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Investigations of Properties of Moulding Sands with Resins Applied in the Alphaset Technology

M. Holtzer, A. Bobrowski, D. Drożyński [a],*, J. Makselon, B. Isendorf [b]

[a] Faculty of Foundry Engineering, AGH University of Science and Technology , Reymonta 23 St., 30-059 Cracow, Poland
[b] CEMA MYSTAL Sp. z o.o., Partyzantów 21 St., 42-300 Myszków, Poland
*Corresponding author. E-mail address: holtzer@agh.edu.pl

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Abstract

In process, known as the ALPHASET process, the alkaline phenol-formaldehyde resin, resol type, containing below 1% of hydrous phenol and below 0.2 % of free formaldehyde - is applied. As hardeners esters are used. An alkaline character of the process allows an application of all kinds of sands, including highly alkaline, This moulding sands can be used for moulds and cores of all alloys, and are especially advantageous for steel castings, in which hot cracks can occur. The following systems of a basic character containing phenol-formaldehyde resins were selected for investigations: REZOLIT AM resin + Prestal R-1/5 hardener; ESTROFEN resin + PR6 hardener; AVENOL 700 NB resin + Katalysator 4040 hardener. High-silica sand from Biała Góra was used as a matrix. Laboratory tests were performed under the following conditions: temperature 20-22^{o}C, humidity 35-50%. Selection of the proper resin as a binding agent for moulding sands must be preceded by the economic analysis of costs of resins and hardeners. This selection should be done on the grounds of the moulding sand technological requirements and the produced assortment of castings and their weight.

Keywords: Mechanical properties, Technological properties, Moulding sands, Alphaset technology, Alkaline organic binder

1. Loose self-hardening moulding sands with phenolic resin hardened by esters

In this process, known as the ALPHASET process, the alkaline phenol-formaldehyde resin, resol type, containing below 1% of hydrous phenol and below 0.2% of free formaldehyde - is applied. As hardeners esters are used, by means of which a hardening rate can be regulated. An alkaline character of the process allows an application of all kinds of sands, including highly alkaline, as matrices. Using of more coarse sands requires an application of protective coatings (hydrous or alcoholic).

The reclaimed material obtained from these moulding sands by means of mechanical reclamation should not have more than 1.5% ignition losses and alkali content of maximum 0.15%.

The described above moulding sands can be used for moulds and cores of all alloys, and are especially advantageous for steel castings, in which hot cracks can occur [1-10].

Phenol-formaldehyde resins are obtained as a poly-condensation product of phenol and formaldehyde. The synthesis process of this resin occurs in the presence of a catalyst, which can be either of a basic or acidic character. Depending on the kind of the applied catalyst, that is on the environment kind (acidic or basic) and the ratio of phenol to formaldehyde, products of different properties are obtained. In an acidic environment the polycondensation is performed with a formaldehyde shortage and novolak (compound of a linear built) is obtained. In a basic environment an excess of formaldehyde is used and resols are obtained (of a linear built).

Phenol-formaldehyde resins of a resol type are used for making no-bake sands: loose self-hardening sands, loose fast-hardening sands and loose self-setting sands. In case of loose self-hardening sands acidic hardeners are used, mainly sulphonic acids. In these sands a resin can enter into a two-component binder (e.g. with phenolic polyisocyanate – Ashland's process) and then amines are catalysts. Loose self-setting sands are used in the hot box method. Hardening occurs due to a high temperature influence.

In recognition of the European Union requirements of limiting the furfuryl alcohol content in furan resins, which is related with classification of this compound as toxic, some companies producing binding agents for foundry industry suggest introducing the alphaset technology as a substitute of moulding sands with furan resins. However, a significant limitation in introducing the Alphaset technology is a fact that spent sands from this technology are difficult to be subjected to the mechanical reclamation [11].

Therefore within the frames of the NOT project (the Central Technical Association) together with the CEMA MYSTAL Company the investigations aimed at comparing properties of moulding sands from the Alphaset technologies using resins originated from various producers [12], were undertaken.

2. Own investigations

2.1. Materials used in investigations

The following systems of a basic character containing phenol-formaldehyde resins were selected for investigations:

- REZOLIT AM resin + Prestal R-1/5 hardener;
- ESTROFEN resin + PR6 hardener;
- AVENOL 700 NB resin + Katalysator 4040 hardener.

High-silica sand from Biała Góra was used as a matrix. Laboratory tests were performed under the following conditions: temperature 20-22^{o}C, humidity 35—50%.

2.1.1. Moulding sands with the Rezolit AM resin

The Rezolit resin is a highly condensed basic resol applied in the loose self-hardening sands technology. Hardening occurs with a participation of the Prestal R hardener at a room temperature. It is especially suitable for making moulds and cores for castings of high quality cast steel. It is characterised by the following parameters: free phenol content < 0.8%; free formaldehyde content < 0.1%, viscosity 60-100 mPa·s; pH = 12 – 14; The initial moulding sand composition: high-silica sand 100 parts by mass; Prestal R1 hardener – 0.3 parts by mass; Rezolit AM resin – 1.5 parts by mass. In addition, the resin contains potassium hydroxide in an amount < 20% and methanol in an amount $3.0 \le c \le 10\%$. The Prestal R1 hardener (basic hardener of a middle reactivity) is prepared on the basis of esters and other enriching additions. It is usually added in an amount of 15 – 25 mass% in relation to a resin. Hardeners R are divided into two groups:

a) R 1/2; R 1/3; R ¼ ; R 1/5 – a group of these hardeners indicates an increasing reactivity in relation to the R1 hardener (it means that R 1/5 hardener is the most reactive – it is the fastest binder);
b) R 2/1; R 3/1; R 4/1; R 5/1 – a group of these hardeners indicates a decreasing reactivity in relation to the R1 hardener (it means that R 5/1 hardener is the least reactive – the slowest).

2.1.2. Moulding sands with the Estrofen resin

The Estrofen resin is the basic resol resin applied for production of moulds and cores. This resin contains 35-50% of phenol, 10 –12.5% of KOH, and 0.1 – 0.2% of formaldehyde. This resin is not flammable, has pH > 11, and its dynamic viscosity - at 25^{o}C - equals 70 mPa·s.

The PR5 hardener is used for resol type resins. It contains 15 –25% of butyrolactone and 20 – 25% of propylene carbonate.

2.1.3. Moulding sands with the Avenol NB 700 resin

The Avenol resin is the - modified in a basic solution of pH app. 14 - phenol-resol resin, cold hardened. It is intended for mould and core production for all kinds of foundry alloys. It is usually applied in amount of 1.5% with an addition of a catalyst from series 4000 in amounts of 0.25 – 0.30%. This resin contains < 5 <10 % NaOH, < 5< 10% KOH, methyl alcohol < 3 < 10%; free phenol < 1.50%.; formaldehyde < 0.1 < 0.2%. The moulding sand working time can be regulated, from a few to a dozen or so hours, in dependence on the applied hardener (catalyst). The catalyst 4040 is a modified mixture of esters of pH app. 4-7.

3. Results of investigations and their discussion

3.1. Moulding sand with the Rezolit AM resin and Prestal R1/5 hardener

The obtained results for moulding sands with the Resolit resin, at various fractions of resin and hardener, are presented in Figures 1a – d, respectively of: bending strength (Fig 1a), tensile strength (Fig. 1b), permeability (Fig. 1c) and abrasive wear (Fig. 1d).

The applied Prestal R 1/5 hardener belongs to the group of the fastest (the most active) hardeners for this resin. This was of an essential meaning for tests, in which a larger fraction of a hardener was used (13% and more in relation to the resin amount), since in such case the moulding sand working time was so short that it was not possible to perform the full series of investigations e.g. bending strength, permeability or abrasive wear (the tests were carried out at an ambient temperature: 20-22°C, while at a lower temperature the working time will be - for sure - prolonged). Laboratory tests should be made in the future with using slower hardeners.

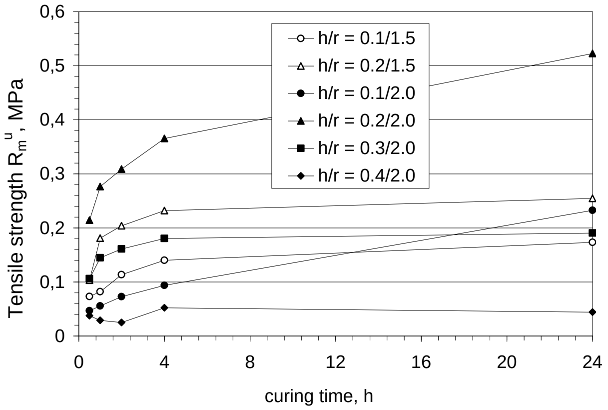

Fig. 1a. Dependence of the tensile strength on the hardening time of the moulding sand with the Rezolit resin and Prestal R-1/5 hardener (r - resin, h - hardener)

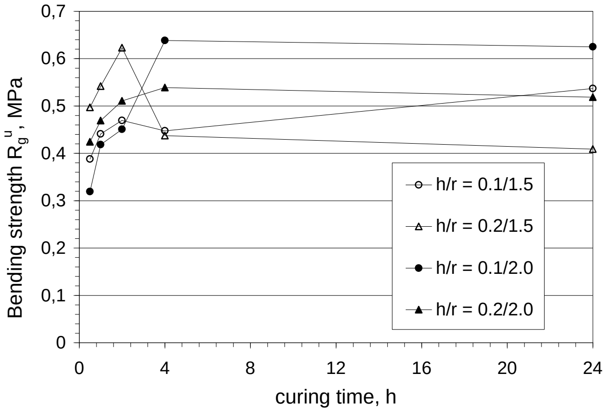

Fig. 1b. Dependence of the bending strength on the hardening time of the moulding sand with the Rezolit resin and Prestal R-1/5 hardener (r - resin, h - hardener)

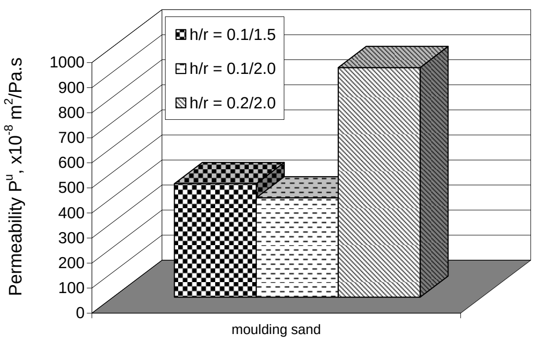

Fig. 1c. Dependence of the permeability on the moulding sand with the Rezolit resin and Prestal hardener (r - resin, h - hardener)

The tensile strength values after 24 hours were quite small and did not exceed 0.25 MPa. Only the moulding sand with addition of 2.0 parts by mass of resin and 0.2. parts by mass of hardener (10%) exhibited higher strengths both of bending and tension (above 0.50 MPa).

This moulding sand was characterised by a high permeability. Two times decrease of the hardener amount (to 0.1 parts by mass) caused drastic decrease of a bending strength (to app. 0.20 MPa), in spite of maintaining a high tensile strength. Such moulding sand had also significantly lower permeability than the sand which had 0.2 parts by mass of a hardener.

A high permeability of moulding sands was caused by their low apparent density (weak condensation of sands - they were setting too fast and their fluidity decreased).

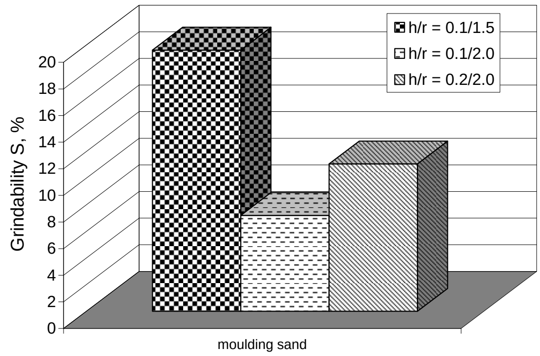

Fig. 1d. Dependence of the grindability on the moulding sand with the Rezolit resin and Prestal hardener (r - resin, h - hardener)

3.2. Moulding sand with the Estrofen resin and PR6 hardener

These moulding sands, containing 13-20 % of the hardener (in relation to the resin) and at least 1.5 – 2.0 parts by mass of the resin indicated the highest strength values. Thus, the tensile strength was 0.70 – 0.80 MPa (Fig. 2a), while bending strength app. 1.50 MPa (Fig. 2b). However, both an excess of the hardener (27%) and its too low amount (6%) caused significant decreases of the tensile strength.

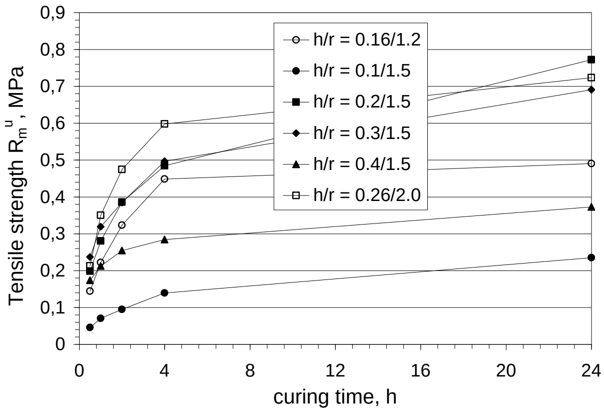

Fig. 2a. Dependence of the tensile strength on the hardening time of the moulding sand with the Estrofen resin and PR6 hardener (r - resin, h - hardener)

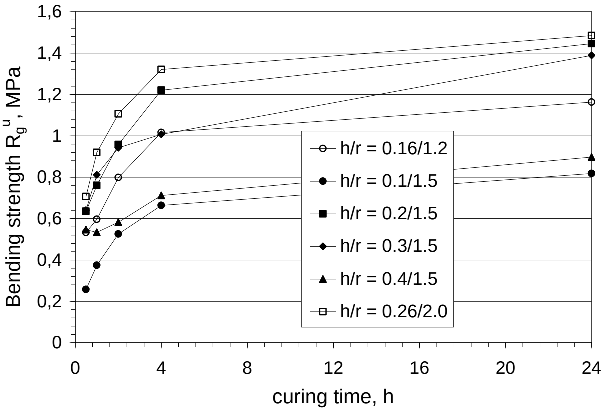

Fig. 2b. Dependence of the bending strength on the hardening time of the moulding sand with the Estrofen resin and PR6 hardener (r - resin, h - hardener)

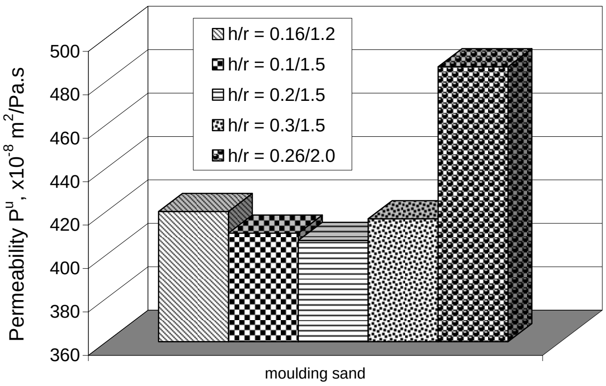

Fig. 2c. Dependence of the permeability on the moulding sand with the Estrofen resin and PR6 hardener (r - resin, h - hardener)

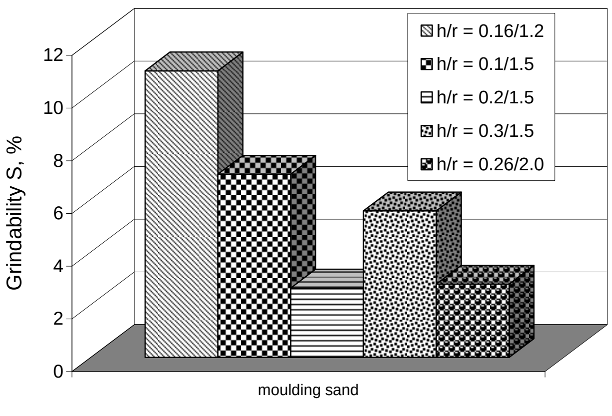

Fig. 2d. Dependence of the grindability on the moulding sand with the Estrofen resin and PR6 hardener (r - resin, h - hardener)

The moulding sand should contain 1.5 parts by mass of the resin and 13% of the hardener. Simultaneously, the moulding sand containing 2 parts by mass of the resin and 13% of the hardener had permeability of an order of 500 units (Fig. 2c), and grinability 2.78% (Fig. 2d). Resin lean moulding sands or containing below 13% of the hardener showed an increased grinability approaching even 11% for sand containing 1.2 parts by mass of the resin and 13% of the hardener.

3.3. Moulding sands with the Avenol NB 700 resin and Katalysator 4040 hardener

Out of the tested 7 moulding sands of various compositions, from 6% to 31% additions of a hardener, only the moulding sand containing 1.6 parts by mass of the resin and 0.1 parts by mass of the hardener (6% in relation to the resin) had a tensile strength equal 0.40 MPa (Fig. 3a). Remaining moulding sands had a tensile strength of 0.60 – 0.80 MPa. As far as the permeability is concerned, all sands have this parameter very similar, at a level of 350 – 400 units (Fig. 3c). In practice, all moulding sands with this resin exhibited an grinability of 2 – 3% (Fig. 3d). The highest bending strength values (above 1.20 MPa) (Fig. 3ab), and tensile strength were achieving sands, which contained at least 25% of the hardener in relation to the resin amount.

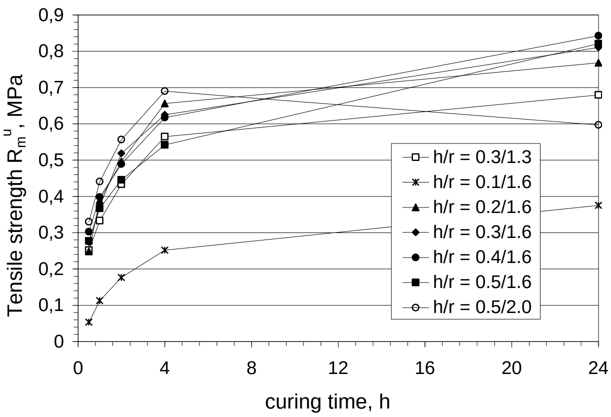

Fig. 3a. Dependence of the tensile strength on the hardening time of the moulding sand with the Avenol NB 700 resin and 4040 hardener (r - resin, h - hardener)

Moulding sands of the same resin content (1.6 parts by mass) and various hardener contents (from 0.1 to 0.5 parts by mass) exhibited an increased tensile strength, up to app. O.3 parts by mass of the hardener (app. 19%), after which a stabilisation of this parameter occurred. An increased resin amount (at 0.5 parts by mass of the hardener) causes a decrease of tensile and bending strengths.

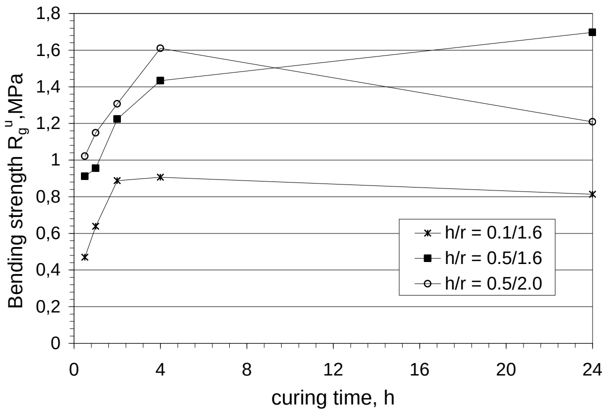

Fig. 3b. Dependence of the bending strength on the hardening time of the moulding sand with the Avenol NB 700 resin and 4040 hardener (r - resin, h - hardener)

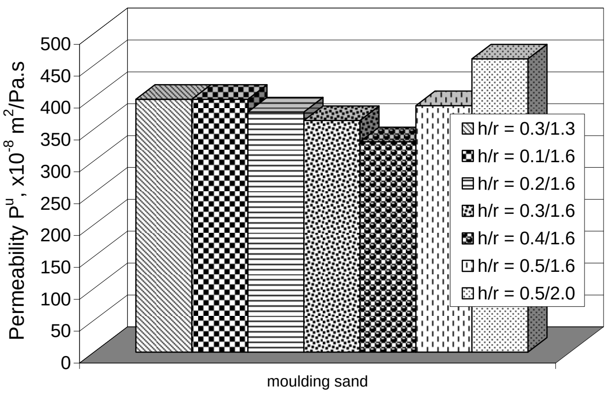

Fig. 3c. Dependence of the permeability on the moulding sand with the Avenol NB 700 resin and 4040 hardener (r - resin, h - hardener)

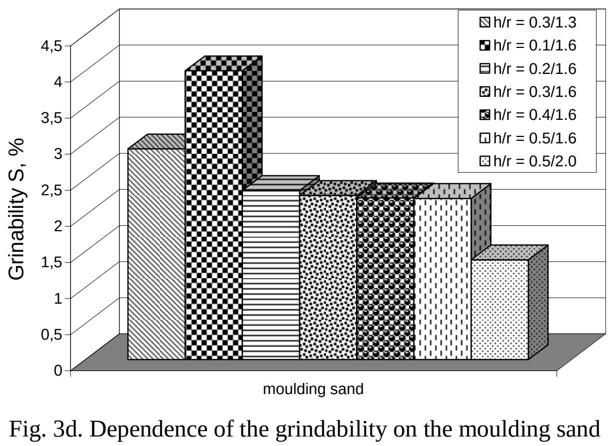

Fig. 3d. Dependence of the grindability on the moulding sand with the Avenol NB 700 resin and 4040 hardener (r - resin, h - hardener)

4. Summary of the obtained results

In order to estimate the tested resins the properties of moulding sands were compared at their optimal compositions (it means at the composition at which each moulding sand had its best parameters). The highest tensile strength values were obtained by the sand with the Avenol resin in the whole investigated time range, and then with the Estrofen and Rezolit resins (Fig. 4a). The sequence of the bending strengths was similar (Fig. 4b).

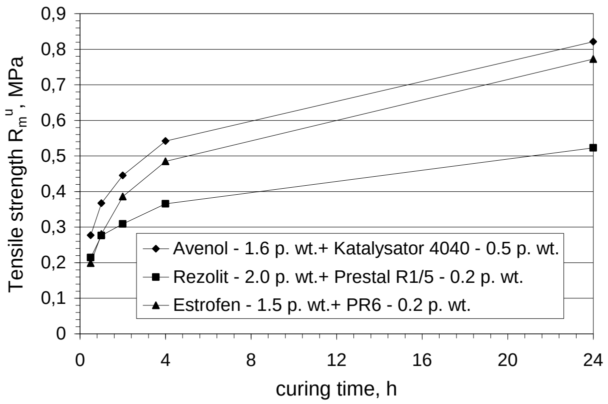

Fig. 4a. Comparison of the bending strength of the tested moulding sands at their optimal compositions

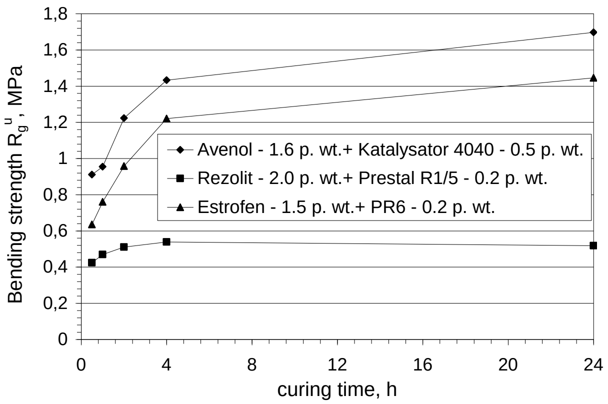

Fig. 4b. Comparison of the bendig strength of the tested moulding sands at their optimal compositions

The permeability of moulding sands with the Avenol and Estrofen resins was comparable, at their optimal compositions and visibly lower than with the Rezolit resin (Fig. 4c). Dependence of the grinability for the tested moulding sands was similar (Fig. 4d).

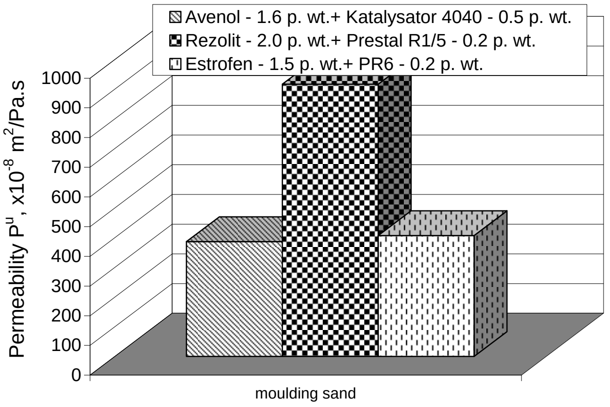

Fig. 4c. Comparison of the permeability of the tested moulding sands at their optimal compositions

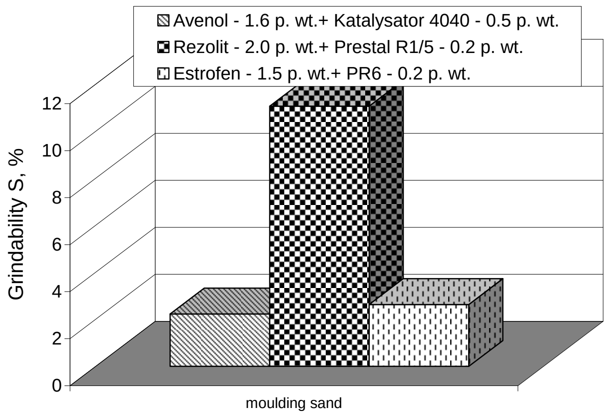

Fig. 4d. Comparison of the grindability for the tested moulding sands at their optimal compositions

Conclusions

On the basis of the performed investigations of moulding sands with 3 highly alkaline phenol resins, resol type, cold hardened and originated from various producers, it can be stated that:

1. Moulding sand with the Rezolit AM resin: The applied hardener Prestal R 1/5 belongs to the group of the fastest (the most reactive) hardeners for this resin. This was of an essential meaning for tests, in which the hardener fraction was larger (13% and more in relation to resin), since then a working time was very short, and performing the full investigation series e.g. bending strength, permeability or grinability was not possible. Investigations were performed at an ambient temperature: 20-22^{o}C, while at lower temperatures the moulding sand working time will be, for sure, longer. A hardener should be selected according to the working time requirements. Tests with the application of slower hardeners should be carried out in the future.
   Tensile strength values after 24 hours were small, not exceeding 0.25 MPa. Only the moulding sand with the resin addition of 2.0 parts by mass and 0.2 parts by mass of the hardener (10%) has higher bending and tensile strength (above 0.50 MPa). This moulding sand was characterised by the high permeability.
2. Moulding sands with the Estrofen resin. These moulding sands with hardener additions in amount 13-20 % (in relation to a resin) and the resin content being at least 1.5 – 2.0 parts by mass, exhibited the highest strength values, thus its tensile strength was app. 0.70 – 0.80 Mpa and its bending strength app. 1.50 MPa. However, both an excess (27%) and too small amount (6.5%) of the hardener were the reason of a significant decrease of the moulding sand tensile strength. This sand should contain at least 1.5 parts by mass of the resin and 13% of the hardener.
3. Moulding sands with the Avenol NB 700 resin. The highest values of a bending strength (above 120 N/cm^2) and a tensile strength achieved moulding sands which contained at least 25% of the hardener in relation to the resin amount.
   Moulding sands of the same resin content (1.6 parts by mass) and various amounts of the hardener (from 0.1 to 0.5 parts by mass) exhibited the tensile strength increase up to app. 0.3 parts by mass (app. 19%), which was followed by the stabilization of this parameter value. An increase of the resin content (at 0.5 parts by mass of a hardener) caused decreases of bending and tensile strength.
4. Selection of the proper resin as a binding agent for moulding sands must be preceded by the economic analysis of costs of resins and hardeners. This selection should be done on the grounds of the moulding sand technological requirements and the produced assortment of castings and their weight.
   According to the data provided by the producers the tested binding systems obtain the following parameters:
   - Rezolit AM resin - 1.5% + Prestal hardener – 0.3% : bending strength after 24 hours: 2.0 MPa;
   - Estrofen resin – 1.3% + PR6 hardener – 0.3% : bending strength after 24 hours: 1.6 MPa;
   - Avenol 700 NB resin – 1.5% + Katalyzator 4040 hardener – 0.25% bending strength after 24 hours: 1.6 MPa.

Acknowledgements

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Badanie właściwości mas z żywicami stosowanymi w technologii Alphaset

Streszczenie

W procesie, znanym szerzej jako **ALPHASET,** stosuje się alkaliczną żywicę fenolowo- formaldehydową typu rezolowego, zawierającą poniżej 1% wolnego fenolu i poniżej 0,2 % wolnego formaldehydu. Jako utwardzacze stosuje się estry, za pomocą których można regulować szybkość utwardzania. Alkaliczny charakter procesu umożliwia zastosowanie wszystkich rodzajów piasku jako osnowy, włącznie z silnie zasadowymi. Powyższe masy mogą być stosowane na formy i rdzenie w zasadzie do wszystkich stopów, przy czym są szczególnie korzystne w przypadku odlewów staliwnych, w których mogą występować pęknięcia na gorąco. Do badań wytypowano następujące układy o charakterze zasadowym zawierające żywice fenolowo-formaldehydowe: żywica Rezolit AM + utwardzacz Prestal R-1/5, żywica Estrofen + utwardzacz PR6, żywica Avenol 700 NB + utwardzacz Katalysator 4040 . Jako osnowę mas stosowano piasek kwarcowy Biała Góra. Badania laboratoryjne wykonywano w następujących warunkach: temperatura 20-22°C, wilgotność 35—50%. Dobór właściwej żywicy, jako spoiwa masy musi poprzedzić analiza ekonomiczna kosztów zakupu żywic i odpowiednich utwardzaczy. Dobór ten musi być dokonany w oparciu na wymagania technologiczne masy oraz produkowany asortyment odlewów i ich ciężar.

Słowa kluczowe: właściwości mechniczne, właściwości technologiczne, masy formierskie, technologia Alphaset, alkaliczne spoiwa organiczne.