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New Pro-ecological Alkyd Binder for Moulding Sands with Limited Solvent Content

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Abstract

Moulding sands with an alkyd binder are used primarily in the production of massive castings, mainly of cast steel, but they can also be used for castings made of other alloys. Moulding sands with an alkyd binder compete with self-hardening sands with phenolic and furfuryl resins. They have several advantages in common with furan moulding sands, such as excellent knock-out properties and very good quality of the casting surface. Additionally, alkyd moulding sands do not contain nitrogen, sulphur, formaldehyde and water, various sands can be used as a matrix: quartz, chromite, zircon or olivine and a high proportion of reclaimed material (up to 90%), moreover the moulding sand has high plasticity. The disadvantages of this technology include limited ability to adjust the hardening time, high binder viscosity and high sensitivity of the moulding sand to the matrix and the ambient humidity. The Prec-Odlew company is a Polish manufacturer of, among others, alkyd resins for the foundry industry. As part of the project: "Development and implementation of technologies for obtaining ecological binders (systems) for bonding highly refractory ceramic materials" (RPMP.01.02.01-12-0636/18) two new alkyd resins were developed with a reduced amount of solvents: SL2017 and SL2019. So far, resins of this type contained approximately 40–50% of solvents, including aromatic ones. The newly developed resins have a reduced amount of solvents in their composition – they contain from 20% to 30% and mainly non-aromatic solvents. The SL 2019 resin contains solvents that do not include any aromatic compounds in the form of hydrocarbons. This article presents the results of testing the properties of moulding sands using the standard alkyd resin and the newly developed resins. The obtained results confirmed the possibility of making moulding sands with innovative binders, and even higher strength values were observed than in the case of the reference moulding sand with the SL 2002 binder.

Keywords:

pro-ecological moulding sand, innovative binder, alkyd binder, solvent content, properties of moulding sand

1. INTRODUCTION TO THE SUBJECT AND PURPOSE OF THE RESEARCH

The alkyd binder consists of an alkyd resin modified with drying oil and a liquid hardener based on polyisocyanate. Alkyd resin belongs to the group of unsaturated polyester resins. The binding process of the moulding sand takes place in two stages. In the first stage, the polyisocyanate reacts with the alkyd resin to produce a urethane binder. This reaction allows the moulding sand to gain strength enough to remove the model from the mould or the core from the core box. The second stage of binding involves the oxidation and polymerization of the drying oil contained in the resin in the presence of air [1–3].

Moulding sands with an alkyd binder are used primarily in the production of massive steel castings, but they can also be used for castings made of other alloys. They compete with self-hardening moulding sands with phenolic and furfuryl resins [2–5].

On December 1, 2010, the Regulation of the European Parliament and of the Council (No. 1272/2008 of December 16, 2008 on the classification, labelling and packaging of substances and mixtures) entered into force, which classifies furfuryl resins with a content of more than 25% free furfuryl alcohol as toxic. Furfuryl resins that contain a smaller amount of free furfuryl alcohol are considered to be harmful. In addition, technological processes that emit harmful substances from the BTEX group, in particular from polycyclic aromatic hydrocarbons (PAHs), should be limited, and such are emitted from currently used technologies like furan no-bake process [2, 6]. This will mean that the self-hardening moulding sands with furfuryl resins, which dominate in the global foundry industry, may lose their current importance due to such a significant reduction in the content of free furfuryl alcohol due to the deterioration of technological properties. They can be successfully replaced by alkyd binders, which will also meet the high requirements regarding environmental hazards. In paper [4] the application of alkyd resin has been proposed as a pro-ecological solution. Increasing legislative restrictions concerning the environment protection as well as the growing social pressure, means that the foundry industry is searching for new, more environment friendly moulding and core sands technologies or modifications of currently used ones, to limit the emission of harmful substances and smells during preparation, pouring, cooling, and knocking out of moulding sands [7].

Alkyd moulding sands have several advantages in common with the furan no-bake process, such as excellent knock-out properties and very good quality of the casting surface. They also have many additional advantages, such as [2–6, 8]:

- do not contain nitrogen, sulphur, formaldehyde and water,
- lower emissions of BTEX compounds than in the case of other technologies, such as furan no-bake or bentonite sands (low toxicity index T_{NDS}),
- possibility of using various types of matrix: quartz sand, chromite, zircon, olivine,
- possibility of using a high percentage of reclaimed sand, up to 90%,
- low tendency to create pinholes and gas bubbles,
- moulding sands show high plasticity during casting shrinkage,
- long bench life, which is very important when producing moulds for heavy castings.

The disadvantages of this technology include limited ability to adjust the hardening time, high binder viscosity and high sensitivity of the moulding sand to the matrix and the ambient humidity. Also problematic are the following processes:

- the affinity of the drying oil to oxygen present in the air that causes the formation of an oxidized layer on the surface of the binder in the container,
- the interaction between isocyanate and moisture contained in the air that creates products of the binding reaction on the surface of the mixed sand [8].

The Prec-Odlew company is a Polish manufacturer of, among others, alkyd resins for the foundry industry. As part of the project: "Development and implementation of technologies for obtaining ecological binders (systems) for bonding highly refractory ceramic materials" (RPMP.01.02.01-12-0636/18) two new alkyd resins were developed with a reduced amount of solvents: SL2017 and SL2019. So far, resins of this type – like SL2002 – contained approximately 40–50% of solvents, including aromatic ones. The newly developed resins have a reduced amount of solvents in their composition – they contain from 20% to 30% and are mainly non-aromatic solvents. The SL 2019 resin contains solvents that do not include any aromatic compounds in the form of hydrocarbons. Reducing the content of solvents in new binders contributes to the lower emission of harmful substances during the moulding process and the thermal decomposition of the moulding sand during pouring and knocking out.

The SL2002 resin contains a mixture of hydrocarbons in its composition, which reduce the viscosity of the binder. These hydrocarbons also contain a certain amount of aromatic hydrocarbons, which have harmful effects on the environment, especially the working environment. Efforts have been made to develop a binder with a reduced amount of solvents, which are hydrocarbons, thereby reducing aromatic compounds. The work carried out in Prec-Odlew's laboratories led to the development of two new binders, SL2017 and SL2019. These are new resins and previously unused. The idea behind these trials was an extensive theoretical analysis of the curing process of polymers, which showed that it is possible to replace part of the solvent with a component that is part of the binder, i.e. linseed oil (its reactant). SL2017 is a resin where the solvent has been partially replaced by linseed oil. The positive results of this research were the development of another new resin SL2019, which contains no solvents in the form of hydrocarbons, an important technological innovation. This was achieved by changing the method of resin synthesis to reduce its viscosity. The complete elimination of solvents usually results in a deterioration of the proper grain wrapping of the sand matrix, which disqualifies such a binder for casting purposes. Therefore, a new original thixotropic additive was introduced into the binder which eliminated this disadvantage. Two new resins were thus obtained and which needed to be tested under broader laboratory conditions.

2. DESCRIPTION OF THE MATERIAL/TEST STAND AND RESEARCH METHODOLOGY

The tests were carried out for moulding sands using three different alkyd resins: the standard SL2002 resin already available on the foundry market and two newly developed SL2017 and SL2019. The following moulding sands compositions were used in the tests (typical for these kinds of moulding sands [7, 9]):

- quartz sand (Grudzeń-Las with medium grain size d_{50} = 0.25 mm) – 100 parts by weight,
- alkyd resin (SL2002, SL2017, SL2019) – 0.8; 1.0; 1.3 parts by weight,
- KL catalyst – 20%; 25%; 35% of the weight of the resin.

In the first stage, moulding sands with a resin content of 1.0 parts by weight were prepared in a laboratory paddle mixer. At the beginning, the matrix and catalyst were put into the mixer bowl and mixed for 90 seconds, then the resin was added and mixed for another 90 seconds. Then, standard samples were prepared on a LUZ-1 vibrating device. The compaction time was 15 seconds and the vibration amplitude was 2 mm. In the second stage, moulding sands of variable composition (resin content from 0.8 to 1.3 parts by weight and catalyst from 20% to 35% of the weight of the resin) were prepared in a laboratory circular mixer, first the matrix and catalyst were mixed for 2 minutes, then the resin was added and mixed for another 2 minutes. Then, standard samples were prepared by manual compaction.

The strength of moulding sands was tested using the universal LRu-2e apparatus for measuring the strength of moulding sands from Multiserw-Morek. The permeability measurement was carried out using the LPiR device. The designation of the loss on ignition was made according to the PN-83/H-04119 standard (withdrawn standard), using a high-temperature furnace at a temperature of 1000°C. The amount of released gases was tested according to the BN-76/4024-05 standard, using an apparatus for determining the gas formation of moulding sands at a temperature of 1000°C. The results presented are the average of three measurements.

3. ANALYSIS AND DISCUSSION OF THE OBTAINED RESULTS

Table 1 shows the physical properties of the tested alkyd resins. Table 2 shows the results of testing the strength and permeability of moulding sands with various alkyd resins: SL2002, SL2017 and SL2019 with a resin content of 1.0 part by weight and a catalyst of 25% to the resin. The results of tensile and bending strength as a function of hardening time are presented graphically (Fig. 1 and Fig. 2). The chart (Fig. 3) shows the results of bench life measurement for the reference moulding sand with SL2002 resin.

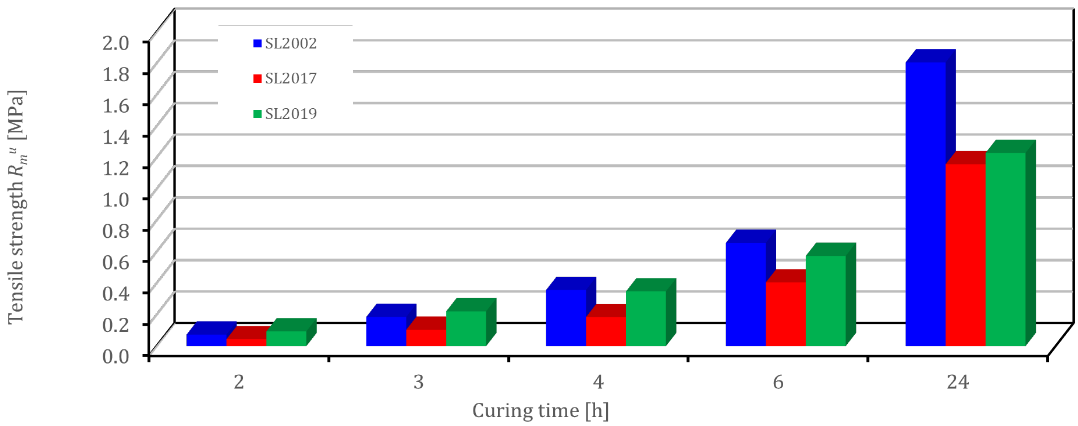

Fig. 1. Tensile strength R_m^u of moulding sand with alkyd resin SL2002, SL2017 and SL2019 as a function of curing time. Moulding sand composition: quartz sand – 100 parts by weight, resin – 1.0 part by weight, KL catalyst – 25% of the weight of the resin (laboratory paddle mixer, vibrating compaction)

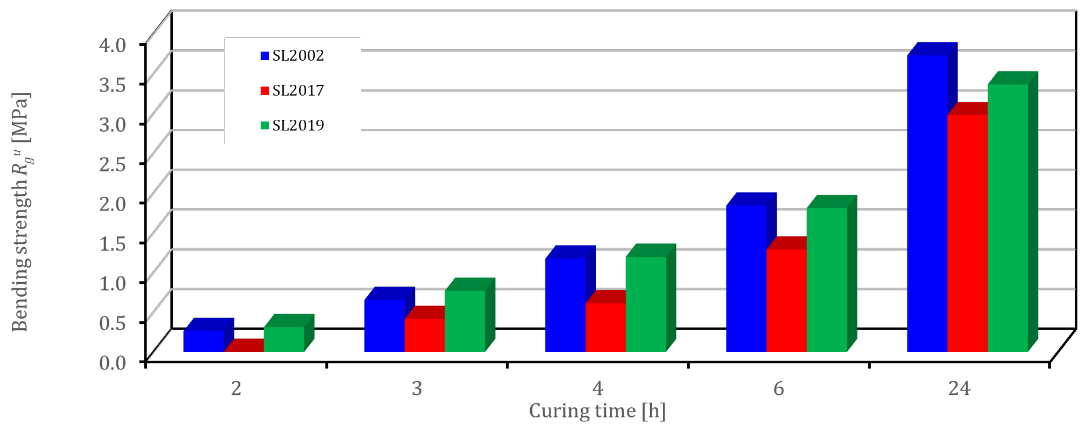

Fig. 2. Bending strength R_g^u of moulding sand with alkyd resin SL2002, SL2017 and SL2019 as a function of curing time. Moulding sand composition: quartz sand – 100 parts by weight, resin – 1.0 part by weight, KL catalyst – 25% of the weight of the resin (laboratory paddle mixer, vibrating compaction)

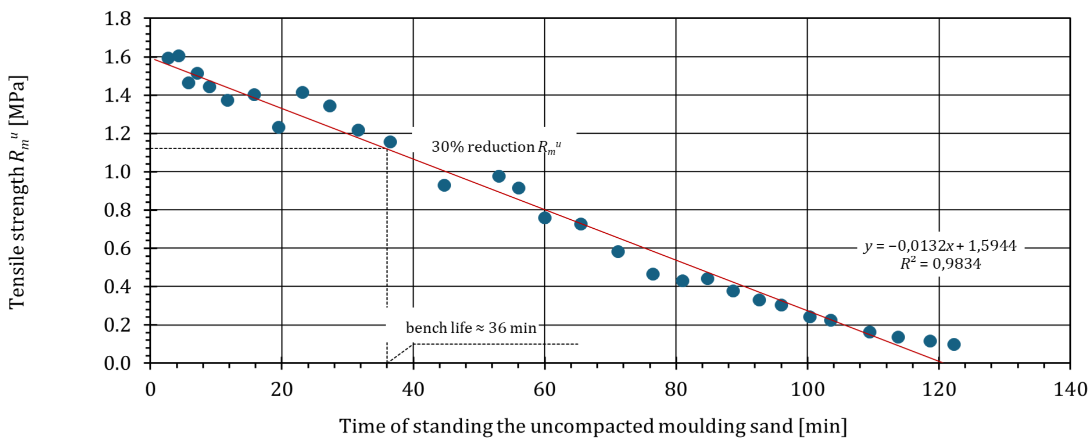

Fig. 3. Tensile strength R_m^u of moulding sand with SL2002 alkyd resin as a function of time of standing the uncompact moulding sand. Moulding sand composition: quartz sand – 100 parts by weight, resin – 1.0 part by weight, KL catalyst – 25% of the weight of the resin (laboratory paddle mixer, vibrating compaction)

The physical properties of the newly developed SL2017 and SL2019 alkyd resins are different to those of the reference resin SL2002 (Table 1). The SL2019 alkyd resin has a higher density than the standard SL2002, but the viscosity is similar. The SL2017 has the same density as standard resin, but a significantly lower viscosity compared to SL2002 and SL2019.

The lowest strength parameters among the tested moulding sands were obtained by the new SL2017 resin with the assumed composition, and the highest – after 24 hours of hardening – by the moulding sand with SL2002 resin: tensile strength R_m^u = 1.81 MPa and bending strength R_g^u = 3.73 MPa. The moulding sand with SL2019 resin had lower strength values compared to SL2002, i.e. tensile strength R_m^u = 1.23 MPa and bending strength R_g^u = 3.37 MPa. The moulding sands with the new binder have binding kinetics typical for self-hardening moulding sands with alkyd resin, achieving high strength after 24 hours of curing. The moulding sands prepared with the new SL2017 and SL2019 alkyd resins have approximately 25% higher permeability than the reference moulding sand with the SL2002 resin (Table 2).

A very important parameter of the moulding sand is its bench life. To evaluate this property, a method was chosen which involves measuring the standing time of the uncompacted moulding sand, resulting in a 30% reduction in its strength after 24 hours of hardening. The marking was made on samples compacted on a laboratory tamper. The results of these studies are presented in Figure 3.

The bench life of the moulding sand with SL2002 alkyd resin in laboratory conditions was approximately 36 minutes. Moulding sands with new SL2017 and SL2019 resins have a slightly longer bench life of approximately 50–60 minutes. Bench life is a feature that reflects the kinetics (rate) of moulding sand binding. In the case of small forms, this value is satisfactory. For large moulds, when we need to prepare great amounts of moulding sand, it may be too short. The research was conducted in a laboratory setting and thus, when selecting the composition of the sand, the individual conditions of the foundry and its production profile should be taken into account.

The charts (Fig. 4 and Fig. 5) present the results of testing the strength of moulding sands with a variable share of resin and catalyst for all three tested alkyd resins. Table 3 shows the results of measuring gas formation and loss on ignition for moulding sands with various alkyd resins.

Then, extensive tests were carried out on new moulding sands with varying proportions of their individual ingredients (Figs. 4 and 5). This was used to select sand composition for the individual needs of a specific foundry.

With a content of 1.3 parts by weight, the tensile strength R_m^u after 24 h of the moulding sand with SL2019 resin was 1.6 MPa, with SL2017 resin was 1.3 MPa, and for the reference moulding sand with SL2002 – 1.4 MPa. The bending strength R_g^u after 24 h of the moulding sand with SL2019 resin was 4.1 MPa, with SL2017 resin – 3.3 MPa, and for the reference moulding sand with SL2002 – 3.4 MPa, with the same resin content of 1.3 parts by weight. Very high strength values were obtained for the moulding sand with SL2019 alkyd resin. Only with the content of 0.8 parts by weight was the bending strength lower than for the moulding sand with SL2017 and SL2002 resin. Analyzing the obtained strength properties of the moulding sand, it can be concluded that very good results were obtained for the SL2019 binder. A reduction in the hardening time was also achieved compared to those currently used on the market, with a resin content of 1.0 and 1.3 parts by weight.

Table 1
Physical properties of the tested alkyd resins

Parameter	Test method	SL2002	SL2017	SL2019
Density at 20°C [g/cm³]	ISO 2811-1 standard (pycnometric method)	0.94–0.95	0.94–0.95	0.99–1.00
Kinematic viscosity at 20°C [s] average of 5 measurements	ISO 2431 standard (flow cup with diameter 4 mm)	166	48	179

Table 2
Results of the strength and permeability of moulding sands with various alkyd resins

Curing time [h]	SL2002	SL2017	SL2019	SL2002	SL2017	SL2019	SL2002	SL2017	SL2019
	Tensile strength R_m^u [MPa]			Bending strength R_g^u [MPa]			Permeability $P^u \times 10^{-8}$ [m²/(Pa·s)]		
2	0.07	0.04	0.09	0.26	0.00	0.31	190	235	240
3	0.19	0.10	0.22	0.66	0.42	0.77			
4	0.36	0.19	0.35	1.18	0.61	1.20			
6	0.66	0.41	0.57	1.84	1.29	1.81			
24	1.81	1.16	1.23	3.73	2.98	3.37			

Moulding sand composition:
quartz sand – 100 parts by weight, resin – 1.0 part by weight, KL catalyst – 25% of the weight of the resin (laboratory paddle mixer, vibrating compaction)

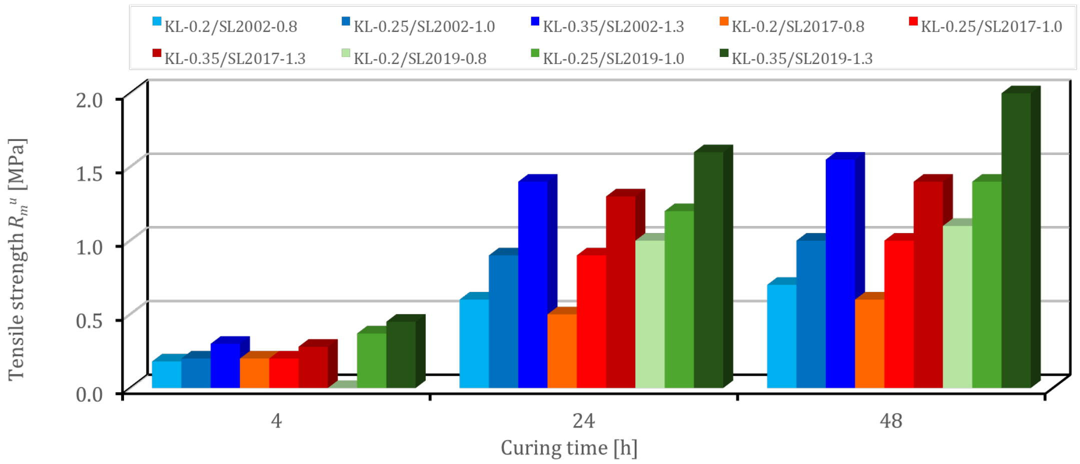

Fig. 4. Tensile strength R_m^u of moulding sand with alkyd resin SL2002, SL2017 and SL2019 as a function of curing time, with different proportions of resin and catalyst (laboratory circular mixer, manual compaction)

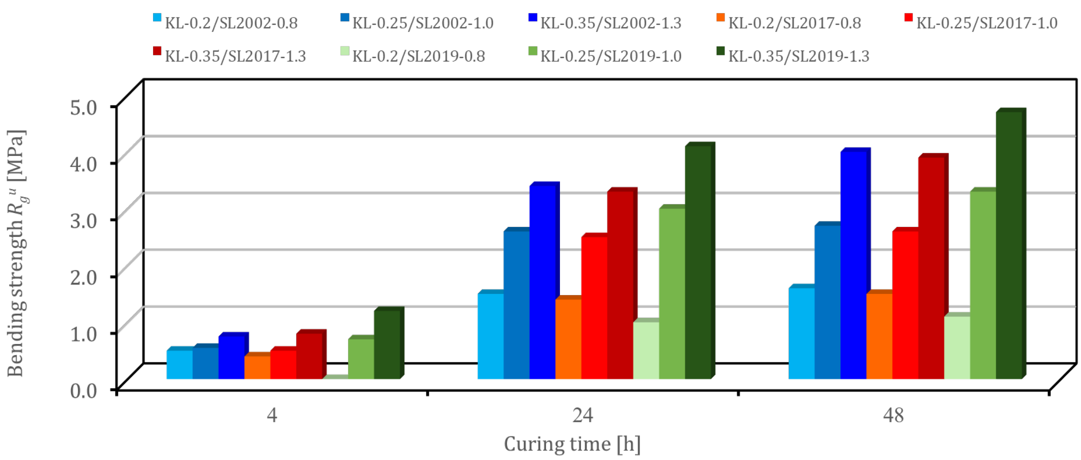

Fig. 5. Bending strength R_g^u of moulding sand with alkyd resin SL2002, SL2017 and SL2019 as a function of curing time, with different proportions of resin and catalyst (laboratory circular mixer, manual compaction)

This is evidenced by the fact that the bending strength of the R_g^u moulding sand with SL2019 after 24 h (resin content of 1.3 parts weight) is 4.1 MPa. However, the moulding sand currently used on the market with the SL2002 resin achieves such strength after 72 hours, with the same resin content.

The last point of the work was the determination of the loss on ignition and gas formation of the tested moulding sands (Table 3).

In the case of moulding sands with newly developed SL2017 and SL2019 resins, slightly higher values of loss on ignition and gas formation were observed, which is related to the modification of the alkyd resin composition towards lowering the solvent content and replacing it with a component that is a part of this binder. The results of loss on ignition testing are similar to those presented in article [7]. However, the results of gas formation testing are higher than presented in [8, 9]. In [8] moulding sand with SL2002 resin has 11 cm^3/g of gas volume.

It is worth adding that moulding sands with SL2002 and SL2017 resins have a specific scent, while the moulding sand with SL2019 alkyd resin is very faint. Another success of the project is the development of a resin with a significantly reduced odor during moulding sand preparation and moulding, which significantly improves conditions in the workplace.

Table 3
Results of the measurement of gas formation and loss on ignition samples of moulding sands with various alkyd resins

Parameter	SL2002	SL2017	SL2019
Loss on ignition [%]	1.30	1.35	1.40
Gas formation [cm^3/g]	16	17	17

Moulding sand composition:
quartz sand – 100 parts by weight, resin – 1.3 parts by weight, KL catalyst – 35% of the weight of the resin

4. CONCLUSIONS AND SUMMARY

The analysis of the results of the carried-out research allowed to formulate the following conclusions:

- Newly developed alkyd resins SL2017 and SL2019 with a reduced amount of solvents in their composition can be used for the preparation of moulding sands. Tests of the properties of the moulding sands confirmed the possibility of their use. The moulding sand with SL2017 resin achieved lower strength values than moulding sand with SL2019 resin. The modification of the composition did not negatively affect the bench life of the moulding sand, but improved its permeability.
- Strength properties are the result of many factors, such as ambient conditions, mixing and compaction method, which can be observed from the results obtained with the rotary or paddle mixer and with vibrating or manual compaction.
- Another success of the project is the development of the SL2019 alkyd resin with reduced odor in the moulding sand, which significantly improves the conditions at the workplace.

Acknowledgments

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