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Influence of Sulphur Diffusion on the Surface of Furan No Bake Casting-A Review

Kashyap V. Mehta**, Shivang S Jani, Dr. G. D. Acharya
Mechanical Engineering Department, AITS, Rajkot, Gujarat, India

Abstract
Casting process is one of the most used processes in manufacturing industries. Furan no bake casting is a fast developing technology for foundry industries. Furan no bake casting process uses resins and acid catalyst to form a binder system. However this process produces castings with high strength and good surface finish. Hence this method is suitable for producing accurate dimensioned castings. This paper deals with effect of resin binder system on dimensional stability and surface finish. This furan resin mould system sometimes produces product with sulphur diffusion on surface of casting. This paper mainly deals with the issue of sulphur diffusion from the moulding sand to the surface of the furan no bake casting. Main constituents of sulphur in furan no bake sand are furfuryl resins produced on the basis of sulphonic acids or sulphuric acid. This paper also deals with degradation of properties of gray iron castings due to sulphur diffusion and also the assessment of degree of diffusion, influence of hardener and the ways to reduce the diffusion.

Keywords: *Furan, moulding sand, no bake casting, sulphur diffusion*

****Author for Correspondence*** E-mail: kavimehta0000@gmail.com

INTRODUCTION

Furan no bake system is commonly known as acid no-bake. It is a two part binder system made up of an acid catalyst and a reactive furan type resin. FNB has high hot strength and excellent shake out characteristics (Figure 1). The amount of furan no bake binder used is usually 0.9 to 1.2% based on sand weight. Catalyst levels are generally 40% based on the weight of the binder. Furfuryl alcohol is the basic raw material for the furan family of acid catalyzed no bakes.

FNB acid catalysts are 75% phosphoric, 85% phosphoric, toluene sulfonic, xylene sulfonic and benzene sulfonic acid. Castings manufactured from furan resin sand and furan binders have higher dimensional accuracy, good surface finish, higher compressive strength, excellent flow ability, predictable polymerization shrinkage, lower smoke and odour, colour change indicates rapid cure and low reject rate [1]. The main factors affecting the compressive strength are amount of resin, ambient temperature and humidity, resin properties, sand grain size, sand quality and permeability. The sand mould affects the casting surface with the assistance of heat of molten metal and reacts with the microstructure and also the diffusion process. Outer surface of the casting gets degraded due to sulphur diffusion of the moulding sand to the outer surface of the casting. Sulphur sources in furan no bake castings are hardeners produced from sulphonic acids or sulphuric acids. Due to high temperature the hardener disintegrates and sulphur diffusion occurs from the moulding sand. Disintegration of sulphonic acid is shown below:

$$C_7H_7SO_3H \rightarrow C_7H_7OH + SO_2$$

LITERATURE REVIEW

Hosadyna *et al.* at faculty of foundry engineering, University of science and technology, AGH analysed, the effect of mechanical reclamation sand in furan no bake mould for appearing of the flake graphite in the outer layer of a nodular iron castings [3]. In their experiment, they made a casting of dimension 175x195x120 mm and U shaped was selected as casting shape. The casting was prepared by no bake moulds with furfuryl resin. This mould contained different amounts of sulphur. Reclamation sand applied in 1R sand contained 0.1% sulphur, 2R sand had 0.15% and 3R sand had 0.2% sulphur.

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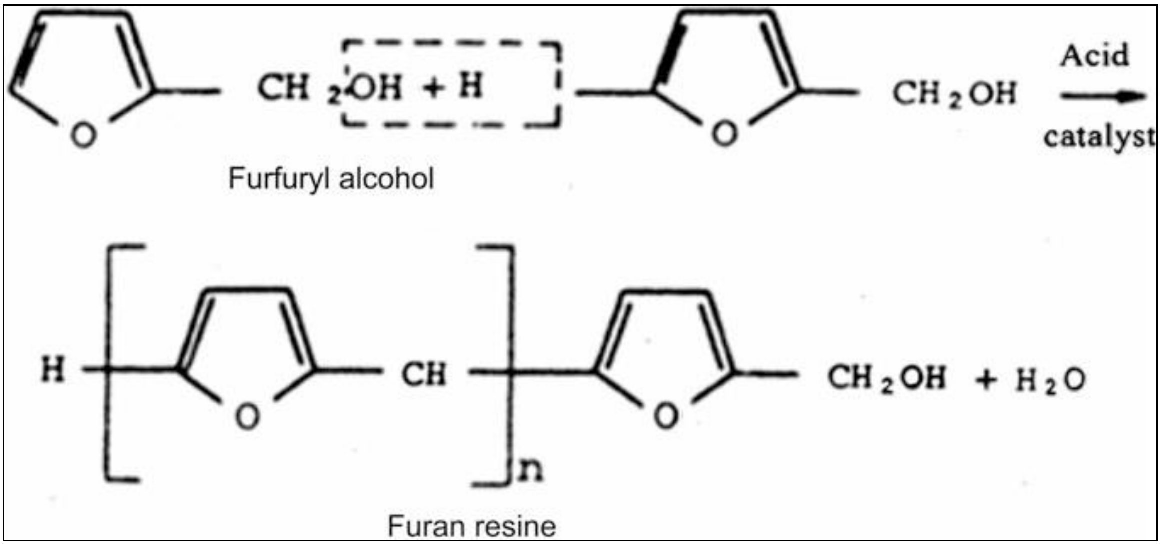

Fig. 1: *The Furan Acid Catalyst No Bake Curing Mechanism [2].*

Individual mould sand had different composition: Reclamation sand =100 p.p.w, Phenol-furfuryl resin Kalhartz =1.1 p.p.w and standard hardener (50–65% PTS acid and <5% sulphuric acid) =0.55 p.p.w. Sulphur content was checked by thermal method with LECO CS 444 apparatus. Three different types of sand were prepared namely; Sand 1R, Sand 2R and Sand 3R. Following Table 1 shows the content of sulphur in reclamation sand and in individual moulding sands.

Table 1: *Content of Sulphur in Reclamation Sand and in Individual Moulding Sands [1].*

Sand nr	Content of Sulphur in Reclamation Sand	Content of Sulphur in Moulding Sand,%
Sand 1R	0.1	0.18+0.018
Sand 2R	0.15	0.22+0.023
Sand 3R	0.2	0.30+0.025

Hosadyna *et al.* at faculty of foundry engineering, University of science and technology AGH studied, influence of over-cooling the nodular cast iron to the graphite form in the surface layer [4]. From their study they analyzed the greater cooling rate, the higher tendency of the cast iron to over-cooling what causes the formation of interdendritic graphite, and in a consequence solidification of the cast iron in the metastable system. Also an increase of the number of eutectic grains was observed by them.

They also studied the factors affecting the cooling rate which were:
1) Shape and dimensions of the casting,
2) Thermophysical properties of metal,
3) The pouring temperature,
4) The structure and dimensions of the mould,
5) Thermophysical properties of moulding material,
6) Coefficient of the heat accumulation, the mould temperature.

The aim of the researchers was to study the impact of cooling rate on the surface of casting for distorted graphite forms existence.

No bake sand called process alphaset was used which contains phenolic resin and esters. The moulding sand composition constituted quartz sand. Grudzeń Las about the main fraction 0.20/0.32/0.40 and the average grain size 0.31 mm in the amount of 100 parts per weight, the phenolic resin sinotherm in the amount of 1.1 parts per weight and the hardener being a mixture of esters in the amount of 0.33 parts per weight. The design of experimental castings was applied in this module of castings. Castings were prepared by pouring the nodular graphite iron EN-GJS 500-7. Chemical compositon of the samples were studied (Table 2) using spectrometer LECO CS46.

Table 2: *Chemical Composition of the Samples [4].*

Element	Content in %
C	3.36
Si	2.65
Mn	0.17
P	0.13
S	0.006
Cr	0.03
Ni	0.07
Cu	0.01
Mg	0.08

Hosadyna *et al.*, at faculty of foundry engineering, University of science and technology AGH studied the diffusion of sulphur from moulding sand, to cast and methods of its elimination [5]. In this paper researchers first studied the degree of sulphur diffusion on the surface of the castings. This process was studied by preparing a casting of 0.6x0.6x0.6 m of cast steel CSN 422712 using bottom pouring and mass 1.65 mg. The self-hardened loose sand used had the following chemical composition: chromite sand 100 part of weight, furfuryl resin TDE20-1.2 part of weight, hardener 500-T1-0.5 part of weight.
After pouring, the sample was cut of 80x80 mm and thickness 50 mm from the surface of the casting. The changes in the content of sulphur were studied and measurements were carried out to a depth of 10 mm, using the EDS technique of microanalyser LINK AN 10/85S coupled with the electron microscope JSM 840. At the same time on milled surfaces at a distance of 1 mm from the casting surface, the carbon and sulphur contents were marked by using the Leco spectrometer. The results of analysis are displayed in the following Table 3.

Table 3: *Changes of Concentration of Carbon and Sulphur in Different Distances from the Casting Surface [5].*

Distance from the Casting Surface(mm)	Content of Sulphur (%)*	Content of Elements (%)**	
		Sulphur	Carbon
0	0.442	-	-
1	0.342	0.153	0.059
2	0.055	0.014	0.110
3	-	0.0097	0.153
4	0.050	0.0098	0.183
5	-	0.0097	0.202
6	0.020	0.0096	0.210
7	-	0.0094	0.212
8	-	0.0099	0.214
9	-	0.0098	0.217
10	0.021	0.0096	0.219

**Microanalyser, Average from 6 Markings,*
***Spectrometer LECO (S, C).*

As we can see there is high amount of sulphur diffusion so researchers developed method to reduce the sulphur diffusion (Figure 2).

Hosadyna *et al.*, at faculty of foundry engineering, University of science and technology AGH, studied influence of the hardener type on the sulfur diffusion from moulding sand to the casting surface [6]. The researchers prepared a sample by studying research materials; and material used for casting was EN GJS 500-7 type. For making moulding sands, Grudzeń Las quartz sand was used, it had different granulation of 0.20/0.32/0.40; d 50=0.31 mm and pH=7. Phenol-formaldehyde Kaltharz resin, about the low content of the free formaldehyde (0.1–0.2%), furfuryl alcohol ~50% and nitrogen (0.35–0.5%). Four different hardeners were used by researchers and their compositions are displayed in the Table 4.

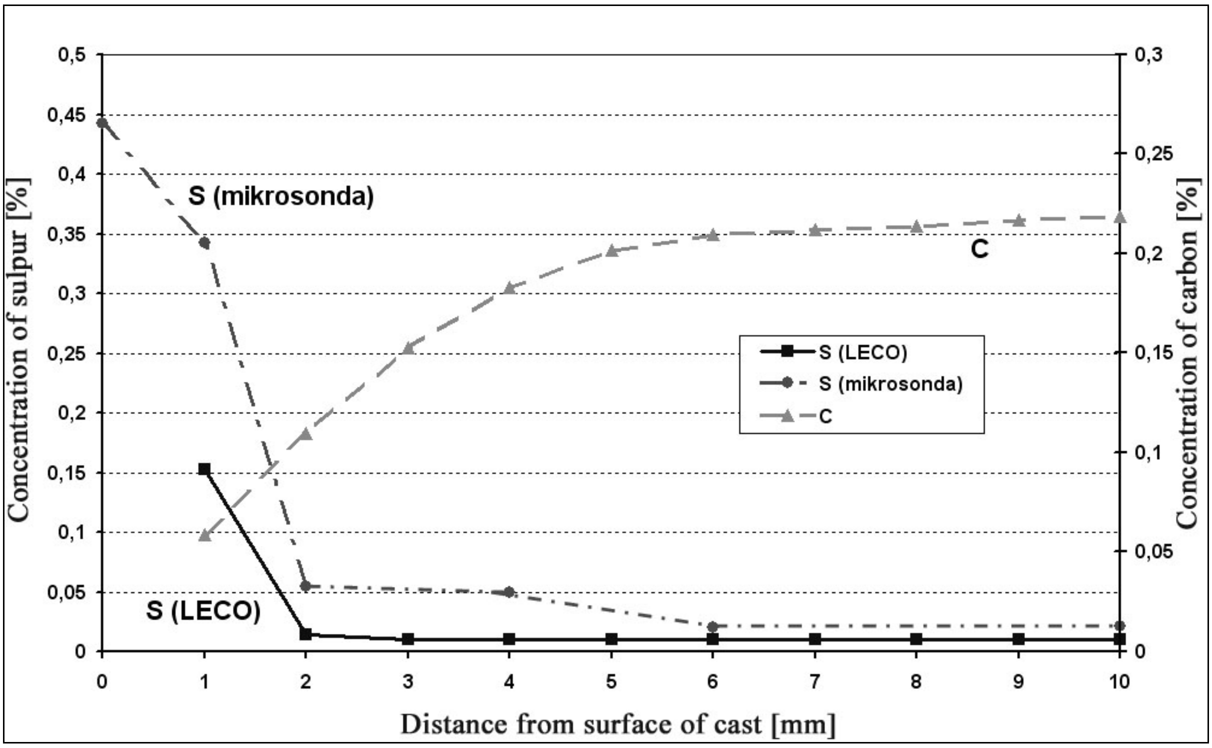

Fig. 2: *Change of the Chemical Content of the Cast-Iron (Content of C and S) in Reference to the Distance from the Casting Surface [5].*

Table 4: *Compositions of Individual Hardeners [6].*

Type of the Hardener	PTS%	Sulphuric Acid (%)	Phosphoric Acid (%)
Activator 1	50–65	<5+10% (solution 69%)	-
Activator 2	40–50	<1, 5	20–25
Activator 3	65	<0, 5	-
Activator 4	30–40	<0, 23	-

Individual moulding sands was being carried out, about the following composition:
Quartz sand 100 parts by weight,
Kaltharz resin 1.1 part by weight,
Hardener 0.55 part by weight,
Sand 1: Activator 1,
Sand 2: Activator 2,
Sand 3: Activator 3, and
Sand 4: Activator 4.
Samples of sand this way prepared were taken for indication the sulphur content with thermal method with Leco CS 444 apparatus (Table 5).

Table 5: *Content of Sulphur in Individual Moulding Sands [6].*

Sand No.	Content of Sulphur in Moulding Sand (%)
Sand-1	0.080±0.006
Sand-2	0.070±0.008
Sand-3	0.072±0.006
Sand-4	0.045±0.007

George *et al.* at American foundry society studied the emission factors of hazardous air pollutants or HAP's and gave the emissions factor table for chemical binders [7]. Holtzer and Danko studied molds and cores in foundry industry and explained the influence of sulphur on casting skin formation [2]. Jiyang, professor, Dalian University of technology, China, studied colour metallography of cast iron and explained effect of segregation on the properties and structure of gray cast iron [8]. Choudhari *et al*. specified that one of the many reasons in the intricate sand casting process, is the absence of theoretical regulation. Current casting process depends on design engineer's knowledge, awareness and experience. Recalculations, repetitions and adjustments repeatedly increase scraps and higher cost [9]. Ravi *et al.* analyzed that reasons for poor design of cast part connected with manufacturability are multiple casting shrinkage defects which are ill reduced by making changes to tooling and method parameters [10]. Suleiman *et al.* used FORTRAN to study the thermal antiquity of the sand casting process. Area near the junction is the lastly solidifying area in casting [11]. Mirbagheri *et al.* have deliberated the molten metal flow and result of roughness of mold of sand mold [12]. Kermanpur *et al.* investigated solidification and molten metal flow in the multi-cavity mold for casting components made of grey cast iron including a flywheel and a disc brake. They determined that it is essential to consider balanced arrangement for finding a similar heat transfer and casting solidification conditions for all cast parts in each multi-cavity mold [13]. Pathak *et al*. deliberated that the solidification boundary is influenced by the properties of mold filling on progress of the solid-liquid boundary during casting solidification and concluded that the remaining flow resulting from the filling process also influences it considerably [14]. Masoumi *et al.* deliberates the impact of gating design on mold filling for light-weight metal casting processes. The pattern of mold filling is excessively influenced by the size, shape and location of the gate and the ratio of the gating system [15]. Hsu *et al.* (2009) applied computational methods for studying the multiple-gate runner system for gravity casting in sand molds. Fras *et al.* premeditated the evolution from grey to white during casting solidification process, both experimentally and analytically, for plate and wedge shaped castings of various dimensions. The modulus of the casting and the heat flow through the casting mold determines the casting solidification rate [16]. In the literature survey, it has been determined that MAGMASOFT Software can be used to study the impeller shaped casting. Influence of location, shape and size of feeders and parameters such as filling pattern, pressure and velocity, cooling rate, solidification and related defects were studied. The forecasted data were then matched with experimental conclusions and an excellent contract between them was tested. Ravi *et al.* focused on casting design and simulation using computer aided tools [10]. Research describes a comparably good and quicker perception for optimizing the feeder and gating design of castings. Behera *et al.* has recommended that to minimize the bottleneck sand non-value added time in casting improvement; the application of computer aided methoding and casting simulation is recommended which ultimately helps in reducing the number of tryouts casting required on the shop floor [17].

RESULTS AND DISCUSSION

Microstructures were examined using the light microscope Zeiss and electron scanning Hitachi 3500 N. Also the examinations of the content and elements of outer layers of castings in chosen areas were done with EDS microanalyzer of the Noran company. It was observed that casting carried out by sand 3R had thickness of lamellar graphite of 600 µm. Apart from flake graphite sulphide and ferrite emissions were also observed. Sulphides were observed on the petals of graphite [3].

Samples were immersed in conducting bakelite, then grinding and polishing was done. Then samples were etched with 3% nital to reveal differences of the structure between the surface layer and the casting interior. Sample 3 had extended substituents which were subjected to detailed analysis [4].

Research was carried out for various hardener contents within the limits: 40, 50, 55 and 60% in relation to the quantity of resin. Mechanical properties were measured as a function of hardening time: 2, 6 and 24 h [5]. The optimal content of hardener for all tested moulding sands is 50%. Only for the sand 2 the highest strength was achieved at 40% of hardener. Furthermore, it was found that all used hardeners give similar binding kinetics.

The content of sulphur in sands was observed by LECO CS444 apparatus using the thermal method. The results of the observation are as follows.
Sand 1: Activator 1: 0.077% S,
Sand 2: Activator 2: 0.053% S,
Sand 3: Activator 3: 0.045% S,
Sand 4: Activator 4: 0.052% S.

The use of hardeners with reduced content of sulphur-derivative acids resulted in a significant reduction in the sulphur content in the sands tested.

EDS analysis showed little tracks of this element for the sample of the casting made in Sand 3 about the content of sulphur 0.072%. Below a chosen scanning image was placed for this sample of the experimental casting with four areas marked, in which chemical composition analysis was performed [6].

CONCLUSIONS

Reviewing these papers we can conclude that: Applying no-bake sand with furfuryl resin on reclamation sand warp, in which the content of sulphur is higher, leads to the degradation of graphite in the surface of the cast iron. The evenness and the size of this zone will depend on the sulphur content in reclamation sand [3]. An influence of the casting module was observed by the researchers on the kind of metallic matrix. In the structure of castings, especially in Sample 3 and in Sample 4, extended constituents appeared. Their chemical composition mainly showed the presence of coal, iron and silicon, as well as magnesium, aluminium and oxygen [4].

The possibility of diffusion of sulphur, coming from the hardeners to the castings surface depends on casting alloy type. This interaction can cause changes in the casting structure, both in the form of fracture initiation and in the phase deformation. Hence development of new types of hardeners with reduced emission of sulphur is done. The new types of hardeners which decreased the emission of sulphur were produced [5]. The content of sulphur in sand upto 0.080% does not cause appearance of the defect of spheroid graphite deformation in the external layer of the casting. Even relatively high content of sulphur in hardeners, when preparing sand based on fresh quartz sand, isn't threatening with negative consequences in forming degenerate graphite [6].

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