	–	14.01	–	–
6	Benzene	71–43–2	78	–	14.39	–	14.37
7	Diacetyl	431–03–8	86	–	15.24	–	–
8	Butyric acid	107–92–6	88	–	18.12	–	–
9	Pentan-1-ol	71–41–0	88	–	18.24	–	–
10	Toluene	108–88–3	92	–	19.01	–	–
11	Glycerol	56–81–5	92	–	19.48	–	19.50
12	Phenylethyne	536–74–3	102	–	20.01	–	–
13	Styrene	100–42–5	104	–	21.12	–	–
14	Ethylbenzene	100–41–4	106	–	22.04	–	–
15	Indene	95–13–6	116	–	22.58	–	–
16	Chloroform	67–66–3	119	–	23.24	–	–
17	Azulene	275–51–4	128	–	23.48	–	24.01
18	Naphthalene	91–20–3	128	–	24.12	–	–
19	Benzo[c]thiophene	270–82–6	134	25.12	25.28	25.11	25.30
20	α-pinene	80–56–8	136	27.35	27.48	27.29	27.51
21	Caprylic acid	124–07–2	144	29.35	29.48	29.40	29.54
22	Acenaphthylene	208–96–8	152	31.33	32.08	31.29	32.10
23	Benzophenone	119–61–9	182	33.57	34.12	34.01	34.15
24	Bibenzyl	103–29–7	182	35.48	36.01	35.51	36.02
25	Lauric acid	143–07–7	200	37.01	37.25	37.03	37.31
26	Myristic acid	544–63–8	228	–	39.48	38.57	39.54
27	Hexadecan-1-ol	36653–82–4	242	–	41.34	–	41.28
28	Palmitic acid	57–10–3	256	–	42.59	–	43.01
29	Isopropyl myristate	110–27–0	270	45.01	44.58	–	44.52
30	Stearic acid	57–11–4	284	–	46.12	–	46.15
31	Lignoceric acid	557–59–5	368	48.03	47.48	–	47.54
32	1-Triacontanol	593–50–0	438	–	49.37	–	49.41
33	Biphenyl	92–52–4	154	–	53.48	–	53.50

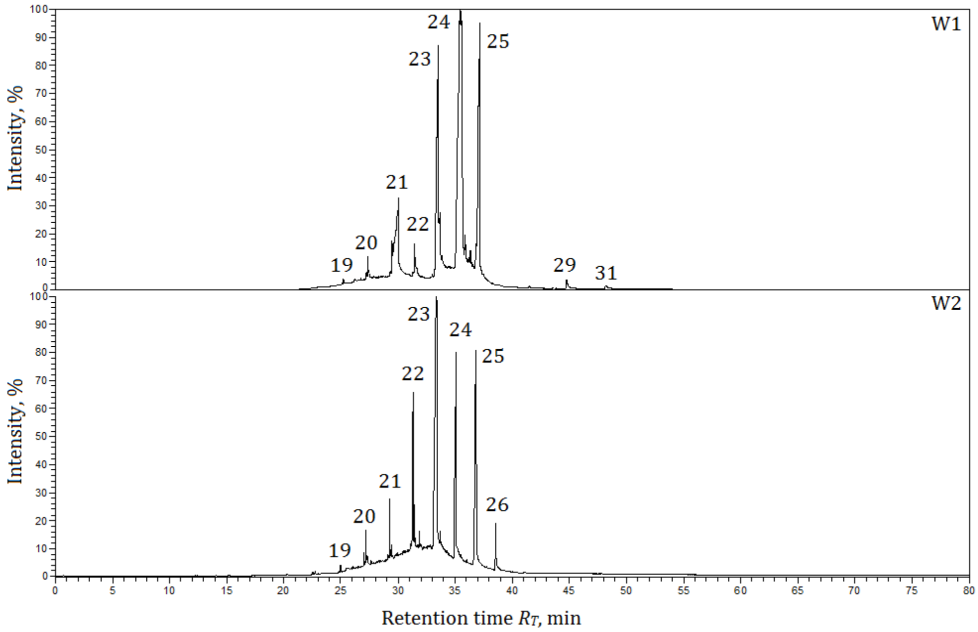

Fig. 2. Chromatograms for samples at 150°C

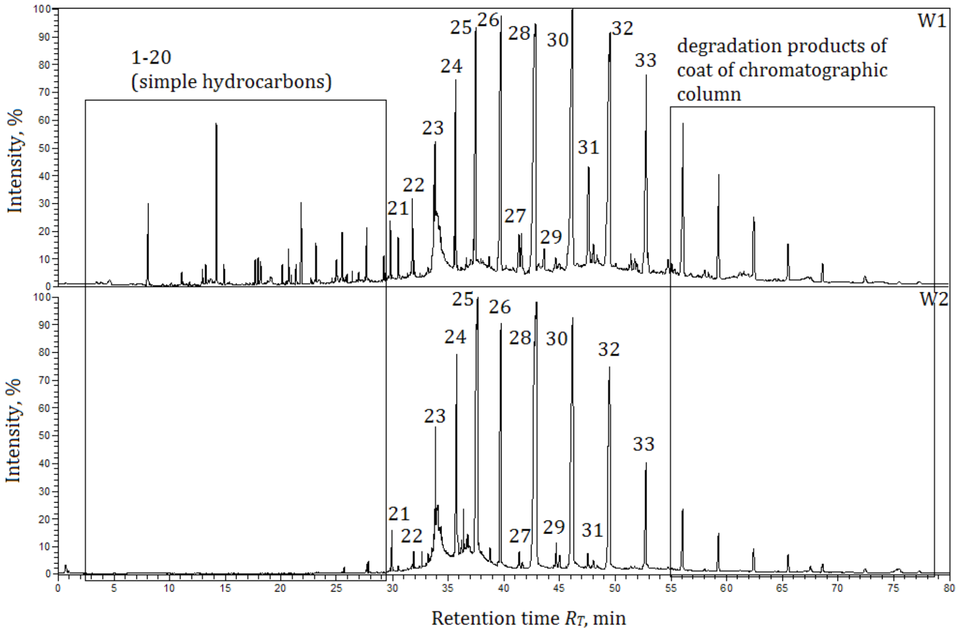

Fig. 3. Chromatograms for samples at 1000°C

4. CONCLUSIONS

The wax mixtures are all chemicals that can affect human health. The gases that the waxes produce during burnout and pouring are dangerous. Heat (definitely a part of the casting process) causes chemical reactions to accelerate (and sometimes starts them). Specific chemicals include wax and plastic fumes from the burnout. When waxes burn, they release many toxic and irritating compounds (including aromatic hydrocarbons). Burning the organic chemicals added to wax such as rosin, glycerin, petroleum jelly, azulene, fatty acid, etc. will release carbon monoxide and other toxic decomposition products.

In connection with the research and taking into account the parameters of the wax mixtures, the use of wax mixture W2 would be more beneficial for safety reasons. It generates fewer toxic gases, mainly due to the aromatic hydrocarbons. During the burnout and pouring steps, it is recommended to use exhaust gas installations with filters that can absorb the gases.

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