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Improving Steel Casting Quality Using Resins With Increased Thermal Stability

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Abstract: This study presents the feasibility of altering the phenol-formaldehyde resins through a modifier increasing their heat resistance. The presence of strong benzene rings that form a networked spatial structure of the polymer is the determining factor of the thermal stability of binders on a fenr base and the stability of the myelene groups. The results have revealed that utilizing resocin produces the intended outcomes concerning maximizing the thermal oxidizing ability of resins. This material is remarkably impervious to thermo-oxidative degradation, additionally, it has two hydroxyl groups. Resocin as a modifier of the heat-resistance-increasing resin binder compositions has proved its efficiency experimentally which focuses our attention on accomplishing thermal stability indicators surpassing furan resins due to the fact that furfuryl alcohol is not one of their components which ensures more health conditions and improved environmental performance in manufacturing large-scale steel casting.

Key words: Phenol-formaldehyde resins, heat resistance, resocin, thermo-oxidative degradation, residual strength, furan resins, environmental indicators

INTRODUCTION

The utilization of resin bonding materials currently occupies the first place in the wide variety of technologies that have been developed for the production of castings. When small and medium-sized castings are mass produced, around 93-96% of the foundry cores are made by utilizing resins. As a matter of fact, these are different molded or improved polyurethane resins utilized in the amine process (Engels *et al*., 2013).

When the mass of castings increases, different technical challenges arise, for example, the design becomes more complicated and geometric dimensions increase. These alterations inevitably impose new requirements such as checking the manufacturability of these changes and using new materials which must be taken into consideration. A good example here is the production of castings of transport (railway) engineering. These castings are characterized by enormous masses, considerable dimensions, complex joints of surfaces and different thicknesses of mating walls. Moreover, these castings are made of steel which requires a higher thermal resistance of the molds and cores, accordingly, this necessitates a new methodology to select the bonding materials that enjoy these characteristics (Seetharaman, 2005; Holtzer *et al*., 2015).

Now a days, the use of furan resins can be attributed to having the following properties: its ability to be processed (Holtzer *et al*., 2015), producing high-quality castings (Holtzer *et al*., 2015; Anonymous, 2018a, b) and their increased toxicity (Anonymous, 2005).

The areas of castings production are tied to toxicity where its damaging impact is clearly reflected in the poor sanitary and hygienic conditions and the deterioration of the ecological situation (Westberg *et al*., 2005; Lofstedt *et al*., 2009).

The primary objective of this research is to provide technical solutions that boost the process of manufacturing high-quality castings, meanwhile keeping into consideration preserving the environment by utilizing resin binders which are relatively environment-friendly.

In spite of the large number of developed compositions of cold curing mixtures depending on synthetic resins such as phenolic, phenol-formaldehyde, urea-formaldehyde, furan and epoxy not all of them are appropriate for manufacturing massive large-dimension steel castings because of lacking sufficient heat resistance. The most suitable materials in this context are carbocyclic polymers and phenol-formaldehyde resins. Figure 1 clearly shows the nature of the structure formation of these materials. It is worth noting that their high thermal stability depends on the structural features of the molecular links of the resin and the oxidative thermal destruction processes that take place when pouring the steel melt into the hollow of the mold. The thermal stability of the binders on a fenr base is controlled by the strong benzene rings that form a networked spatial structure of the polymer and the stability of the myelene groups.

As a side note, high temperature plays a vital role in the course of destruction that it causes the majority of the carbon of the methylene groups to take part in forming the

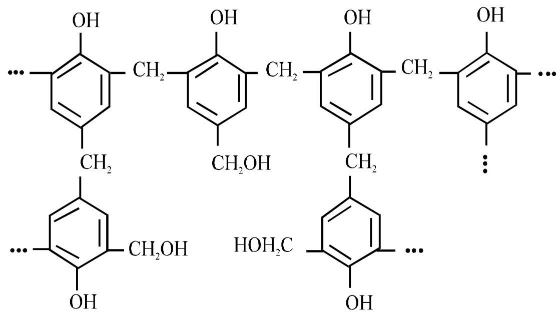

Fig. 1: Typical structure of the phenol-formaldehyde resin of the resolving type

coke skeleton where there is a contact between the elements of the mold and the molten metal. Consequently, the filler seeds are bound which determines the sufficient strength properties of the walls of the mold and cores for high-quality casting.

Thermo oxidative destruction of phenolic binders involves changing methylene groups into carboxyl groups. These converted groups have the ability to form a solid polymeric skeleton that offers high thermal resistance. In particular, hydroxyl groups play a vital role in forming a thermally stable polymeric matrix of phenolic-formaldehyde resins since they act as the adhesive strength in the filler-binder system (Zymankowska-Kumon *et al*., 2016).

Nevertheless, the heat resistance of phenol-formaldehyde resins is deemed insufficient in respect of large-sized castings or casting of thick-walled.

It seems that creating and developing binding compositions based on phenol-formaldehyde resins with increased heat resistance for large-size and massive steel casting is advantageous. This improvement involves developing a number of modifying additives with the aim of maximizing the thermal stability of phenol-formaldehyde resins and casting mixtures based on them.

To develop the thermo-oxidative ability of resins, resocin is a good choice due to the fact that it has two hydroxyl groups moreover, it is most impervious to oxidative degradation (Zymankowska-Kumon *et al*., 2016). Figure 2 shows the structural formula of the resonance molecule. Resorcinol is used in making synthetic dyes and synthetic polymeric materials, resorcinol-aldehyde resins have tanning properties for instance, thus, used as a disinfectant in curing skin diseases.

Basically, resorcinol aldehyde resins are phenol-formaldehyde resins, these resins are achieved either by polycondensation of resorcinol or its homologs with aldehydes (main formaldehyde) (Yurkevichyute *et al*., 2016).

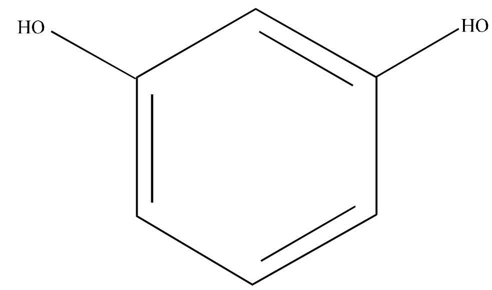

Fig. 2: Structural formula of resorcinol molecule)

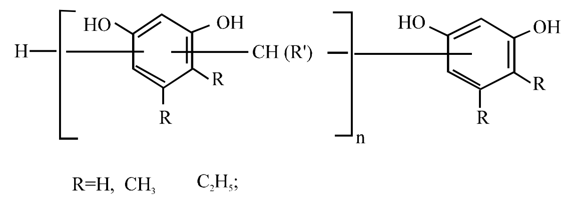

Fig. 3: Structural formula obtains resorcinol-aldehyde resin (Yurkevichyute *et al*., 2016)

Regarding synthesis of resorcinol-aldehyde resins (Yurkevichyute *et al*., 2016), methylene bridges that adhere dihydroxyphenylene nuclei occupy in most cases, ortho and para-positions in both OH groups. In comparison with phenol, resorcinol is more active when reacts with formaldehyde. Polycondensation reacts simply at room temperature without any catalyst. The activation energy of the process found to be 4.3-4.5 kJ/mol and the minimum speed is at pH 3.5.

The most widely recognized thermoplastic resorcinol-formaldehyde resins are produced in aqueous or aqueous-alcohol medium (cation-NaOH, Zn acetate or others), utilizing overabundance of resorcinol (1 mole per 0.5-0.65 mole of formaldehyde). This process goes through different stages in the first stage, isomeric dihydroxybenzene alcohols are obtained at 40-60°C, then in the second stage, at 100°C, they gather with each other and with resorcinol to shape oligomers (Fig. 3) (Yurkevichyute *et al*., 2016). Sometimes the need arises for drying the obtained resin under vacuum to a solid state. In this research, this substance is employed as a modifier of the starting resins.

The residual free phenol of synthetic resins which have been developed to be used in the foundry industry, take part in the polycondensation process with acid curing of cold-hardening mixtures. In that connection in comparison with conventional Tylenol-formaldehyde resins, resorcinol-aldehyde resins are the most reactive elements. Resins are characterized by having adhesive

Sproperties which are responsible for strength formation of molds and cores that are held to be responsible for resisting high temperatures because they are located in the chains of molecules of hydroxyl groups as has been conclusively shown in different studies (Holtzer *et al*., 2015; Zymankowska-Kumon *et al*., 2016). Accordingly, the modifying agent suggested here is resorcinol containing two hydroxyl groups in the molecule.

MATERIALS AND METHODS

The possibility of utilizing the customary phenol-formaldehyde resin of the brand SFZH-301 with a modified resonant which has been used to maximize heat resistance has been examined to ensure its feasibility as a replacement of furan resins derived from the product line of Mason (Anonymous, 2018a) but differing in containing no furfuryl alcohol, the primary source of harmful emissions into the environment (Anonymous, 2018b). The materials utilized in the tests are listed in Table 1.

Table 2 shows the Physicochemical properties of the resonance employed in the experiments of this research. To provide a basis for comparison, furan resin Askuran, grade F 336/1 (Table 3, isolated in gray) has been used and the manufacturer-ASK chemicals. ASK chemicals is a German company, it is one of the leading pioneers of the furan resins manufacturers and suppliers in Europe. Furan resins are dense items composed of furfuryl alcohol, urea and formaldehyde. In any standard Askuran furan resins, the vital component furfuryl alcohol ranges from 60-90% (Anonymous, 2018a, b).

If the percentage of furfuryl alcohol reaches up to 90% in the resin, definitely there will be carcinogenic emissions during the stages of the process as has been revealed by the Directive of European Parliament and Council in 2010). Accordingly, the amount of this constituent must not be more than 30%.

Taking these reasons into consideration, a test of the heat resistance of these mixtures has been conducted. A comparison between the formulations based on phenol-formaldehyde resins modified with resin (Resin SFZH-301, Table 1) and compositions based on Askuran resin, grade F 336/1 has been designed.

To fulfill these purposes, experimental research has been conducted on the model compositions of mixtures; a mixture of quartz sand - 100%, resin SFZH301 -2.0% with the amount of modifier 2.4.6.8, 10 parts by weight, respectively were made. Moreover, cylindrical samples were shaped using the gotten sand mix 50×50 mm, this sand solidifies within 24 h.

Table 1: Basic materials for carrying out experimental studies

Material	Specifications
Resin SFF 301--phenol-formaldehyde	Composition, mass%: basic substance 73.2, water 18.5, impurities 8.3 Physical-chemical properties: T. b. 122-126°C Fire-hazardous properties: flammable liquid, autoignition T. 620°C Extinguishing media: water, air-fur. foam
Resorcinol	$C_6H_4(OH)_2$-colorless crystalline substance, easily soluble in ethanol, diethyl ether, acetone, water, it is hardly soluble in chloroform, carbon disulfide, benzene Resorcinol has the properties of phenols when reacted with halogens and nitric acid, forms the corresponding trisubstituted derivatives Resorcinol readily condenses with aldehydes to form the corresponding resorcinol-aldehyde resins
Furan resin	Resin Askuran, brand F 336/1, manufacture ASK chemicals, Germany

Table 2: Physicochemical properties of resonator (Yurkevichyute *et al*., 2016)

Indicators	Quantity
Appearance	White or pale yellow flakes
Mass of the main substanc (%)	99.5
Mass of water (%)	0.01
Mass of nonvolatile substances (%)	0.01
Density (kg/m^3)	1.27
Melting point (°C)	109-110
Flash point (°C)	127
Boiling point (°C)	280.8
Auto ignition temperature (°C)	608

Table 3: Nomenclature of furan resins for cast iron and steel casting (Anonymous, 2018a, b)

					Alloys			
Resin Askuran	Specific weight (g/cm^3)	Furfuryl alcohol (%)	Phenol (%)	Nitrogen (%)	Steel	Cast iron (gray and high-strength)	Color	Application
381	1.14-1.16	92	0	1	x	x	x	High reactivity
FH 040	1.16-1.18	75-77	0	3.5		x		Standard resin, annual use
F 336/1	1.14-1.18	83-87	0	<0.5	x	x		Low reactivity, high ductility, suitable for large castings
NB 7915 D	1.16-1.18	67	0	5		x		Low reactivity, suitable for large castings
EP 4179	1.14-1.16	82	0	1		x		Standard reactance

Table 4: Compositions of mixtures for comparison of indicators of heat resistance

Components of the composition	Experimental composition, mass fraction	Mixture on furan resin, mass fraction
Sand quartz, 1K02B, mass fraction	100	100
Resin SFZH-301 with a resonator modifier, (8 parts by weight)	2.0	-
Resin Askuran	-	1,2
Curing agent, phosphoric acid	0.4	0.2

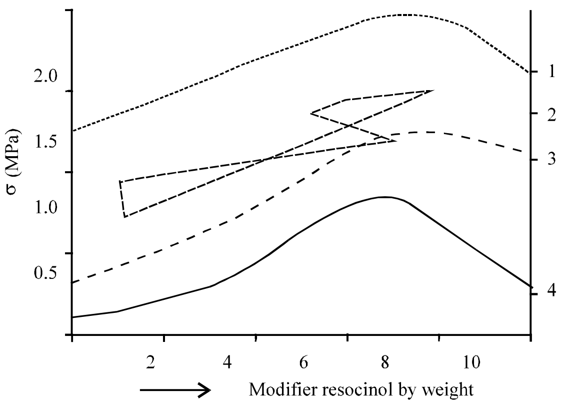

Fig. 4: Results of heat resistance of the mixture in terms of the residual strength of the samples, on the phenol-formaldehyde resin SFZH301 with different components of the modifier and different calcination temperatures: 1) At room temperature; 2) At 400, 3) 600 and 4 -800°C, respectively

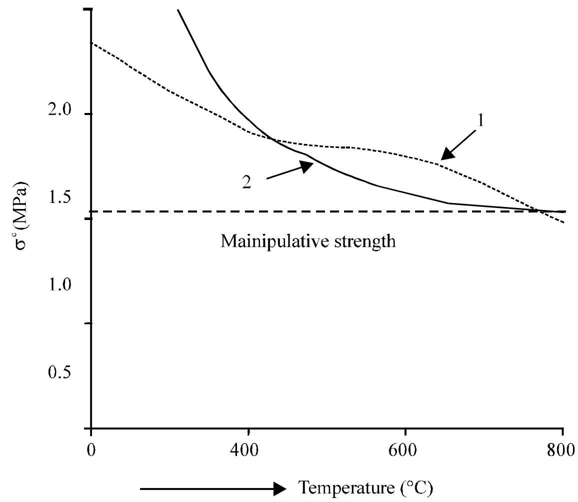

Fig. 5: Munipulative strength

RESULTS AND DISCUSSION

Regarding Thermostability, it has been identified by the residual strength of the mixture as a result of calcination of cylindrical samples at different temperatures, namely: 400, 600 and 800 °C. Then the residual strength of the samples has been identified for compression (according to ASTM E9 - 09(2018) (Fig. 4). Experimental investigations have explored that the ideal amount of the modifier ranges from 7.7-8.5 parts by weight. In the tests that have been conducted to compare it with furan resin, the amount of the modifier has been of 8.0 parts by weight. Table 4 shows the constituents of the test substances. A related point to consider is that the hardener orthophosphoric acid has been taken.

It is worth noting that it cannot be said that the chosen constituents are the ideal ones, i.e., it is not optimal in terms of having the required complex of properties either manufacturability (vitality, formability, tenacity, etc.) or the even the quality of the casting. The intended role of these compositions is nothing but to measure heat resistance of the used resins.

The thermal stability has been determined as the same as the earlier experiments by evaluating the residual strength of the mixtures after their calcination where they have been heated at the same temperatures. Figure 5 clearly shows the results.

The modified mixture which is based on the usual phenol-formaldehyde resin but modified with a resonance (8% by weight), resists heat as equal as the standard furan resin does.

What distinguishes the suggested composition is that it is free of furfuryl alcohol which is the primary source of toxic emissions into the environment. Accordingly, this composition has a crucial role in protecting the environment, i.e., it improves the working conditions for foundry researchers and minimizes noxious emissions.

CONCLUSION

The following conclusions can be drawn from the present research: based on the detailed highlights, a technique for choosing modifiers of phenol-formaldehyde resins to maximize their heat resistance has been proposed by this research.

Based on the theoretical background of the process of the formation of phenol-formaldehyde resins, this research has chosen a modifier to improve the thermal stability of the mixture and then tested it experimentally. Moreover, a resonator modifier has been suggested and tested for the resin SFZH 301.

The results show that the optimum concentrations of the modifier in the resin are 7.7-8.5 parts by weight. The utilization of modifiers that work to improve the heat resistance of resins has proved its effectiveness. The possibility of producing high-quality steel castings by using modifiers for improving the heat resistance of resins has been proved. The developed resins have proved its ability to minimize damage to the environment, i.e., it excluded substances that generate toxic emissions during the manufacturing process of large-sized steel castings.

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