COATING COMPOSITIONS FOR INORGANIC CASTING MOLDS AND CORES AND USE THEREOF AND METHOD FOR SIZING

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ABSTRACT
The invention relates to coating compositions, comprising specific clays, an aqueous carrier fluid and refractory materials in powder form, and to the use thereof for casting molds and cores, in particular those that are produced using water glass as a binder. The invention further relates to a method for producing the sizing agents and for applying same to inorganically bound casting molds and cores.
COATING COMPOSITIONS FOR
INORGANIC CASTING MOLDS AND CORES
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SIZING

[0001] The invention relates to a coating composition for casting molds and the use thereof. The coating composition is suitable for casting molds and cores, in particular those that are produced using water glass as a binder. The coating composition comprises certain clay materials. A sizing method is also claimed.

PRIOR ART

[0002] Casting molds can be produced from a refractory material, for example quartz sand, by shaping into a casting mold and binding using a suitable binder to guarantee adequate mechanical strength. Thus casting molds are produced using a refractory basic material and a suitable binder. The refractory basic mold material is preferably present in the molding mixture, so that it can be packed into a suitable hollow mold and compacted there. The binder produces firm cohesion between the particles of the basic mold material, so that the mold form achieves the necessary mechanical stability.

[0003] Both organic and inorganic binders can be used for producing casting molds, and they can be cured by cold or hot processes. Cold processes are those that are essentially performed at room temperature without heating the casting molds. In these cases the curing is usually performed by a chemical reaction, initiated, for example, by passing a gas as a catalyst through the mold to be cured. In hot processes, the molding mixture, after forming, can be heated to a temperature high enough, for example, to expel the solvent present in the binder or to initiate a chemical reaction by which the binder is cured, for example by cross-linking.

[0004] Regardless of the curing mechanism, all organic systems share the fact that they undergo thermal decomposition when the liquid metal is filled into the casting mold and in this process may release toxic materials, such as benzene, toluene, xylene, phenol, formaldehyde and other cracking products, some of which have not been identified.

[0005] It has become possible to minimize these emissions by various measures, but they cannot be avoided altogether in the case of organic binders. To minimize or prevent the emission of decomposition products during the casting process, binders may be used which are based on inorganic materials or which contain a very small fraction of organic compounds. Such binder systems have long been known.

[0006] Binder systems have been developed which can be cured by passing gases into them. A system of this type is described, for example, in GB 782205, in which an alkali water glass is used as the binder and can be cured by passing in CO₂. In U.S. Pat. No. 6,972,059 B1 an exothermic feeder mass containing an alkali silicate as binder is described. In addition, binder systems that are self-curing at room temperature have been developed. One such system, based on phosphoric acid and metal oxides, is described for example in U.S. Pat. No. 5,582,232. Finally, inorganic binder systems that are cured at higher temperatures, for example in a hot tool, are also known. Such hot-curing binder systems are known, for example, from U.S. Pat. No. 5,474,606, in which a binder system consisting of alkali water glass and aluminum silicate is described.

[0007] In U.S. Pat. No. 7,022,178 B1 a binder system for molding sands for producing cores is described. The binder system, based on water glass, consists of an aqueous alkali silicate solution and a hygroscopic base, for example sodium hydroxide, which is added in a ratio of 1:4 to 1:6. The water glass has a SiO₂/MgO modulus of 2.5 to 3.5 and a solids fraction of 20 to 40%. To obtain a free-flowing molding material mixture that can also be packed into core molds with complicated shapes, and to control the hygroscopicity, the binder system also contains a surface-active material, such as silicone oil, which has a boiling point ≥250°C. The binder system is mixed with a suitable refractory material, such as quartz sand, and can then be shot into a core box using a core shooting machine. The curing of the molding material mixture is accomplished by withdrawing the remaining water. The drying or curing of the casting mold can also take place with the aid of microwaves.

[0008] However, inorganic binders also have drawbacks compared with organic binders; for example, the known inorganic binders result in low stability of the casting molds produced by using them toward high atmospheric humidity and toward water. Thus storage of the moldings over a long period of time, as is customary with organic binders, is not definitely possible. To achieve higher initial strengths, better resistance of the casting molds toward atmospheric moisture and better results on the surface of the casting, in U.S. Pat. No. 7,770,629 B2 a molding mixture is suggested in addition to a refractory basic mold material contains a water glass-based binder. A fraction of a particulate metal oxide is added to the mold material mixture. Preferably, precipitated silica or pyrogenic silica is used as the particulate metal oxide.

[0009] The methods described for producing casting molds and cores generally also include the application of a refractory mold coating, also known as sizing agent, at least to the surfaces of the basic mold that come into contact with the cast metal. The mold coatings are primarily intended to influence the surface of the molded part, to improve the appearance of the casting, to influence the casting metallurgically, and/or to prevent casting defects.

[0010] The sizing agents generally used contain as their basic materials, for example, clays, quartz, diatomaceous earth, cristobalite, tridymite, aluminum silicate, zirconium silicate, mica, fireclay and also coke and graphite. These basic materials are the defining parts of the sizing agent, which cover the mold surface and close the pores against the penetration of the casting metal.

[0011] With the aid of these coatings, therefore, the surface of the casting mold can be modified and tailored to the properties of the metal being processed. For example, the sizing agent can improve the appearance of the casting by producing a smooth surface, since the sizing agent smooths out irregularities caused by the different sizes of the granules of the molding material. In addition, the sizing agent can metallurgically influence the casting in that, for example, through the sizing agent, additives at the surface of the casting are selectively transferred into the casting, improving the surface properties of the casting.

[0012] In addition, the sizing agents form a layer that chemically isolates the casting mold during the casting of liquid metal. In this way, any adhesion between the casting and the casting mold is prevented, so that the casting can be removed from the casting mold without problems. However, the sizing agent can also be used to control the heat transfer
between liquid metal and casting mold, in order for example to accomplish the formation of a certain metal microstructure via the cooling rate.

Today, the curing of the inorganic binders used takes place increasingly via a condensation reaction initiated by elevated temperatures, in which the formation of the binder bridges occurs through splitting off of water. Like many chemical reactions, this is a reversible reaction, i.e., the bonds can be broken by contact and reaction with water, wherein the extent of this reaction depends heavily on the process parameters for core production. Under the process parameters typically used in mass production (rapid cycling, high temperatures), the casting molds lose their strength due to contact with water and to some extent also, to contact with alcohol; the surface softens and the casting mold loses its shape.

**STATEMENT OF THE PROBLEM**

The invention was based on the task of suggesting a sizing agent through which the most defect-free possible coating, especially of inorganic cores and molds, can be assured, without negatively impacting the stability of the cores or molds and thus their processing and storage.

**SUMMARY OF THE INVENTION**

This task is accomplished with the features of claim 1; advantageous embodiments form the subject matter of the dependent claims or are described in the following.

In a preferred embodiment, the sizing composition according to the invention is prepared in the form of a paste or a suspension. In this embodiment, the sizing composition contains a carrier fluid.

Surprisingly, it has been found that through the combination of certain clays as constituents of the sizing agents, sizing agents with an unusually high solids content can be produced, the viscosity of which is nevertheless comparable to that of commercial ready-to-use sizing agents such as Trofle® W-LS-1. The quality of cores and molds coated with these sizing agents and bonded with inorganic binders is lastingly improved by the combination of clays according to the invention and, for example, in this way several days' storage stability of the cores and molds can be achieved. It should be particularly emphasized that despite the unusually high solids content, the viscosity of the sizing agent is in the customary range for sizing agents with substantially lower solids contents. The sizing agents can be brought into the ready-to-use condition without the use of special additives or large amounts of water.

**DETAILED DESCRIPTION OF THE INVENTION**

The clay material used was a combination of

(A1) 1 to 10% by weight, especially 1 to 5% by weight, of palygorskite

(A2) 1 to 10% by weight, especially 1 to 5% by weight, of hectorite and

(A3) 1 to 20% by weight, especially 1 to 5% by weight, of sodium bentonite

(incase each relative to one another), especially in a weight ratio of palygorskite to hectorite of 1:0.5 to 2, especially 1:0.8 to 2 and a palygorskite to sodium bentonite ratio of 1:0.5 to 3, especially 1:0.8 to 2 and of hectorite to sodium bentonite of 1:0.5 to 2, especially 1:0.8 to 2.

The total content of the above-mentioned clays in the sizing agent amounts to 0.1 to 4.0% by weight, preferably 0.5 to 3.0% by weight, and particularly preferably 1.0 to 2.0% by weight.

Palygorskite is a magnesium-aluminum hydrosilicate listed under CAS No. 8031-18-3. Palygorskite is a constituent of commercial products sold as attapulgite. Attagulgite does contain palygorskite, but should not be used because of other interfering constituents and the absence of rod-shaped crystals.

Palygorskite exists in the form of rod-shaped crystals. The particles have the following dimensions: 1 to 3 nm, especially 1.5 to 2 nm in length at a diameter of 1 to 5 nm, especially about 3 nm.

For example, the product Acti-Gel® 208 from the "Active Minerals" company can be used as the palygorskite. For example, Bentone CT from the "Elements" company can be used as the hectorite.

For example, Vol clay from the "Stöchchemie" company can be used as the sodium bentonite. This natural raw material consists primarily (>80%) of montmorillonite; accompanying minerals can be quartzite, calcite, feldspar and mica.

Depending on the desired use of the sizing composition, e.g., as a base coat or top coat, and the desired layer thickness of the coating produced from the sizing composition, additional characteristic parameters of the sizing composition can be set.

The carrier fluid may be partially or completely composed of water. The carrier fluid is the component that can be evaporated at 160° C. and normal pressure and in this sense, by definition, is primarily the component that is not the solids content. The carrier fluid contains water to the extent of more than 50% by weight, preferably 75% by weight, especially more than 80% by weight, and optionally greater than 95% by weight of water.

The additional constituents in the carrier fluid may be organic solvents. Suitable solvents are alcohols, including polyalcohols and polyether alcohols. Examples of alcohols are ethanol, n-propanol, isopropanol, butanol and glycol.

The solids content of the ready-to-use sizing composition is preferably adjusted to the range of 10 to 90% by weight, especially more than 80% by weight to 85% by weight.

In addition to the constituents already named, the sizing agent according to the invention can contain additional constituents customary for sizing agents.

Thus the sizing composition according to the invention contains at least one powdered refractory material. This refractory material serves to block the pores in a casting mold against the penetration of the liquid metal. In addition, the refractory material achieves thermal insulation between the casting mold and the liquid metal. Examples of suitable refractory materials are quartz, aluminum oxide, zirconium oxide, aluminum silicates such as pyrophyllite, kyanite,
andalusite or fireclay, zirconium sands, ziconium silicates, olivine, talc, mica, graphite, coke, feldspar, diatomite, kaolins, calcined kaolins, kaolinite, metakaolinite, iron oxide and/or bauxite.

[0034] The refractory material is prepared in powdered form. The particle size is selected such that a stable structure is formed in the coating and that the sizing agent preferably can be distributed without problems on the wall of the casting mold using a spray device. Suitably, the refractory material has a mean particle size (measured by light scattering according to DIN/ISO 13320) in the range of 0.1 to 500 μm, particularly preferably in the range of 1 to 200 μm. Particularly suitable as refractory materials are those that have a melting point that is at least 200°C above the temperature of the liquid metal and independently of this, do not react with the metal.

[0035] The fraction of the refractory material (in each case contributing only to the solids content), e.g., in the commercial form of a paste, relative to the solids fraction of the sizing material composition, is advantageously more than 70% by weight, preferably more than 80% by weight, and particularly preferably more than 85% by weight.

[0036] According to another embodiment (in each case contributing only to the solids content), the fraction of the refractory material for the case of application following dilution (e.g., of the paste) with water is selected to be less than 80% by weight, according to an additional embodiment less than 70% by weight and according to a further embodiment less than 60% by weight.

[0037] In another embodiment the sizing material according to the invention may contain at least one suspending agent. The suspending agent brings about an increase in the viscosity of the sizing agent, so that the solid constituents of the sizing agent do not drop to the bottom in the suspension, or do so only to a slight degree. Organic or inorganic materials or mixtures thereof can be used to increase the viscosity. Suitable inorganic suspending agents are, for example, strongly swelling clays, such as sodium bentonite.

[0038] Alternatively or additionally, the suspending agent may also include organic thickeners, since after application of the protective coating, these can be dried to such an extent that they scarcely release any water after application of the protective coating. Possible organic suspending agents are, for example, swellable polymers such as carboxymethyl-1, methyl-1, ethyl-1, hydroxethyl-1, and hydroxypropylcelluloses, plant mucilages, polyvinyl alcohols, polyvinylpyrrolidone, pectin, gelatin, agar-agar, polypeptides and/or alginites.

[0039] The fraction of the suspending agent, based on the total sizing composition, is advantageously selected as 0.1 to 5% by weight, preferably 0.5 to 3% by weight, particularly preferably 1 to 2% by weight.

[0040] According to a preferred embodiment, the sizing agent according to the invention contains at least one binder as an additional component. The binder makes possible better fixation of the sizing agent or the protective coating made from the sizing agent onto the wall of the casting mold. In addition, the binder increases the mechanical stability of the protective coating, so that less erosion is observed under the influence of the liquid metal. Preferably the binder cures irreversibly, so that an abrasion-resistant coating is obtained. Particularly preferred are binders that do not soften again under contact with atmospheric humidity. Fundamentally any binder used in sizing agents may be present. Both inorganic and organic binders may be used. Suitable binders for use include, for example, clays, especially bentonite.

[0041] The fraction of the binder is preferably selected in the range of 0.1 to 20% by weight, particularly preferably 0.5 to 5% by weight, based on the solids content of the sizing composition.

[0042] According to an additional, preferred embodiment, the sizing agent contains a graphite fraction. This supports the formation of lamellar carbon at the interface between casting and casting mold. The fraction of the graphite is preferably selected in the range of 1 to 30% by weight, especially preferably 5 to 15% by weight, based on the solids content of the sizing agent. In iron casting, graphite has a beneficial effect on the surface quality of the casting.

[0043] Optionally, the sizing composition according to the invention may contain other constituents customary in sizing agents, for example wetting agents, defoamers, pigments, colorants or biocides. The fraction of these additional constituents in the ready-to-use coating composition is advantageously less than 10% by weight, preferably less than 5% by weight and particularly preferably less than 1% by weight.

[0044] For example, wetting agents may include anionic and non-anionic surfactants, especially those with an HSB value of at least 7. One example of such a wetting agent is disodium diocetylsulphosuccinate. The wetting agent is preferably used in a quantity of 0.01 to 1% by weight, preferably 0.05 to 0.3% by weight, based on the ready-to-use sizing composition.

[0045] Defoamers, also known as antifoamers, can be used to prevent foam formation during the production or application of the sizing composition. Foam formation during application of the sizing composition can lead to lack of uniformity in the layer thickness and to holes in the coating. For example, silicone oil or mineral oil may be used as defoamers. The defoamer is advantageously present in a quantity of 0.01 to 1% by weight, preferably 0.05 to 3% by weight, based on the ready-to-use sizing composition.

[0046] In the sizing composition according to the invention, the usual pigments and colorants may be used if desired. These are added to achieve contrast, e.g., between different sizing agents, or to create a stronger separating effect of the sizing agent from the casting.

[0047] Examples of pigments are red and yellow iron oxide and graphite. Examples of colorants are commercial colorants such as the Lucenyl® colorant series from BASF AG, Ludwigshafen, DE. The colorants and pigments are preferably present in a quantity of 0.01 to 10% by weight, preferably of 0.1 to 5% by weight, based on the solids content of the sizing composition.

[0048] According to an additional embodiment, the sizing composition contains a biocide to prevent bacterial attack and thus avoid a negative effect on the rheology and the binding strength of the binder. This is especially preferred when the carrier fluid contained in the sizing composition is made up essentially (on a weight basis) of water, and thus the sizing agent according to the invention is supplied in the form of a so-called aqueous sizing agent. Examples of suitable biocides are formaldehyde, 2-ethyl-4-isothiazolin-3-one (MIT), 5-chloro-2-methyl-4-isothiazolin-3-one (CIT) and 1,2-benzisothiazolin-3-one (BIT). Preferably, MIT, BIT or a mixture thereof is used. The biocides are usually used in a quantity of 10 to 1000 ppm, preferably of 50 to 500 ppm, based on the weight of the ready-to-use sizing composition.
The sizing composition according to the invention may be made by the usual methods. For example, a sizing composition according to the invention can be prepared by initially taking water and then dispersing clay, acting as a suspension agent, in it using a high-shear agitator. Then the refractory components, pigments and colorants, as well as the metallic additive are mixed in until a homogeneous mixture forms. Finally, wetting agents, antifoamers, biocides and binders are mixed in.

The sizing composition according to the invention can be prepared and sold as a ready-to-use formulated sizing agent. However, the sizing agent can also be prepared and sold in concentrated form. In this case, to produce a ready-to-use sizing agent, the quantity of the carrier fluid needed to establish the desired viscosity and density of the sizing agent is added. In addition, the sizing agent according to the invention can also be prepared and sold in the form of a kit, wherein for example the solid component(s) and the solvent component(s) are present side by side in separate containers.

The solid component(s) can be supplied as a powdered solids mixture in a separate container. Additional liquid component(s) optionally to be used, for example binders, surfactants, wetting agents/defoamers, pigments, colorants and biocides, can also be present in this kit, once again in a separate container. The solvent component(s) can either include the optional additional components for use, e.g., in a single container, or they can be present separate from other optional components in a separate container. To produce a ready-to-use sizing agent, the suitable quantities of the solids components, the optional additional components and the solvent components are mixed together.

The sizing compositions according to the invention are suitable for coating casting molds. The term “casting mold” used here includes all types of solid bodies needed for producing a casting, e.g., cores, molds and dies. The use of the sizing agent according to the invention also includes partial coating of casting molds.

The sizing agents are used for casting molds for metal processing, obtainable from inorganic molding material mixtures containing at least one refractory basic mold material, a water glass-based binder and preferably a fraction of a metal oxide selected from the group of silicon dioxide, especially amorphous silicon dioxide, aluminum oxide, titanium oxide or zircon oxide and mixtures thereof, wherein this is preferably present in particulate form and especially has particle sizes of less than 300 μm (screen analysis). For example, amorphous silicon dioxide can be obtained through precipitation processes starting from water glass, which can be obtained by solubilizing quartz sand with sodium carbonate or potassium carbonate. Depending on the process conditions, SiO₂ obtained in this way is called precipitated silica. Another important manufacturing variant is the production of so-called pyrogenic SiO₂ in an oxyhydrogen gas flame, starting from liquid chlorosilanes such as silicon tetrachloride.

The molding material mixtures and a method for producing casting molds for metal processing using the cured molding material mixtures are described in WO 2006/024540 (+U.S. Pat. No. 7,770,629 B2), and this publication is incorporated in the content of this application to this extent. Preferred molding material mixtures are the subject matter of the claims of WO 2006/024540.

Thus the casting molds to be coated typically comprise:

a) More than 80% by weight of a refractory basic mold material (including additives that behave like refractory basic mold materials).

b) 0.01 to 5% by weight of cured water glass as a binder, and
c) optionally 0 to 5% by weight of the above-named metal oxide or metal oxides.

In addition, the invention relates to a method for producing sized casting molds for metal processing with application of sizing agents to the above-mentioned, partially or completely cured inorganic molding material mixtures. The application or preparation of the sizing agents can take place as follows:

In the case of dipping as an application method, the casting mold, in the mold cavity of which a base coat of sizing agent has been applied, is dipped for about 2 seconds to 2 minutes in a container that is filled with a ready-to-use sizing composition according to the invention.

The casting mold is then removed from the sizing composition and excess sizing composition is allowed to run out of the casting mold. The time taken for the excess sizing composition to run out after dipping depends on the run-off behavior of the sizing composition used.

In the case of spraying as the application method, commercial pressure tank spraying devices are used. In this process the sizing composition, in a diluted state, is filled into a spray tank. Through the positive pressure to be applied, the sizing agent can be forced into a spray gun, where it is sprayed with the aid of separately controllable atomizing air. During spraying, the conditions are advantageously selected such that the pressure for the sizing composition and atomizing air are selected on the spray gun is set so that the sizing composition that is sprayed atomizing air strikes the mold or the core while said sizing composition is still wet, but results in a uniform application.

In the case of flow coating as the application method, the casting mold, optionally with a base coat applied in the mold cavity, is covered with a ready-to-use sizing composition with the aid of a tube, a lance or similar instruments.

In this process, the casting mold is covered completely with the sizing composition and the excess sizing composition runs out of the casting mold. The time taken for the excess sizing composition to run off after flow coating depends on the flow behavior of the sizing composition used.

In addition, the sizing agent can also be applied by painting.

The carrier fluid contained in the sizing agent is then evaporated, so that a dry sizing agent layer is obtained. Drying methods used may include all conventional drying methods, for example allowing to dry in air, drying with dehumidified air, drying with microwave or infrared radiation, drying in a convection oven and comparable methods. In a preferred embodiment of the invention, the coated casting mold is dried in a convection oven at 20 to 250° C., preferably 50 to 180° C.

When alcohol-based sizing agents are used, the sizing composition according to the invention is preferably dried by burning off the alcohol or the alcohol mixture. In this case the coated casting mold is additionally heated by the heat of combustion. In an additional preferred embodiment, the coated casting mold is dried in air without further treatment or using microwaves.
The sizing agent can be applied in the form of a single layer or in the form of several layers arranged one on top of the other. In this process the individual layers may be the same or different in terms of their composition. For example, first a base coat can be produced from a conventional commercial sizing agent that contains no metal additive according to the invention. For example, water-based sizing agents or alcohol-based sizing agents may be used. It is also possible to prepare all layers from the sizing composition according to the invention. The layer that will later come into contact with the liquid metal, however, is always produced from the sizing agent according to the invention. When several layers are applied, each individual layer may be dried completely or partially after application.

The coating prepared from the sizing composition advantageously has a dry layer thickness of at least 0.1 mm, preferably at least 0.2 mm, particularly preferably at least 0.45 mm, especially preferably at least 0.55 mm. According to one embodiment, the thickness of the coating is selected to be less than 1.5 mm. The thickness of the dry layer in this case is the layer thickness of the dried coating obtained by essentially completely removing the solvent component and optionally curing subsequently. The dry layer thickness of the base coat and the top coat are preferably determined by measuring with the wet layer thickness comb. The casting mold can then be assembled completely if desired. The casing is advantageously performed to make iron and steel castings.

Example 1

In this example, the effect of the increased solids content of the sizing agents used on the strengths of the sized cores was tested. The core sizing agents 1 and 2 have the compositions and physical properties indicated in Tables 1 and 2.

<table>
<thead>
<tr>
<th>Name, company (designation)</th>
<th>Sizing agent 1</th>
<th>Sizing agent 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>15.0%</td>
<td>21.0%</td>
</tr>
<tr>
<td>Attigel 40: Solvadis (attapulgite)</td>
<td>1.2%</td>
<td>1.2%</td>
</tr>
<tr>
<td>Actigel 208: Activene Minerals (pyrogorskite)</td>
<td>0.3%</td>
<td>---</td>
</tr>
<tr>
<td>Bentonite CT: Elementics (hectorite)</td>
<td>0.4%</td>
<td>---</td>
</tr>
<tr>
<td>Voslavy, Silikon (sodium bentonite)</td>
<td>0.6%</td>
<td>0.6%</td>
</tr>
<tr>
<td>Zircon flour 45 µm</td>
<td>30.5%</td>
<td>24%</td>
</tr>
<tr>
<td>Zircon flour 75 µm</td>
<td>51%</td>
<td>51%</td>
</tr>
<tr>
<td>PVA solution (25%)</td>
<td>1.2%</td>
<td>1.2%</td>
</tr>
<tr>
<td>1.25Surlyn &amp; SEF (wetting agent 1)</td>
<td>0.2%</td>
<td>0.2%</td>
</tr>
<tr>
<td>D.O. Synol &amp; 604 (wetting agent 2)</td>
<td>0.05, 0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Fomular @ MF 324 (defoamer).005</td>
<td>0.2%</td>
<td>0.2%</td>
</tr>
<tr>
<td>Anticid @ F30 (preservative 1)</td>
<td>0.4%</td>
<td>0.4%</td>
</tr>
<tr>
<td>Anticid ® MBS (preservative 2)</td>
<td>0.15%</td>
<td>0.15%</td>
</tr>
</tbody>
</table>

The mold casting sizing agent was produced as follows: water is placed in a vessel and the clay(s) broken up using a high-shear unit and a chopper disk for at least 15 minutes. Then the refractory components, pigments and colorants are mixed in for at least 15 minutes until a homogeneous mixture forms. Finally, additives such as wetting agents, defoamers and preservatives as well as the binder are mixed in for 5 minutes.

For the experiments that follow, the sizing agents were adjusted to a viscosity in the range of 0.6 Pas, suitable for application. The adjustment was done by adding appropriate amounts of water to the original composition and then homogenizing. The main characteristic in this case is the viscosity, measured with a Brookfield viscometer (DIN EN ISO 2555) and with a DIN 4 mm viscosity flow cup (DIN EN ISO 2431), at 20°C. in each case.

<table>
<thead>
<tr>
<th>Application parameters</th>
<th>Sizing agent 1</th>
<th>Sizing agent 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brookfield [Pas]</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Flow time [s]</td>
<td>15.5</td>
<td>15.5</td>
</tr>
<tr>
<td>Solids content [%]</td>
<td>77.1</td>
<td>66.9</td>
</tr>
<tr>
<td>Penetration depth [mm]</td>
<td>0.1</td>
<td>2</td>
</tr>
</tbody>
</table>

It was observed that less water penetrates into the sized molds and cores compared with conventional sizing agents. Consequently, as a result, the scope of effect of the carrier fluid, water, on the inorganic binder can be decisively reduced and the stability of the cores and molds produced can be increased.

The products available from the ASK Chemicals company, Triolite® WK-HP or Solite® W 3 can be cited as additional examples of sizing agents not in accordance with the patent.

In the following, the performance of the corresponding series of experiments, which served as the basis for the findings presented, will be described.

Producing and Testing the Molding Materials Test Pieces

Two different core geometries were investigated for experimental purposes. One geometry, the so-called Georg Fischer test bar, illustrates the behavior of the sized test pieces on thicker core geometries, while the other geometry, so-called long cores, illustrates the behavior of the sized test pieces on thin geometries. Georg Fischer test bars are defined as rectangular test bars with dimensions of 150 mm x 22.36 mm x 22.36 mm. The long cores have dimensions of 13 mm x 20 mm x 235 mm.

The composition of the molding material mixture is shown in Table 3. The following procedure was used for producing the Georg Fischer test bar: the components listed in Table 3 were mixed in a laboratory paddle vane type mixer (from Vogel & Schenmann AG, Hagen DE).

For this purpose, first the quartz sand was placed in a vessel and the water glass was added while stirring. A sodium water glass containing some potassium was used as the water glass. The SiO2-MgO modulus of the water glass was about 2.2, wherein M is the sum of sodium and potassium. After the mixture was agitated for one minute, amorphous silicon dioxide was optionally added under further agitation. The amorphous silicon dioxide is pyrogenic silica from the RW Silicium company. Then the mixture was agitated for an additional minute.

The molding composition mixture was transferred to the storage bunker, an H 2.5 Hot Box core shooting machine from the Röperwerk-Giessereimaschinen GmbH, Viersen, DE, the molding tool of which was heated to 180°C. The molding composition mixture was introduced into the molding tool using compressed air (5 bar) and remained in the molding tool for an additional 35 seconds. To accelerate the curing of the mixture, hot air (2 bar, 150°C) upon entry into
the tool) was passed through the molding tool for the last 20 seconds. The molding tool was opened and the test bar removed.

[0080] The coating compositions were applied to the test bar by dipping; the application parameters are listed in Table 2. The test bars were coated either immediately after removal from the molding tool or after a 30 min cooling time.

[0081] After application of the coating, the coated test bars were held in a drying oven for 30 min at 150°C.

[0082] To determine the bending strengths, the test bars were placed in a Georg Fischer strength testing apparatus equipped with a 3-point bending device (DISA Industrie AG, Schaffhausen, CH) and the force resulting in breakage of the test bar was measured.

[0083] The uncoated bending strengths were measured according to the following plan:

- 10 seconds after removal (hot strength)
- 1 hour after removal (cold strength).

[0084] The bending strengths were coated according to the following scheme:

- coated 1 minute after removal (hot coating)
- coated 30 minutes after removal (cold coating)

[0085] The coated bending strengths were measured according to the following plan:

- 10 seconds after removal from the drying oven
- 30 minutes after removal

[0086] (hot strengths, hot-coated)

<table>
<thead>
<tr>
<th>TABLE 3</th>
<th>Composition of the molding mixtures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz sand (G1)</td>
<td>Alkali elay (A2)</td>
</tr>
<tr>
<td>1 100 GT</td>
<td>2.0</td>
</tr>
<tr>
<td>2 100 GT</td>
<td>2.0</td>
</tr>
<tr>
<td>3 100 GT</td>
<td>2.0</td>
</tr>
</tbody>
</table>

[0087] (cold strengths, hot-coated)

<table>
<thead>
<tr>
<th>TABLE 4</th>
<th>Strengths on Georg Fischer test bars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot strength, cold coated [N/cm²]</td>
<td>Cold strength, cold coated [N/cm²]</td>
</tr>
<tr>
<td>1 400</td>
<td>450</td>
</tr>
<tr>
<td>2 295</td>
<td>300</td>
</tr>
<tr>
<td>3 270</td>
<td>275</td>
</tr>
</tbody>
</table>

[0088] Comparison, not according to invention

[0089] According to invention

<table>
<thead>
<tr>
<th>TABLE 5</th>
<th>Strengths on long cores</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot strength, cold coated [N/cm²]</td>
<td>Cold strength, cold coated [N/cm²]</td>
</tr>
<tr>
<td>1 250</td>
<td>280</td>
</tr>
<tr>
<td>2 180</td>
<td>220</td>
</tr>
<tr>
<td>3 -(broken)</td>
<td>-(broken)</td>
</tr>
</tbody>
</table>

| Hot strength, hot coated [N/cm²] | Cold strength, hot coated [N/cm²] |
| 1 250            | 280                     |
| 2 180            | 220                     |
| 3 -(broken)      | -(broken)               |

Results

[0090] The use of an alcohol-containing coating is undesirable because of the drawback presented by the release of emissions during the casting process. Using standardized water-based coating agents, the test pieces made of water glass-containing molding material agents lose considerable strength (sizing agent 2).

[0091] Surprisingly it was found that by using a combination of certain clays, sizing agents with an unusually high solids content can be produced, the viscosity of which is comparable to that of commercial ready-to-use sizing agents such as Trioflex® WK-LS 1.

[0092] The quality of the inorganic cores and molds coated with these sizing agents is lastingly improved, and thus for example, storage stability of the cores and molds for several days can be achieved. It should be mentioned in particular that despite the unusually high solids content, the viscosity of the sizing agents lies in a customary range for sizing agents. The agents can be brought into the condition suitable for application without using special additives or large amounts of water.

[0093] The high strengths of cores coated with sizing agent 2 according to the invention provide evidence of the positive effect.

1. A sizing composition comprising

(A) at least the following clays:

(A1) 1 to 10 parts by weight of palygorskite, which is a magnesium-aluminum hydroxilicate, present in the form of rod-shaped crystals with particle dimensions of 1 to 3 μm in length and of 1 to 5 μm in diameter;

(A2) 1 to 10 parts by weight of hectorite; and

(A3) 1 to 20 parts by weight of sodium bentonite, based on the ratio of the components (A1), (A2) and (A3) relative to one another;

(B) a carrier fluid comprising water that can be fully evaporated at up to 160°C and 1013 mbar; and

(C) refractory materials different from (A).

2. The sizing composition according to claim 1, comprising, independently of one another:

(A1) 1 to 5 parts by weight of palygorskite

(A2) 1 to 5 parts by weight of hectorite and

(A3) 1 to 10 parts by weight of sodium bentonite.
3. The sizing composition according to claim 1, wherein the total clay content A1, A2 and A3 of the sizing agents combined amounts to 0.1 to 4.0% by weight, based on the solids content of the sizing composition.

4. The sizing composition according to claim 1, wherein the carrier fluid comprises more than 50% by weight of water.

5. The sizing composition according to claim 1, wherein the solids content of the sizing composition amounts to 20 to 90% by weight.

6. The sizing composition according to claim 1, wherein the sizing composition comprises 10 to 85% by weight of refractory material, based on the solids content of the sizing composition.

7. The sizing composition according to claim 1, wherein the refractory materials are selected from the group consisting of: quartz, aluminum oxide, zirconium dioxide, aluminum silicates, zirconium sands, zirconium silicates, olivine, talc, mica, graphite, coke, feldspar, diatomite, kaolins, calcined kaolins, kaolinite, metakaolinite, iron oxide, bauxite and mixtures thereof.

8. The sizing composition according to claim 1, in which the refractory materials have particle sizes of 0.1 to 500 μm, measured by light scattering according to DIN/ISO 13320.

9. The sizing composition according to claim 1, wherein the sizing composition comprises 0.1 to 20% by weight of at least one binder, based on the solids content of the sizing composition.

10. The sizing composition according to claim 1, wherein the sizing composition is used as a concentrate and the fraction of the refractory solid (C) in the sizing composition is more than 70% by weight, based on the solids fraction of the sizing composition.

11. (Canceled)

12. A method for sizing molds and cores cured with an inorganic binder, comprising the steps of:
   a) providing a sizing composition by combining at least:
      (A) the following clays:
         (A1) 1 to 10 parts by weight of palygorskite, which is
               a magnesium-aluminum hydrosilicate, present in
               the form of rod-shaped crystals with particle
               dimensions of 1 to 3 μm in length and of 1 to 5 nm
               in diameter;
         (A2) 1 to 10 parts by weight of hectorite; and
         (A3) 1 to 20 parts by weight of sodium bentonite,
               based on the ratio of the components (A1), (A2)
               and (A3) relative to one another;
      (B) a carrier fluid comprising water that can be fully
           evaporated at up to 160°C and 1013 mbar; and
      (C) refractory materials different from (A)
   b) sizing molds and cores with the sizing composition,
      wherein the molds and cores consist of molding material
      mixtures cured with an inorganic binder.

13. (Canceled)

14. The method according to claim 12, wherein:
   the binder is water glass; and
   the molding material mixtures comprise particulate silicon
dioxide, particulate aluminum oxide, particulate titanium oxide,
particulate zinc oxide and mixtures thereof.

15. The sizing composition according to claim 3, wherein the total clay content A1, A2 and A3 of the sizing agents combined amounts to 0.5 to 3.0% by weight, based on the solids content of the sizing composition.

16. The sizing composition according to claim 3, wherein the total clay content A1, A2 and A3 of the sizing agents combined to 1.0 to 2.0% by weight, based on the solids content of the sizing composition.

17. The sizing composition according to claim 4, wherein the carrier fluid further comprises at least one alcohol, including polyalcohols and polyether alcohols.

18. The sizing composition according to claim 5, wherein the solids content of the sizing composition amounts to 80 to 85% by weight.

19. The sizing composition according to claim 8, in which the refractory materials have particle sizes of 1 to 200 μm, measured by light scattering according to DIN/ISO 13320.

20. The sizing composition according to claim 9, wherein the sizing composition comprises 0.5 to 5% by weight, of at least one binder, based on the solids content of the sizing composition.

21. The sizing composition according to claim 10, wherein the sizing composition is used as a concentrate and the fraction of the refractory solid (C) in the sizing composition is more than 80% by weight, based on the solids fraction of the sizing composition.

22. The sizing composition according to claim 10, wherein the total clay content A1, A2 and A3 of the sizing agents combined amounts to 0.1 to 4.0% by weight based on the solids content of the sizing composition.

23. The sizing composition according to claim 10, wherein the solids content of the sizing composition amounts to 20 to 90% by weight.

* * * * *