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(54) Moulding sand and a method of curing of moulding sand

(57) A moulding sand comprising water, a binder and a silica sand matrix, characterised in that it further comprises sodium salt of carboxymethyl starch (CMS-Na) having a degree of substitution (DS) in the range of 0.2 to 0.9, in the amount of 0.2 to 2.5 parts by weight per 100 parts by weight of the matrix.

$$\text{Starch-OH} + \text{Cl-CH}_2\text{-COONa} \xrightarrow[\text{-NaCl, -H}_2\text{O}]{\text{NaOH}} \text{Starch-OCH}_2\text{-COONa}$$

Fig. 1

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Description

TECHNICAL FIELD

[0001] The present invention relates to moulding sand comprising a modified biopolymer and a method of curing thereof.

BACKGROUND

[0002] Moulding sands are used in the foundry industry for production of moulds and cores, which are then used to produce castings.

[0003] A typical process of producing a casting comprises filling a mould (prepared from a moulding sand) with a liquid material (such as metal alloy, gypsum, wax or plastic) in order to obtain a product having desired structure and properties. After the casting is solidified, the mould is subject to the process of striking, wherein the material of the mould is separated from the casting.

[0004] The moulding sand is typically composed of a matrix, usually in the form of an inorganic, loose material, such as silica sand, and a binder for "connecting" the grains of the matrix; green sands additionally comprise water.

[0005] The main requirements for the moulding sands are the ability to be moulded while maintaining appropriate cohesion, as well as the strength of the bonds between sand grains - i.e. lack of tendency of the mould to be friable, both while waiting for filling, and during thermal and erosive impact on the mould of liquid material introduced into the mould.

[0006] The functional properties of moulds and cores made of moulding sand are highly influenced by the type of the binder applied. One typical binder used for moulding sands is bentonite. There are also known binders in the form of hydrocarbon resins, wherein bonding process of the binder is carried out by a chemical reaction. Further, mixtures of synthetic polymers and biopolymers can be used as binders as well.

[0007] In order to improve the functional properties of casting moulds and cores, various types of additives can be introduced into moulding sands at the stage of their preparation, such as pulverised coal or sulphite lye, which are aimed at reducing mould friability and at reducing the tendency of casting defects to be formed, such as streaks, scars or dusting.

[0008] In order to reduce the negative impact on the environment, some of the synthetic additives for moulding sands can be replaced by additives of natural origin, such as starch, cellulose or modifications thereof, including dextrins, carboxymethyl starch or carboxymethyl cellulose.

[0009] For example, native starch can be used as an auxiliary substance which improves hardness and durability of moulding sands with bentonite, and reduces friability. Native starch can also be introduced in the form of boiled starch, which helps to prevent casting defects associated with expansion. A side effect of the presence of starch in the composition of the moulding sand is, however, deterioration in liquidity and in resistance of the sand to erosion and to penetration of metal into the mould.

[0010] Native starch is composed of glucose mers linked by α-1,4-glycosidic bonds in amylose, and by α-1,4- and α-1,6-glycosidic bonds in amylopectin. In terms of its chemical composition, native starch is not homogeneous and is composed of amylose (20-25%, $(C_6H_{10}O_5)_n$ with n=5000) and amylopectin (75-80%, $(C_6H_{10}O_5)_n$ with n=50000). Amylose forms viscous solutions at the temperature of 90°C, and amylopectin forms hydrogel at the temperature of 70°C. A disadvantage of native starch is its insolubility in cold water. Native starch begins to partially dissolve and swell at the temperature of about 70°C. In order to improve solubility of native starch in water, it is typically modified by introducing polar groups, such as hydroxyl groups.

[0011] The Polish Standard PN-87/A-74820 defines a modified starch as a natural starch in which one or more of its initial physical or chemical properties are changed by an appropriate treatment. Modification of starch aims at improving functional properties of starch or at giving it new characteristics.

[0012] Starch properties can be changed within a wide range by interacting with chemical agents, physical agents or enzymatically. Products of chemical modification of starch by esterification, etherification and oxidation are widely used in the industry, including products with modified molar mass, gelatinisation temperature, solubility, viscosity, water binding capacity, temperature stability and resistance to acids and enzymes.

[0013] Products of starch modification, such as, for example, etherified starch, i.e. comprising hydroxyethyl, hydroxypropyl or carboxymethyl groups, for example, carboxymethyl starch, can be used as binder components of moulding sands in the form of multicomponent mixtures.

[0014] Modified biopolymers, including modified products of starch and cellulose, introduced into binders due to their natural origin (as renewable raw materials), relatively low price and biodegradability, do not have a negative impact on the natural environment.

[0015] There are known numerous examples of using starch and its etherified derivatives in the technology of moulding sands.

[0016] For example, a publication "Preparation and experiments for a novel kind of foundry core binder made from modified potato starch" (Wenbin Yu, Hong He, Nanpu Cheng, Bingtai Gan, Xuelian Li, Materials and Design 30 (2009) pp.210-213), discloses water-soluble modified starch binder (WMSB) is described, which consists of 28-30% of potato starch, 1% of formaldehyde, 0.1% of phosphoric acid, 2% of polyvinyl alcohol, 1% of urea and water. The binder is introduced into the sands with bentonite (2-3%) in the amount of 4-7%. The sand after drying (self-curing under ambient conditions) has a tensile strength at the level of 0.7-2.5 MPa, depending on the amount of WMSB in the sand. The sand has a tendency to absorb moisture from the environment and is a gas generant (14.2 ml/g).

[0017] A publication "Study on synthesis and properties of modified starch binder for foundry" (Xia Zhou, Jinzong Yang, Guohui Qu, Journal of Materials Processing Technology 183 (2007) pp. 407-411) describes a technology for synthesising carboxymethyl starch (CMS) with a degree of substitution DS of 0.25-0.78, and for preparing sands with a starch binder based on carboxymethyl starch having DS of 0.3-0.5. The sand consists of bentonite 0.5%, pulverised graphite 0.3%, phosphate 0.01%, water 12-15% and synthetic residues of fatty acids 1.0%. Curing of the sand is carried out by heating the mould for 1 h in the temperature of 160-180°C. The sand is characterised by tensile strength after curing of 1.5-2.2 MPa, gas generation capacity at the level of 14-16 ml/g and coefficient of moisture absorption of 43-50%.

[0018] A publication "Synthesis and Application of Modified Starch as a Shell-Core Main Adhesive in a Foundry" (Xia Zhou, Jinzong Yang, Feng Qian,Guohui Qu, Journal of Applied Polymer Science, 116/5 (2010), pp. 2893-2900, DOI 10.1002/app.31781) describes a method for obtaining sand for the preparation of shell cores with the participation of corn-based binder CMS having DS of 0.25-0.78. The sand consists of matrix, CMS, bentonite, graphite powder, phosphates, surfactants and water in the ratio of 100:4.0:0.5:0.3:0.01:0.03:(14-20). The shell cores are prepared in a core box having the temperature of 100-200°C.

[0019] Publications "The high-temperature resistant mechanism of α-starch composite binder for foundry" (Xia Zhou, Jinzong Yang, Depeng Su, Guohui Qu, Journal of Materials Processing Technology 209 (2009) pp. 5394-5398), "Hygroscopicity-resistant mechanism of an α -starch based composite binder for dry sand molds and cores" (Xia Zhou , Jiyang Zhou , Guohui QU, China foundry, (2) 2005, pp. 97-101) and "Adhesive Bonding and Self-Curing Characteristics of α-Starch Based Composite Binder for Green Sand Mould/Core" (Xia Zhou ,Jinzong Yang ,Guohui QU., J. Mater. Sci. Technol., (20/05)2004,) pp. 617-621) describe a binder consisting of α-starch, kaolin, sodium silicate, dextrin, phosphate and water in the respective proportions of: 2.5-4.0%, 1.5-3.0%, 0.55%, 0.35%, 0.04% and 2.5-3.5%. Curing is carried out by annealing at the temperature of 160-200°C for 1 h. This sand is resistant to absorption of moisture from the environment and to high temperatures, bending strength of the sand at about 1000°C is maintained at the level of about 0.4 MPa.

[0020] A publication "The Use of Yarn Flour (Starch) as Binder for Sand Mould Production in Nigeria", (T. Shehu and R.S. Bhatti, World Applied Sciences Journal (16/6) 2012, pp. 858-862) describes a technology for producing sands with the use of starch of yarns as an independent binder introduced into the sand in the amount of 25-30% (water content in the sand of 6-7%). The obtained maximum strength of the dried sands under ambient conditions is 309 KN/m^2.

[0021] A publication "Synergistic effects of starch and rubber-latex as core binders for foundry sand cores production" (A. Oyetunji , S.O. Seidu , Acta Technica Corvininesis - Bulletin of Engineering; (5/4) 2012, pp. 103) describes a binder in the form of mixture of tapioca starch and latex rubber (at the ratio of 1:2). The suggested share of the binder in the sand is 2-9 % in relation to the matrix. The sand is dried under ambient conditions for 3 days. Compressive strength of the sand produced in wet and cured states is respectively 72 N and 65 N. This sand is an alternative to sands with bentonite.

[0022] Publications "Evaluating the Baked Compressive Strength of Produced Sand Cores Using Cassava Starch as Binder for the Casting of Aluminium Alloy T-Joint Pipe" (Opaluwa A. I and Oyetunji A., Journal of Emerging Trends in Engineering and Applied Sciences (JETEAS) (3/1), pp. 25-32) and "Littlestudy on the shear strength of foundry sand cores using clay and cassava starch as binder" (Oyetunji A., Seidu S.O. and Opaluwa A. I., DAFFODIL INTERNATIONAL UNIVERSITY JOURNAL OF SCIENCE AND TECHNOLOGY, (8/2) 2013, pp. 77- 84) describe a technology for preparing core sands of 4-12% of tapioca starch, 6-12% of water and 5% of locally occurring clay. Curing of the sand is carried out at the temperature of 180°C for 2 hours. The maximum compressive strength of the sand (10% of water, 10% of starch) in wet state is 290 N/mm^2, and that for the dried sand is, respectively, 4122 N/mm^2.

[0023] There are also known compositions of moulding sands which contain biopolymers in the form of products of chemical modification of starch and cellulose.

[0024] A Japanese patent application JPS5731439 describes a binder for moulding sands which are obtained by esterification by adding, to the starch, chloroacetic acid and NaOH solution, and then cold water. However, this publication does not relate to moulding sands as such and methods for their preparation and curing.

[0025] A Polish patent application PL285979 describes a moulding sand consisting of a matrix in the form of silica sand, carbon additive in the amount of 0-6% by weight, starch and cellulose formulations in the amount of 0.5-3.0% by weight, basaltic loam acting as a binder in the amount of 5-20% by weight and water.

[0026] A Polish patent application PL93595 describes an additive for moulding sands, based on silica sand, bentonite and water, reducing the tendency of the sand to friability. The additive consists of formamyle in the amount of 40% by weight, flocculant in the amount of 30% by weight, glycol in the amount of 5% by weight and wood flour or harl flour in the amount of 25% by weight.

[0027] A Chineese patent application CN101898226 describes a use of carboxymethyl starch as an additive to the binder in the form of a multicomponent mixture for binding moulding sands. The moulding sand consists of sand, modified starch, malt sugar, glycerine, sodium hydroxide, pulverised coal, iron oxide, starch, carboxymethyl cellulose and water. These components are of natural origin, which ensures lack of negative impact of the sand on the environment and its nontoxicity.

[0028] A Dutch patent application NL6913413 describes a moulding sand consisting of bentonite, water-soluble grafted polymer of acrylic acid on a base of carboxymethyl cellulose.

[0029] A Chinese patent application CN103521696 describes a composition of moulding sand, consisting of china clay, pulverised coal, aluminum powder, carboxymethyl cellulose, sodium hexametaphosphate, stearic acid, chlorinated paraffin, borax, boron oxide, boric acid and water. The moulding sand is characterised by good gas permeability and cohesiveness.

[0030] A Polish patent application PL396105 describes a composition of moulding sand with a biodegradable polymeric binder, consisting of 100 parts by weight of refractory matrix and of 1-5 parts by weight of organic binder. The organic binder applied consists of a mixture of aqueous solutions of poly(acrylic acid) or poly(sodium acrylate) in the amount of 30-70% by weight and of biopolymer from the group of polysaccharides in the form of modified starch or dextrin in the amount of 30-70% by weight.

[0031] It follows from the above-mentioned publications, that the known compositions of moulding sands with biopolymers are characterised by multicomponent nature of the binder, which is associated with the need to meet specific performance and strength parameters by the moulding sand. A multicomponent nature of the binder negatively affects also prolongation of preparation of the sand and its price.

[0032] It would, therefore, be advisable to develop a composition of moulding sand which would not contain multiple components and would contain primarily substances which are non-toxic and neutral to the environment. It would also be advisable for such a composition to exhibit good performance and durability parameters.

SUMMARY

[0033] The object of the invention is a moulding sand comprising water, a binder and a silica sand matrix, wherein it further comprises sodium salt of carboxymethyl starch (CMS-Na) having a degree of substitution (DS) in the range of 0.2 to 0.9, in the amount of 0.2 to 2.5 parts by weight per 100 parts by weight of the matrix.

[0034] Preferably, CMS-Na is a binder in the amount of 1.5 to 2.5 parts by weight per 100 parts by weight of the matrix.

[0035] Preferably, the moulding sand is a bentonite-bound sand and CMS-Na is an additive in the amount of 0.2 to 2.0 parts by weight per 100 parts by weight of matrix.

[0036] Preferably, the moulding sand comprises a binder in the form of activated bentonite comprising montmorillonite in the amount of 70% to 90% by weight.

[0037] Another object of the present invention is a method of curing a moulding sand as described above by evaporating water from the sand by subjecting the moulding sand to electromagnetic waves of microwave frequency in the range of 2 GHz to 3 GHz.

DETAILED DESCRIPTION

[0038] The moulding sand according to the invention comprises a single-component binder, a matrix and a solvent or it may contain a normally used binding material, such as an activated bentonite. One of the sand components is a biodegradable sodium salt of carboxymethyl starch (CMS-Na), wherein depending on the amount of CMS-Na introduced into the moulding sand, it may serve only as an additive to the sand, improving certain utility properties, or it may serve as an additive and a binder. As the matrix, silica sand is used, preferably acidic, and the solvent is constituted by water capable of solvating CMS-Na, which is generally available, does not influence the environment negatively, and has a low price.

[0039] CMS-Na for the moulding sand according to the invention can be obtained in any known manner, for example by etherification of starch, for example potato starch, and then by neutralization of the etherification product by means of an aqueous solution of sodium hydroxide (NaOH), preferably having the concentration of: 2-10%, and more preferably having the concentration of 5%.

[0040] Fig. 1 shows a reaction scheme for obtaining CMS-Na from starch by etherification of native starch slurry in ethyl alcohol by means of sodium salt of monochloroacetic acid in the presence of NaOH (Williamson synthesis). Products having different properties can be obtained, depending on the conditions for conducting modification. Changes that take place in the starch molecule are determined based on the degree of substitution (DS) which defines the average number of carboxymethyl groups ($-CH_2-COOH$) or sodium carboxymethyl groups ($-CH_2-COONa$) attributable to a single link of starch in each glucopyranose ring. Viscosity, water solubility and durability of CMS-Na increase proportionally to the degree of substitution (DS).

[0041] In order to produce the moulding sand according to the invention, CMS-Na is introduced in a loose form into the matrix, optionally with another loose material, such as for example activated bentonite, and all the components are stirred. The time of stirring may be adapted depending on the needs, for example, depending on the efficiency of the stirrer applied. Preferably, the stirring time is 1 to 2 minutes, and more preferably the stirring time is 1 minute. After the loose components have been mixed, a polar solvent (e.g. water) is introduced into the mixture, and the components are stirred until the mass becomes consistent. Preferably, the stirring time of the loose components with water is 1 to 2 minutes, and more preferably the stirring time of the loose components with water is 2 minutes. Addition of the solvent ensures wetting of matrix grains, which provides appropriate adhesion of the binder-matrix system.

[0042] Research conducted for moulding sands with CMS-Na having various compositions has shown that CMS-Na introduced into the sand as an additive in minor amounts, i.e. in the range of 0.2 to 2, and more preferably in the amount of 0.5 parts by weight per 100 parts by weight of the matrix, results in reduction of friability of the moulding sand. Further, it appeared that CMS-Na serves as a carrier of lustrous carbon in the moulding sand, and therefore it can be used as a bio-substitute for pulverised coal and hydrocarbon resins, which allows for achieving a simple composition of the moulding sand and ensures elimination of components from the sand, which could negatively affect the natural environment.

[0043] In turn, CMS-Na can also serve as a binder, when introduced into the moulding sand in the amount of 1.5 to 2.5 parts by weight per 100 parts by weight of the matrix - it exhibits the ability to bind the moulding sand permanently.

[0044] Research has shown unexpectedly that the binding properties of sodium salt of carboxymethyl starch (CMS-Na) are better than the binding properties of other known binding biopolymers, such as carboxymethyl cellulose (CMC) and carboxymethyl starch (CMS), which allows the use of CMS-Na as the main "binding agent" of the moulding sand - without the need to introduce auxiliary binding substances or to use binding mixtures having complex compositions.

[0045] Further research has shown that the degree of substitution (DS) has an impact on the binding properties of CMS-Na, wherein the best binding properties are achieved with the degree of substitution (DS) in the range of 0.2 to 0.9, and preferably 0.6 to 0.8. This is caused by the impact of DS on solubility of CMS-Na in polar solvents: the higher DS (i.e. the greater share of side polar groups within a polymer chain - starch), the higher the solubility of CMS-Na in polar solvents. Therefore, an increase in solubility of CMS-Na improves the binding properties of this substance.

[0046] It further appeared that the type of matrix applied has an impact on the increase in binding properties of CMS-Na. Research results have shown that the best binding properties of CMS-Na are achieved with acidic matrix materials, including for example silica sand.

[0047] For example, addition of 1.5-2.5 parts by weight of binder CMS-Na and 3-5 parts by weight of water to 100 parts by weight of silica sand, very good functional parameters of sand and very good durability parameters of moulds and cores are achieved.

[0048] In case CMS-Na serves as a binder, the moulding sand can be cured physically - by evaporating part of the water contained in the sand. The evaporation can be performed by supplying energy in a thermal way, i.e. by heating the moulding sand until it solidifies. For example, the moulding sand can be annealed through thermal drying in the temperature of 80 to 150°C, and preferably in the temperature of 100°C.

[0049] Optionally, with a view to solidification, the sand with CMS-Na binder can be subjected to electromagnetic radiation having a microwave frequency, preferably in the range of 2 to 3 GHz, and more preferably 2.45 GHz and with the power of 600 W to 1200 W, preferably 800 W. Radiation exposure time is selected depending on the amount and/or the weight of the sand.

[0050] For the composition of the moulding sand which contains CMS-Na as an additive, various types of typically used binding materials can be used, such as for example activated bentonite having montmorillonite content of 70 to 90%. For example, the moulding sand can be composed of 100 parts by weight of mineral matrix, 5-8 parts by weight of bentonite, 0.5-2 parts by weight of CMS-Na and 1.5-4 parts by weight of water.

[0051] One of the advantages of the moulding sand according to the invention is its simple composition; the sand can be composed of only three components: CMS-Na binder, mineral matrix and solvent; introduction of CMS-Na as a binder allowed obtaining the effect of better binding of the matrix, and therefore obtaining moulds and cores having better functional parameters.

[0052] The simple composition of the moulding sand according to the invention is also related to the multifunctionality of CMS-Na in the sand. This substance can simultaneously serve in the moulding sand as a binder and as an additive, providing reduction in friability of the bentonite-bound sand and allowing elimination from the system of substances such as pulverised coal or hydrocarbon resins, which significantly simplifies the composition of the sand.

[0053] The ability to control the properties of CMS-Na binder, such as degree of substitution (DS) or viscosity, already at the stage of its production (starch modification) provides additionally the possibility of producing, depending on the needs, the moulding sand with desired properties, such as bending strength or friability.

[0054] Further, the moulding sand according to the invention does not negatively affect the environment. CMS-Na is a biodegradable polymer, and products of CMS-Na decomposition are substances which occur naturally in the environment and are harmless.

[0055] The moulding sand with CMS-Na according to the invention is characterised by allowing easy striking of the products out of the mould and by a high quality of the castings produced.

[0056] The moulding sand according to the invention is further characterised by good recoverability. CMS-Na binder can be retrieved from the sand after a technological process.

[0057] The CMS-Na bound sand is characterised by insignificant harmfulness to the environment and workers (the used sand can be utilised in the industry).

[0058] An important advantage of the CMS-Na bound sand is the possibility of its preparation with acidic matrices.

[0059] The CMS-Na bound sand may be an alternative for the sands used in foundry industry due to the physicochemical characteristics of its components, and technological, ecological and economic aspects. Further, the starch component of CMS-Na sand can be produced from cheap raw materials, such as for example potato starch, or from vegetable waste containing starch (e.g. potato processing waste).

EXAMPLE I

Synthesis of CMS-Na:

[0060] Modification of potato starch with the moisture content of up to 14.0% was conducted in a glass reactor equipped with a mechanical stirrer, a thermocouple and capillaries supplying nitrogen to the reaction system. The starch was etherified in a mixture of isopropanol (IPOH) and water in a single-step process. Monochloroacetic acid (MCA) was dissolved in IPOH in the reactor, and then was introduced in aqueous solution of NaOH. The molar ratio of NaOH/(S)MCA was 2.25:1. After stirring for 90 min and homogenisation of the mixture, a fine fraction of NaOH was introduced into the reactor. The reaction was conducted for the period of about 150 - 180 min in the temperature of 50°C. The product obtained was filtered off and neutralised with acetic acid, then it was washed several times with methanol solution, once with pure methanol, and then it was left on a heated surface to be dried in the air.

[0061] The above example of the synthesis of CMS-Na should only be considered as illustrative, while CMS-Na to be used in further examples can be also obtained by other known methods.

EXAMPLE II

Preparation and curing of the sand with starch binder:

[0062] 1.5 parts by weight of non-crosslinked CMS-Na in a loose form having DS=0.87 (properties for 5% solution: pH=12 and viscosity is 4500 mPa·s) and 100 parts by weight of acidic silica sand having an average grain size in the range of 0.16-0.32 mm, were introduced into a roll mixer and the components were stirred for 1 min. Next, 3 parts by weight of water were added to the mixer and the sand was stirred for another 2 min, and then the liquidity of the sand was measured. The process of sand preparation was performed under ambient conditions - humidity of the air: 35% and the temperature of: 23°C.

[0063] From the moulding sand produced, two longitudinal moulded pieces, each weighing 150g, and four octal moulded pieces, each weighing 75g, were prepared.

[0064] The moulded pieces were subjected to curing under the influence of microwave radiation with power of 800W and frequency of 2.45 GHz for 120s, an then properties of the cured sand were examined.

The sand with the following properties was obtained:

Tensile strength R_m^u in the cured state after storage time:

- 1 h: 1.4(± 0.1) MPa
- 24 h: 1.4 (± 0.1) MPa

Bending strength R_g^u in the cured state after storage time:

- 1 h : 2.4 (± 0.1) MPa
- 24 h : 2.0 (± 0.1) MPa

Sand permeability in the cured state after storage time:

- 1 h: 218 (± 2) 10^{-8} m^2/Pa·s
- 24 h: 268 (± 3) 10^{-8} m^2/Pa·s

Abrasion resistance of sand in the cured state after storage time:

- 1 h: 1.92 (± 0.13) %
- 24 h: 1.63 (± 0.11) %

Dietert liquidity of sand in the uncured state
95 ((± 0.23) %

EXAMPLE III

Preparation and curing of the sand with starch binder:

[0065] 2.5 parts by weight of non-crosslinked CMS-Na in a loose form having DS=0.2 (properties for 5% solution: pH=11.3 and viscosity = 22000 mPa·s) and 100 parts by weight of acidic silica sand having an average grain size in the range of 0.16-0.32 mm, were introduced into a roll mixer and the components were stirred for 1 min. Then, 5 parts by weight of water were added to the mixer and the sand was stirred for another 2 min, and then liquidity of the sand was measured. The process of sand preparation was performed under ambient conditions - humidity of the air: 35% and the temperature of: 23°C.

[0066] From the moulding sand produced, two longitudinal moulded pieces, each weighing 150g, and four octal moulded pieces, each weighing 75g, were prepared.

[0067] The moulded pieces were subjected to curing under the influence of microwave radiation with power of 800W and frequency of 2.45 GHz for 120s, an then properties of the cured sand were examined.

The sand with the following properties was obtained:

Tensile strength R_m^u in the cured state after storage time:

- 1 h: 1.3 (± 0.1) MPa
- 24 h: 1.2 (± 0.1) MPa

Bending strength R_g^u in the cured state after storage time:

- 1 h: 2.4 (± 0.1) MPa
- 24 h: 2.0 (± 0.1) MPa

Sand permeability in the cured state after storage time:

- 1 h: 210 (± 3) 10^{-8} m^2/Pa·s
- 24 h: 222 (± 2) 10^{-8} m^2/Pa·s

Abrasion resistance of sand in the cured state after storage time:

- 1 h: 1.26 (± 0.15) %
- 24 h: 1.5 (± 0.10) %

Dietert liquidity of sand in the uncured state
89 ((± 0.2) %

EXAMPLE IV

Preparation and curing of the sand with starch binder:

[0068] 2.5 parts by weight of non-crosslinked CMS-Na in a loose form having DS=0.2 (properties for 5% solution: pH=11.3 and viscosity = 22000 mPa·s) and 100 parts by weight of acidic silica sand having an average grain size in the range of 0.16-0.32 mm, were introduced into a roll mixer and the compontents were stirred for 1 min. Then, 5 parts by weight of water were added to the mixer and the sand was stirred for another 2 min, and then liquidity of the sand was measured. The process of sand preparation was performed under ambient conditions - humidity of the air: 42% and the temperature of: 22°C.

[0069] From the moulding sand produced, two longitudinal moulded pieces, each weighing 150g, and four octal moulded pieces, each weighing 75g, were prepared. The moulded pieces were cured by thermal annealing in the temperature of 100°C for 30 min, and then their properties were examined.
The sand with the following properties was obtained:

Tensile strength R_m^u in the cured state after storage time:

- 1 h: 1.2 (± 0.06) MPa
- 24 h: 1.2 (± 0.04) MPa

Bending strength R_g^u in the cured state after storage time:

- 1 h: 2.6 (± 0.1) MPa
- 24 h: 2.2 (± 0.1) MPa

Sand permeability in the cured state after storage time:

- 1 h: 172 (± 2) 10^{-8} m^2/Pa·s
- 24 h: 192 (± 2) 10^{-8} m^2/Pa·s

Abrasion resistance of sand in the cured state after storage time:

- 1 h: 11.9 (± 0.2) %
- 24 h: 14.9 (± 0.2) %

Dietert liquidity of sand in the uncured state
91.2 (± 0.5) %

EXAMPLE V

Preparation of bentonite-bound green sand moulding with a starch additive:

[0070] 6 parts by weight of activated bentonite containing montmorillonite in the amount of 70-90%, 100 parts by weight of acidic silica sand having an average grain size in the range of 0.16-0.32 mm and 0.5 parts by weight of non-crosslinked CMS-Na in a loose form having DS=0.87 (property of 5% solution having pH of 10.2 and viscosity of 4500 mPa·s) were introduced into a roll mixer, the entirety was stirred for 1 min, then water was added to achieve moisture content at the level of 1.5 to 4% (optimal operating moisture content is 2.54%), and then the entirety was stirred for 2 min. The process of sand preparation was performed under ambient conditions - humidity of the air: 54% and the temperature of: 19.7°C. Then, certain parameters of the sand were measured.
The sand with the following properties was obtained:

Compressive strength of green sand
R_c^w = 0.1 MPa

Shear strength of green sand R_t^w = 0.03 MPa

Tensile strength of green sand R_m^w = 0.02 MPa

Permeability P_w= 300 x108 m^2/Pa·s
Dietert flowability P_D= 72%
Free flowability P_S= 25%
Friability S = 10.3%
Compatibility Z = 52.0%
Properties for optimal operating moisture content of the sand being 2.54% determined on the basis of an indicator of moulding properties Wf = 75%.

EXAMPLE VI

Preparation of bentonite-bound green sand moulding with a starch additive:

[0071] 6 parts by weight of activated bentonite containing montmorillonite in the amount of 70-90%, 100 parts by weight of acidic silica sand having an average grain size in the range of 0.16-0.32 mm and 0.5 parts by weight of non-crosslinked CMS-Na in a loose form having DS=0.2 (property of 5% solution having pH of 11.4 and viscosity of 22000 mPa·s) were introduced into a roll mixer, the entirety was stirred for 1 min, then water was added to achieve moisture content at the level of 1.5 to 4% (optimal operating moisture content is 2.10%), and then the entirety was stirred for 2 min. The process of sand preparation was performed under ambient conditions - humidity of the air: 47.0% and the temperature of: 26.1°C. Then, certain parameters of the sand were measured. The sand with the following properties was obtained:

Compressive strength of green sand R_c^w = 0.09 MPa
Shear strength of green sand R_t^w = 0.02 MPa
Tensile strength of green sand R_m^w = 0.02 MPa
Permeability P_w = 300 x108 m^2/Pa·s
Dietert flowability P_D = 76.8 %
Free flowability P_S = 17.0 %
Friability S = 13.5 %
Compatibility Z = 55.0 %
Properties for optimum operating moisture content of the sand being 2.10% determined on the basis of an indicator of moulding properties Wf = 75%.

Claims

1. A moulding sand comprising water, a binder and a silica sand matrix, **characterised in that** it further comprises sodium salt of carboxymethyl starch (CMS-Na) having a degree of substitution (DS) in the range of 0.2 to 0.9, in the amount of 0.2 to 2.5 parts by weight per 100 parts by weight of the matrix.

2. The moulding sand according to claim 1, **characterised in that** CMS-Na is a binder in the amount of 1.5 to 2.5 parts by weight per 100 parts by weight of the matrix.

3. The moulding sand according to claim 1, **characterised in that** the moulding sand is a bentonite-bound sand and CMS-Na is an additive in the amount of 0.2 to 2.0 parts by weight per 100 parts by weight of matrix.

4. The moulding sand according to claim 3, **characterised in that** it comprises a binder in the form of activated bentonite comprising montmorillonite in the amount of 70% to 90% by weight.

5. A method of curing a moulding sand according to any of claims 1-4 by evaporating water from the sand by subjecting the moulding sand to electromagnetic waves of microwave frequency in the range of 2 GHz to 3 GHz.

$$\text{Starch-OH} + \text{Cl-CH}_2\text{-COONa} \xrightarrow[\text{-NaCl, -H}_2\text{O}]{\text{NaOH}} \text{Starch-OCH}_2\text{-COONa}$$

Fig. 1

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EUROPEAN SEARCH REPORT

Application Number
EP 14 19 6636

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	18 December 2015	Lombois, Thierry

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

Application Number
EP 14 19 6636

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The present search report has been drawn up for all claims

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