CASTING MOULD AND METHOD FOR THE PRODUCTION THEREOF

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ABSTRACT

A water-dispersible casting mould, particularly a core, for the manufacture of castings is proposed. The mould contains a water-insoluble, particulate material, such as moulding sand, a binder, which has a first binder component based on a condensed phosphate, and optionally a flux. In order to ensure an increased flexural strength and abrasion resistance, there is a second binder component based on polyamines. It is also possible to provide a flux based on alkali metal carbonate, which gives the mould an increased thermal stability. The invention also relates to a method for the manufacture of such a mould, in that the aforementioned components are mixed, accompanied by the addition of water, the mixture is moulded and at least part of the added free water is removed.

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Graph showing stress vs. time (σ [N/cm²] vs. t [min]) with data points labeled A, B, C, etc.
Fig. 6

[Diagram with bars labeled A, B, C, D, E, F, G, H, I, J, K, L, M, N. Axes labeled with [cm^2/N] on the x-axis and bars with time points (0, 1, 2, 3, 4, 5) on the y-axis.]

Legend:
- A: 0, 1: 2: 3: 4
- B: 0, 1: 2: 3: 4
- C: 0, 1: 2: 3: 4
- D: 0, 1: 2: 3: 4
- E: 0, 1: 2: 3: 4
- F: 0, 1: 2: 3: 4
- G: 0, 1: 2: 3: 4
- H: 0, 1: 2: 3: 4
- I: 0, 1: 2: 3: 4
- J: 0, 1: 2: 3: 4
- K: 0, 1: 2: 3: 4
- L: 0, 1: 2: 3: 4
- M: 0, 1: 2: 3: 4
- N: 0, 1: 2: 3: 4]
CASTING MOULD AND METHOD FOR THE PRODUCTION THEREOF

[0001] The invention relates to a water-dispersible casting mould, particularly core, for the manufacture of castings, which contains a water-insoluble, particulate material, particularly moulding sand, and a binder having as a first binder component at least one condensed phosphate. The invention also relates to a method for the manufacture of such a casting mould, in that a water-insoluble, particulate material, particularly moulding sand is mixed with a binder having as a first binder component at least one condensed phosphate and accompanied by the addition of water, the mixture is moulded and at least part of the added, free water is removed.

[0002] Cores of the aforementioned composition are known. They are generally manufactured in core boxes by means of core shooters for mass production. The core boxes are provided with corresponding mould cavities into which issue feed openings by means of which and by means of a so-called shooting head, a water-insoluble, particulate material provided with a binder is shot into the mould cavities using compressed air. The particulate material is generally in the form of moulding sands, such as silica, zircon, chromite sands and the like, which are compactable by the binder. For the manufacture of cores having a complex geometry the moulding sand should have a good flowability.

[0003] Conventionally liquid synthetic resins and additional additives are used as moulding sand binders. In order to avoid the disadvantages of synthetic resin binders, namely the formation of health-prejudicial vapours during production, partial burning of the binder during casting, complicated and costly core removal, disposal of the used core sand, the use of at least to some extent water-soluble, inorganic binders has been proposed.

[0004] Thus, DE 195 49 469 A1 discloses a core based on moulding sand compacted by means of a water-soluble binder, phosphoric acid or condensed phosphates, such as sodium polyphosphate and sodium hexametaphosphate being used as binders.

[0005] WO 92/06808 A1 discloses a core which, for compacting the moulding sand, has a binder of a water-soluble phosphate glass having polyphosphate chains or water-soluble borate glass. For manufacturing the core the moulding sand is mixed with the binder accompanied by the addition of water, the mixture is shot into the core boxes and the excess water is expelled from the mould by heating.

[0006] The known cores are water-dispersable following casting, i.e. they dissolve again after immersion in water, so that there is no need for complicated core removal. It is also an advantage of cores of this type that both during the manufacture of the cores and on casting the castings, as well as in the case of casting core removal no environmentally prejudicial substances are given off. The binders used also have an inorganic chemism, so that a burning of the binder during the casting process is reliably avoided.

[0007] However, it has been found that binders of the aforementioned type give the core an inadequate bending or flexural strength for many applications. Thus, the core can become deformed or even break on removal, during storage after moulding, on inserting in the mould or during the casting process, so that the castings obtained can be faulty and constitute waste material. In addition, cores of this type frequently have an inadequate abrasion resistance, so that during casting sand grains are deposited on the core surface and lead to a rough surface and/or to sand contamination of the casting. When using a binder based on pure, condensed phosphates, an additional problem is that the binder does not have an adequate thermal stability for alloys with a relatively high melting point, so that it is not possible to manufacture castings from such alloys. It is not possible to effectively counteract the indicated disadvantages by varying the process parameters during the manufacture of the core, such as the core composition, the drying temperature, the residual water content, etc.

[0008] The problem of the invention is to provide a casting mould, particularly a core, with a first binder component based on condensed phosphates and which is given an increased flexural strength and abrasion resistance, whilst increasing the thermal stability. However, it is also necessary to conserve acceptable cycle times during core manufacture and to release no or only small amounts of environmentally prejudicial substances. It is also directed at the manufacture of such a mould.

[0009] According to the invention this problem is solved in the case of a mould of the aforementioned type in that the binder has as a second binder component at least one polyamine.

[0010] It has surprisingly been found that both the flexural strength and the abrasion resistance of a mould or core from a water-insoluble, particulate material and a binder based on condensed phosphates can be significantly increased by the addition of only small amounts of polyamines, without impairing the water dispersibility of the cast core. In this way it is possible to obtain flexural strengths of more than 150 N/cm², which reliably avoid a failure of the core and the resulting faulty castings. At the same time the abrasion resistance of the mould or core is improved to such an extent that a deterioration of the casting by sand particles is virtually excluded.

[0011] It is assumed that the polar amino groups of the second binder component based on polyamines according to the invention interact with the polar phosphate groups of the first binder component based on condensed phosphates and as a result improve the binder characteristics thereof. In this connection the term “polyamines” means saturated or unsaturated, open-chain or cyclic, organic compounds with several primary, secondary and/or tertiary amino groups, particularly in liquid form. The water-insoluble, particulate materials can in particular be random known moulding sands, e.g. silica, zircon, chromite sands and the like and also thermally stable materials such as alumina, aluminosilicate, quartz glass, etc. in fine particulate form. It is obviously also possible to provide further binder components.

[0012] Whilst fundamentally it is also possible to provide low molecular polyamines, such as ethylene, propylene, butylene diamines, etc. and their condensation products as the second binder component, according to a preferred embodiment the polyamine is chosen from the group of polymeric polyamines. Among these particular advantages have been achieved with polyethylene imines, i.e. branched polymers with primary, secondary and tertiary amino groups, polyvinyl amines (vinyl amine polymers) and/or their copolymers. Thus, it is e.g. possible to virtually double
the flexural strength of a core from a moulding sand and a binder based on sodium polyphosphate through the addition of 0.1 wt. % polyvinyl amine, based on the moulding sand. The polymeric polyamines can in particular have a molecular weight between approximately 400 g/mole and approximately 10³ g/mole. Hereinafter are given in exemplified form the chemical formulas for polyvinyl amine (I) and polyethylene imine (II):

\[
\begin{align*}
(\text{I}) & \quad [\text{CH}_2-\text{CH}]-_n \\
(\text{II}) & \quad [\text{CH}_2-\text{NH}-\text{CH}_2-\text{NH}]_n \\
& \quad [(\text{CH}_2)_2-\text{NH}]_n-[(\text{CH}_2)_2-\text{NH}_2]
\end{align*}
\]

In a preferred variant the polyamine has a nitrogen proportion (N proportion) between 1 and 35 wt. % N/polymer unit, preferably between 10 and 33 wt. % N/polymer unit, particularly between 20 and 33 wt. % N/polymer unit. Particularly good flexural strengths of the core of above 200 N/cm² were obtainable with polymeric polyamines having a relatively high amino group density of around 30 wt. % N/polymer unit, e.g. with polyvinyl amines having a nitrogen proportion of up to 33 wt. % N/polymer unit and in particular with polyvinyl amines with a high proportion of free amino groups.

The quantity of the polyamine provided as the second binder component is preferably between 0.001 and 1 wt. %, particularly between 0.005 and 0.5 wt. % polyamine, based on the particulate material. It is mainly dependent on the nature of the polyamine and in general the polyamine quantity can decrease in proportion to the increase of the free amino group density of the polyamine in order to improve the binder characteristics with respect to the flexural strength and abrasion resistance.

The first binder component based on condensed phosphates can contain or entirely comprise phosphates, preferably alkali metal polyphosphates, particularly sodium polyphosphate, and/or metaphosphates, preferably alkali metal metaphosphates, particularly sodium metaphosphates, e.g. sodium hexametaphosphate. It is also possible for the first binder component to contain or completely comprise a polyphosphate and/or metaphosphate chain-containing, water-soluble phosphate glass, which preferably has between 58 and 75 wt. % phosphorus pentoxide (P₂O₅) and between 25 and 42 wt. % alkali metal oxide, particularly sodium oxide (Na₂O). The indicated binders are known per se and ensure a rapid, lump-free dissolving of the core if the latter is immersed in water with the finished casting. A further advantage of such binders is that they lead to an optimum mixing with the moulding sand in the case of a relatively low moisture content and ensure an adequate initial strength of the core or mould, so that only very short drying times are required and consequently very short cycle times arise.

The quantity of the first binder component based on condensed phosphates is appropriately between 0.25 and 25 wt. %, preferably between 0.5 and 10 wt. %, based on the water-insoluble, particulate material.

A further development of the invention is characterized by at least one flux, preferably in the form of sulphates, carbonates and/or nitrates from the group of alkali metals and/or alkaline earth metals, such as alkali metal carbonates, particularly sodium carbonate (Na₂CO₃). It has surprisingly been found that such a flux leads to a significant improvement of the thermal stability of the mould or core to a value above 800° C., so that it is possible to cast alloys with a relatively high melting point, e.g. aluminium alloys, as well as thermoplastics from high melting point polymers without there being any deformation of the mould or core during the casting process. It has also been found that a proportion of alkali metal carbonates increases the dispersibility of the core in water and consequently facilitates the core removal of the finished casting. As a function of the requisite thermal stability use is preferably made of between 20 and 90 wt. %, particularly between 30 and 85 wt. % alkali metal carbonate, based on the condensed phosphate-based first binder component.

In addition to the water-insoluble, particulate material such as moulding sand, the binder containing both condensed phosphates and polyamines and optionally the flux, particularly the alkali metal carbonates, the moulding material mixture for the mould or core generally also has a moisture proportion between 0.01 and 35 wt. %, particularly between 0.1 and 5 wt. %. After drying the moisture proportion of the mould or core is generally approximately 0.01 wt. % or less.

The method according to the invention is characterized in that a second binder component based on at least one polyamine is added. Preferably use is made of the above-described types of first and second binder components and optionally fluxes in the aforementioned quantities.

According to a preferred embodiment, the second binder component is brought in liquid form into contact with the particulate material and then the first binder component is admixed in dry form, water being added to the mixture. The second binder component can be in the liquid phase or in particular in the form of an aqueous solution. If a flux, such as alkali metal carbonates is desired, it can be dissolved in the water added to the mixture and the solution is then added to the mixture.

According to another preferred embodiment, the first binder component is mixed dry with the particulate material and then an aqueous solution together with the second binder component is added and also here, if desired, the flux can be dissolved in the solution prior to the addition thereof.

It is alternatively possible for the binder and optionally the flux to be dissolved in water and the solution contacted with the particulate material. In each case there should be a maximum homogeneous distribution of the water-soluble binder and optionally the flux with the particulate material.

Appropriately up to 35 wt. % water, based on the particulate material, are added and following shaping, the mould or core is e.g. dried to a residual moisture content of approximately 0.01 wt. %, based on the particulate material. The water quantity used is preferably kept as low as possible so as to ensure short cycle times during manufacture, which once again decisively depend on the drying time. However,
the flexural strength of the mould or core can be influenced within certain limits by the water proportion and the latter ensures the necessary flowability of the mixture on shooting into the core boxes. It has proved advantageous to add between 0.1 and 5 wt. %, particularly between approximately 0.1 and 3 wt. % water, based on the particulate material, in order to ensure short cycle times accompanied by a satisfactory flowability of the moulding material mixture.

[0024] According to a further development, the mixture is initially dried to a predetermined residual moisture content, water is then again added to the mixture and is moulded and at least part of the added, free water is removed again. The mixture is preferably initially dried to a predetermined residual moisture content of approximately 0.1 wt. %. In this way it is possible to further reduce the cycle times for the manufacture of the inventive mould or casting, in that the total proportion of added water can be reduced.

[0025] In addition, the moulding material mixture dried to a predetermined residual moisture content can easily be stored and easily processed as a result of the repeat addition of water. Here again, after shaping, the mould or core is appropriately dried to a residual moisture content of approximately 0.01 wt. %, based on the particulate material.

[0026] The invention is described in greater detail hereinafter relative to embodiments and the attached drawings, wherein show:

[0027] FIG. 1A graph for illustrating the flexural strength of a core with a sodium polyphosphate binder and without the addition of polyamines (A) and with the addition of 0.1 wt. % polyvinyl amine (B) at different residence times t.

[0028] FIG. 2A comparison graph for illustrating the flexural strength σ of a core with a binder exclusively formed from polyvinyl amine at different residence times t.

[0029] FIG. 3A graph to illustrate the flexural strength σ of a core of composition (B) according to FIG. 1 and which additionally contains a flux in the form of sodium carbonate at different residence times t.

[0030] FIG. 4A graph for illustrating the flexural strength σ of a core having the composition according to FIG. 3 after different storage times t1 of the moulding material mixture and following different residence times t2.

[0031] FIG. 5A graph for illustrating the flexural strength σ of in each case one core with a binder of sodium polyphosphate and different polyamines with different amino group densities (A, B, C, D, E) at different residence times t.

[0032] FIG. 6A graph for illustrating the flexural strength σ of in each case one core with the compositions (A, B, C, D, E) according to FIG. 5 after different storage times t for the moulding material mixture and after different residence times t2.

EXAMPLE 1

[0033] Cores having the following composition were manufactured.

[0034] Composition A:

[0035] moulding sand,

[0036] 2 wt. % sodium polyphosphate, based on the moulding sand (binder),

[0037] 1.4 wt. % moisture, based on the moulding sand.

[0038] Composition B:

[0039] moulding sand,

[0040] 2 wt. % sodium polyphosphate (binder component 1), based on the moulding sand,

[0041] 0.1 wt. % liquid polyvinyl amine (binder component 2), based on the moulding sand,

[0042] 1.4 wt. % moisture, based on the moulding sand.

[0043] For the manufacture of the core according to composition A the binder was admixed dry with the moulding sand. For the manufacture of the core according to composition B the second binder component was mixed in dissolved form and homogeneously with the moulding sand and then the first binder component was admixed dry with the mixture. Subsequently in each case approximately 1.4 wt. % water, based on the moulding sand was added. The moulding material mixture was in each case shot into a core box and dried to a residual moisture content of approximately 0.01 wt. %. The cores produced in this way were tested for their flexural strength after different residence times t.

[0044] As can be gathered from FIG. 1, the flexural strength of composition A exclusively with a conventional sodium polyphosphate binder, was approximately 80 N/cm² immediately following drying (t=0). After roughly 2 hours (t=120 min) there was a substantially constant flexural strength σ of approximately 100 N/cm². The flexural strength of composition B, which in addition to the first binder component in the form of sodium polyphosphate contained small amounts of a second binder component in the form of polyvinyl amine, was more than 150 N/cm² immediately after drying (t=0) and after approximately 4 hours (t=240 min) a substantially constant flexural strength of more than 200 N/cm² was obtained.

[0045] Thus, the bending strength of the core can be virtually doubled by the addition of only small polyvinyl amine quantities (0.1 wt. %, based on the moulding sand).

EXAMPLE 2

[0046] As a comparison test cores were produced in the above-described manner, but only polyvinyl amine was used as the binder. The flexural strength σ of the cores obtained was tested following different residence times t.

[0047] As can be gathered from FIG. 2, immediately following drying (t=0), there was a high flexural strength of more than 250 N/cm² and after approximately 2 hours (t=120 min) this had dropped to approximately 100 N/cm². It was also established that the cores with increasing storage time for the moulding material mixture prior to shooting into the core boxes and drying have an elastic behaviour, which can lead to core deformations during the casting process. Thus, pure polyvinyl amine proved to be relatively unsuitable as a binder for moulding sand.

EXAMPLE 3

[0048] Composition B according to example 1 (moulding sand, 2 wt. % sodium polyphosphate—binder component 1,
0.1 wt. % liquid polyvinyl amine—binder component 2 and 1.4 wt. % moisture, in each case based on the moulding sand) additionally received sodium carbonate (Na₂CO₃) as a flux in order to increase the thermal stability. In the manner described hereinbefore, cores were manufactured from the moulding material mixture obtained and following different residence times were tested for their flexural strength σ.

[0049] As can be gathered from FIG. 3, immediately after drying (t=0) there was a flexural strength of more than 200 N/cm², which for a short time (t=10 min) dropped somewhat and after approximately 2 hours (t=120 min) returned to a substantially constant value above 200 N/cm², which corresponds to the flexural strength of a core without the addition of Na₂CO₃, but with an otherwise corresponding composition (cf. composition B of FIG. 1).

[0050] The example shows that the flexural strength of the core is not impaired by Na₂CO₃ addition. However, the addition of Na₂CO₃ leads to a significantly better thermal stability of the core, so that the latter is e.g. suitable for the manufacture of aluminium castings with a casting temperature of above 800°C and it is possible to reliably avoid core deformation during the casting process. Moreover, Na₂CO₃ addition increases the water solubility of the core, so that core removal for the finished casting is made easier.

EXAMPLE 4

[0051] In order to investigate the storage characteristics of the moulding material mixture for a core according to example 3 moulding sand, 2 wt. % sodium polyphosphate (binder component 1) and 0.1 wt. % liquid polyvinyl amine (binder component 2), in each case based on the moulding sand, as well as sodium carbonate (Na₂CO₃) were homogeneously mixed with approximately 1.4 wt. % water, based on the moulding sand. The thus formed moulding material mixture was shot into a core box following different storage times t₁, of 0, 1, 2 and 3 h and dried to a residual moisture content of approximately 0.01 wt. %, based on the moulding sand. The flexural strength σ following different residence times t₂, namely on the one hand immediately following drying (t₂=0) and on the other after one day (t₂=24 h) was determined.

[0052] As can be gathered from FIG. 4, for moulding material mixture storage times t₁ between one and three hours there were only slightly inferior flexural strengths in the range just below 200 N/cm² as compared with the immediate shooting (t₂=0) of the mixture into the core boxes, which gave a flexural strength of approximately 220 N/cm². The flexural strength of the core immediately after drying (t₂=0) in all cases roughly corresponded to the flexural strength after a residence time of one day (t₂=24 h), which corresponds with the flexural strength pattern shown in FIG. 3.

[0053] This example makes it clear that the moulding material mixture has good storage characteristics and can be dried several hours after the mixing process, accompanied by the formation of the core.

EXAMPLE 5

[0054] Cores with the following composition were manufactured:

[0055] moulding sand,

[0056] 2 wt. % sodium polyphosphate, based on the moulding sand,

[0057] 0.1 wt. % of polyamine, based on the moulding sand,

[0058] 1.4 wt. % moisture.

[0059] As polyamines were on the one hand used different polyethylene imines (A, B), namely water-modified polyethylene imines with a molecular weight of approximately 2 g/mole (A) or 750,000 g/mole (B) and on the other polyvinyl amines (C, D, E) with a molecular weight of approximately 400,000 g/mole and which differ through the proportion of free amino groups, which once again corresponds to the degree of hydrolysis. The polyvinyl amine (C) has the highest degree of hydrolysis, the polyvinyl amine (E) a lower degree of hydrolysis than the latter and the polyvinyl amine (D) the lowest degree of hydrolysis of the polyvinyl amines (C, D, E).

[0060] The cores were manufactured in accordance with the method described in example 1. The thus produced cores were tested for their flexural strength σ after different residence times t₂.

[0061] FIG. 5 shows that the best flexural strengths were obtainable with the polyvinyl amine (C) having a high proportion of free amino groups. It is assumed that the free amino groups of the polyvinyl amine interact with the phosphate groups of the sodium polyphosphate and improve the binder characteristics thereof. FIG. 5 also makes it clear that following a residence time of approximately two hours (t₂=120 min) it was possible to achieve a substantially constant bending strength, which in the case of the polyvinyl amine (C) was at least 200 N/cm².

EXAMPLE 6

[0062] In order to investigate the storage characteristics of the compositions (A, B, C, D, E) for a core according to example 5, the moulding material mixtures were shot into a core box and dried following different residence times t₁ of 0, 1, 2 and 3 h. The flexural strength a was determined following different residence times t₂, namely on the one hand immediately after drying (t₂=0) and on the other after one day (t₂=24 h).

[0063] As can be gathered from FIG. 6, the best values for the flexural strength of the core were obtained after a moulding material mixture storage time t₁ of one hour, and whilst maintaining an only slightly inferior flexural strength, the mixture was processable immediately or at least three hours following the mixing of the individual components, so that here again good storage characteristics were established. In all cases polyvinyl amine (C) with a high free amino group proportion was found to be the most suitable. After a core residence time of one day (t₂=24 h), the flexural strength was improved compared with that immediately after the drying of the mixture (t₂=0), which corresponds to the flexural strength pattern shown in FIG. 5.

[0064] The examples make it clear that through the addition of small polyamine quantities as an additional binder component with respect to a conventional binder based on sodium polyphosphate, it is possible to significantly increase the flexural strength of the core. The flexural strength is also not impaired by the addition of a flux in the form of sodium
carbonate in order to improve the thermal stability of said core. The mixture has good storage characteristics and water solubility and therefore completely satisfactory processability.

1. Water-dispersible casting mould, particularly core, for the manufacture of castings, comprising
   a water-insoluble, particulate material, particularly moulding sand,
   a binder, having as a first binder component at least one condensed phosphate,
   wherein the binder has as a second binder component at least one polyamine.

2. Mould according to claim 1, wherein the polyamine is chosen from the group of polymeric polyamines.
3. Mould according to claim 1, wherein the polyamine is chosen from the group of polyethylene imines, polyvinyl amines and/or their copolymers.
4. Mould according to claim 2, wherein the polyamine has a nitrogen proportion between 1 and 35 wt. % N/polymer unit.
5. Mould according to claim 2, wherein the polyamine has a nitrogen proportion between 10 and 33 wt. % N/polymer unit.
6. Mould according to claim 2, wherein the polyamine has a nitrogen proportion between 20 and 33 wt. % N/polymer unit.
7. Mould according to claim 1, wherein there are between 0.001 and 1 wt. % polyamine, based on the particulate material.
8. Mould according to claim 1, wherein there are between 0.005 and 0.5 wt. % polyamine, based on the particulate material.
9. Mould according to claim 1, wherein the first binder component comprises or entirely consists of a metaphosphate.
10. Mould according to claim 9, wherein the metaphosphate is an alkali metal metaphosphate, particularly sodium polyphosphate.
11. Mould according to claim 1, wherein the first binder component comprises or entirely consists of a metaphosphate.
12. Mould according to claim 11, wherein the metaphosphate is an alkali metal metaphosphate, particularly sodium metaphosphate.
13. Mould according to claim 1, wherein the first binder component comprises or entirely consists of a phosphophosphate and/or metaphosphate-containing water-soluble phosphate glass.
14. Mould according to claim 13, wherein the phosphate glass contains between 58 and 75 wt. % phosphorous pentoxide (P₂O₅) and between 25 and 42 wt. % alkali metal oxide, particularly sodium oxide (Na₂O).
15. Mould according to claim 1, wherein there are between 0.25 and 25 wt. % of the first binder component, based on the particulate material.
16. Mould according to claim 1, wherein there are between 0.5 and 10 wt. % of the first binder component, based on the particulate material.
17. Mould according to claim 1, wherein by at least one flux, preferably in the form of sulphates, carbonates and/or nitrates from the group of alkali metals and/or alkaline earth metals, such as alkali metal carbonates, particularly sodium carbonate (Na₂CO₃).
18. Mould according to claim 17, wherein there are between 20 and 90 wt. % alkali metal carbonate, based on the first binder component.
19. Mould according to claim 17, wherein there are between 30 and 85 wt. % alkali metal carbonate, based on the first binder component.
20. Mould according to claim 1, wherein by a moisture proportion of the moulding material mixture between 0.01 and 35 wt. %, based on the particulate material.
21. Mould according to claim 20, wherein the moisture proportion of the moulding material mixture is between 0.1 and 5 wt. %, based on the particulate material.
22. Method for the manufacture of a water-dispersible casting mould, particularly core, for the manufacture of castings, in that a water-insoluble, particulate material, particularly moulding sand, is mixed, accompanied by the addition of water, with a binder having as a first binder component at least one condensed phosphate, the mixture is moulded and at least part of the added free water is removed, wherein a second binder component based on at least one polyamine is added.
23. Method according to claim 22, wherein a polyamine according to one of the claims 2 to 6 is added.
24. Method according to claim 22, wherein the polyamine is used in a quantity between 0.001 and 1 wt. %, particularly between 0.005 and 0.5 wt. %, based on the particulate material.
25. Method according to claim 22, wherein a first binder component according to one of the claims 9 to 14, is used.
26. Method according to claim 22, wherein the first binder component is used in a quantity between 0.25 and 25 wt. %, particularly between 0.5 and 10 wt. %, based on the particulate material.
27. Method according to claim 22, wherein use is made of at least one flux, preferably in the form of sulphates, carbonates and/or nitrates from the group of alkali metals and/or alkaline earth metals, such as alkali metal carbonates, particularly sodium carbonate (Na₂CO₃).
28. Method according to claim 27, wherein the alkali metal carbonate is used in a quantity between 20 and 90 wt. %, particularly between 30 and 85 wt. %, based on the first binder component.
29. Method according to claim 22, wherein the second binder component in liquid form is brought into contact with the particulate material and then the first binder component is admixed in dry form, water being added to the mixture.
30. Method according to claim 27, wherein the flux is dissolved in water and the solution is added to the mixture.
31. Method according to claim 22, wherein the first binder component is mixed dry with the particulate material and then an aqueous solution is added with the second binder component.
32. Method according to claim 31, wherein prior to the addition of the solution, a flux is dissolved in water and the solution is contacted with the particulate material.
34. Method according to claim 22, wherein up to 35 wt. % water, based on the particulate material, are added.

35. Method according to claim 22, wherein the mixture is initially dried to a predetermined residual moisture content, the mixture is then again mixed with water and the mixture is moulded and at least part of the added free water is removed again.

36. Method according to claim 35, wherein the mixture is initially dried to a predetermined residual moisture content of approximately 0.1 wt. %.

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