



US 20110036528A1

(19) **United States**(12) **Patent Application Publication**  
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§ 371 (c)(1),

(2), (4) Date: **Nov. 2, 2010**(30) **Foreign Application Priority Data**

Dec. 21, 2007 (DE) ..... 10 2007 063 552.6

Mar. 20, 2008 (DE) ..... 10 2008 015 966.2

**Publication Classification**(51) **Int. Cl.**  
**B22C 9/02** (2006.01)  
**B22C 11/00** (2006.01)(52) **U.S. Cl.** ..... **164/23**; 164/159; 164/228(57) **ABSTRACT**

A process for producing a mold includes introducing a composition including a particulate, refractory material and a binder into a hollow model having an interior cavity which determines contours of all surfaces of the mold or a mold part, wherein the model includes at least two separate parts to permit removal of the mold, and applying a second composition containing at least one organosilicon component and at least one solvent to at least one of the separable parts before use.

## PRODUCTION OF MOLDINGS FOR FOUNDRY PURPOSES

### RELATED APPLICATIONS

[0001] This is a §371 of International Application No. PCT/EP2008/010971, with an international filing date of Dec. 19, 2008 (WO 2009/083201 A1, published Jul. 9, 2009), which is based on German Patent Application Nos. 10 2007 063 552.6, filed Dec. 21, 2007, and 10 2008 015 966.2, filed Mar. 20, 2008, the subject matter of which is incorporated by reference.

### TECHNICAL FIELD

[0002] This disclosure relates to a process for producing molds for foundry purposes, in particular, mask molds, sand cores and parts thereof, and compositions and apparatuses suitable for use in this process.

### BACKGROUND

[0003] In foundry technology, heat-resistant molds which can be produced, in particular, from a particulate, refractory material and a binder are required.

[0004] Molds used for foundry purposes are frequently mask molds which can be produced by the Croning process (named for its inventor Johannes Croning). In general, mask molds consist of two halves which when placed together form a mold material shell corresponding to the contour of the model. Mask molds and parts thereof are preferably produced from mixtures of sand and synthetic resin using heated modeling apparatuses. The mixture is introduced into a hollow model whose inner cavity determines the contours of all surfaces of the mold to be produced or of the mold part to be produced. As a result of the action of heat during molding, the synthetic resin binder cures to form a self-supporting, mask-like mold of preferably low thickness which defines the exterior contour of the product to be cast. In the subsequent casting process, this mold can be, for example, backfilled with granular material.

[0005] To produce cavities in the interior of foundry products, cores which can be arranged within a casting mold and whose exterior shape corresponds to the interior contour of the product to be cast are required. The core may thus be a constituent of a mold. After casting, the core can be removed again (dissolved out) from the cast product.

[0006] Like mask molds, cores are usually produced from a particulate, refractory material and a binder. For example, in the core shooting process, sand admixed with binder (known as core sand) can be introduced under defined pressure and at defined temperature into a core box (an apparatus which generally consists of two parts of the mold or mold halves which during use enclose at least one interior cavity known as a mold cavity having the shape of the core to be manufactured). After curing the binder, the finished core (which on the basis of its composition is usually referred to as a sand core) can be removed from the core box and used for its intended purpose.

[0007] Since chemical reactions between the liquid metal and the mold are not allowed to occur in the production of cast metal products, mask molds and cores usually have to be made from very high quality materials, e.g., from pure silica sand. The particle size of the materials is preferably selected so that the surfaces of the cast products do not become too rough.

[0008] In general, organic binders such as liquid phenolic, furan and amino resins (or a combination thereof) are used as binders. With addition of a hardener such as ammonium stearate, a mixture thereof with a suitable particulate, refractory material can cure in a very short time at temperatures in the range from 200° C. to 270° C. However, inorganic binders have been used to an increasing extent in recent times. Possible binders of this type are, in particular, water glass, magnesium sulfate, sodium phosphate, clays, montmorillonite, glauconite, kaolin, aerogels, cement or gypsum plaster. In addition, sheet minerals, in particular, sheet silicates, are generally also suitable as inorganic binders.

[0009] However, both when using organic binders and when using inorganic binders, problems frequently occur. Thus, adhesion of the mixture of the particulate, refractory material and the binder to the walls of the abovementioned interior cavities frequently occurs. Over time, ever thicker caked material is formed and leads to inaccuracies in the moldings, which are later reflected in the finished cast product.

[0010] It is known that such adhering material or caked material can be avoided by means of "Quickpads." A Quickpad is an antiadhesion sticker which can, for example, be based on a Teflon layer. This has to be manually stuck on in the interior cavity and removed again and replaced when the effect diminishes, which is associated with a relatively high outlay. In addition, such Quickpads have only limited use since the very complex contours occurring in some regions of the interior cavities may make their use impossible. In addition, Quickpads have only limited thermal stability and are therefore unsuitable for use in heat-curing processes.

[0011] As an alternative to the Quickpad, it is known that single-use mold release agents, in particular, ones based on wax, can be used. Such mold release agents form a liquid film on walls of the interior cavities. However, they frequently remain ineffective in critical regions since the mixture of the particulate, refractory material and the binder is frequently under high pressure when it enters hollow models and core molds and the mold release agent is thereby mechanically washed off.

[0012] It could therefore be helpful to provide an improved industrial solution for the production of molds, in particular, mask molds and cores, for foundry purposes, in which the abovementioned problems do not occur.

### SUMMARY

[0013] We provide a process for producing a mold including introducing a composition including a particulate, refractory material and a binder into a hollow model having an interior cavity which determines contours of all surfaces of the mold or a mold part, wherein the model includes at least two separate parts to permit removal of the mold, and applying a second composition containing at least one organosilicon component to at least one of the separable parts before use.

### DETAILED DESCRIPTION

[0014] Selected preferred features may be explained in detail hereinafter only in the description of one of the abovementioned subjects. However, the corresponding explanation is nevertheless intended to apply to all subjects. The wording of all claims is hereby incorporated by reference into this description.

[0015] Our process produces molds for foundry purposes, particularly preferably mask molds, cores (in particular, sand cores) and parts thereof. The process thus allows production both of molds which define the exterior contour of a product to be cast and of molds which can be used for creating a cavity (cores).

[0016] In the process, a composition comprising a particulate, refractory material and a binder is introduced, in particular blown, into a hollow model. After the introduction, the binder is generally immediately cured, whereupon the molds produced can be removed. The interior cavity of the hollow model or its shape determines the contours of all surfaces of the mold to be produced or the core to be produced. The mold itself includes at least two parts which can be separated from one another to permit removal of the mold. To produce sand cores, preference is given to using a conventional mold box or a conventional mold flask, as are known in the art.

[0017] A process for producing molds for foundry purposes is particularly characterized in that a composition containing at least one organosilicon component and preferably at least one solvent is applied to at least one of the separable parts before it is used.

[0018] A process for producing cores for foundry processes preferably comprises:

[0019] introduction, in particular, shooting, of a composition containing a particulate, refractory material and a binder (the composition preferably consists essentially of the particulate, refractory material and the binder) through at least one feed opening into the interior cavity,

[0020] curing of the binder, and

[0021] removal of the mold.

[0022] The composition comprising the organosilicon component is preferably applied in such a way that the walls of the interior cavity are at least partly, preferably completely, covered by the layer or coating. In particular, the composition is applied in the regions which are particularly severely mechanically stressed during introduction of the composition comprising the particulate, refractory material and the binder, i.e., particularly the regions which are located opposite the at least one feed opening and are thus struck directly by the composition during shooting-in.

[0023] The composition is preferably applied by spraying on or dipping. It is naturally necessary to use a composition having a suitable consistency in each case. The properties required for this and also other properties of the composition can be adjusted by addition of appropriate additives such as thickeners, rheological additives and the like. Suitable additives are known and require no detailed explanation.

[0024] The composition comprising the organosilicon component can be cured immediately after application. Curing of the composition is preferably carried out thermally, more preferably at temperatures in the range from room temperature to 350° C., particularly preferably from 20° C. to 300° C., in particular from 30° C. to 200° C.

[0025] In this case, the composition preferably comprises at least one constituent which can be crosslinked thermally. This can also be, in particular, the at least one organosilicon component.

[0026] Preferably, curing can also be effected by electromagnetic radiation. The use of radiation having wavelengths in the UV and/or IR region is particularly preferred.

[0027] In this case, the composition preferably comprises at least one constituent which can be crosslinked by radiation. Thus, for example, the at least one organosilicon component

can have side chains which can be crosslinked by radiation (in particular, chains having ethylenic double bonds).

[0028] It is in principle also possible for curing to be carried out both thermally and by using radiation. Thus, components which can be crosslinked thermally and components which can be crosslinked by radiation can both be present in the composition, in which case it is not necessary for all components to be organosilicon components. Thus, for example, polyester resins can also be preferred as a constituent of the composition.

[0029] The organosilicon layer or coating produced in this way has an excellent release function and effectively prevents direct contact of the composition comprising the particulate, refractory material and the binder with at least the critical wall regions of the interior cavity. The layer or coating can therefore also be referred to as release layer. It has high nonwettability. In addition, it is characterized, in particular, by an extraordinarily high abrasion resistance and very good adhesion properties.

[0030] The particulate, refractory material is particularly preferably sand, especially silica sand.

[0031] As binders for the particulate, refractory material, it is possible to use the organic binders mentioned at the outset. However, it is also possible to use inorganic binders, optionally in combination with one or more organic binders. Possible inorganic binders are, in particular, water glass, magnesium sulfate, sodium phosphate, clays, montmorillonite, glauconite, kaolin, aerogels, cement, gypsum plaster, sheet minerals such as sheet silicates and combinations of the components mentioned.

[0032] As mentioned above, we use a composition containing at least one organosilicon component and preferably at least one solvent for producing molds for foundry purposes and parts thereof, in particular, in a process for producing molds for foundry purposes.

[0033] The at least one organosilicon component is preferably a crosslinkable component and thus comprises compounds which can undergo reactions with one another on irradiation and/or on heating. It particularly preferably comprises a silane or a siloxane or a crosslinkable silicone compound. Combinations of silanes and siloxanes or silicones can also be used.

[0034] Particularly suitable silanes are organofunctional silanes such as aminosilanes, epoxysilanes and methacryloxysilanes and isocyanatosilanes. Preferably, the methacryloxysilanes are, in particular, radiation-crosslinkable silanes which can be cured, for example, by UV radiation as has been discussed above.

[0035] Suitable siloxanes and silicones are, for example, polysiloxanes such as, in particular, polydialkylsiloxanes (in particular, polydimethylsiloxane), polyorganosiloxanes, epoxysilicones and polyether silicones. These should each have crosslinkable groups. The crosslinkable groups can be, for example, groups such as free hydroxy groups which can undergo a condensation reaction or, for example, alkoxy groups from which free hydroxy groups can be formed.

[0036] Furthermore, it is preferred that the composition has further organosilicon components. In particular, alkoxysilanes are preferably present. Among the particularly preferred alkoxysilanes, particular mention may be made of alkylalkoxysilanes such as trimethylethoxysilane or trimethylmethoxysilane.

[0037] In summary, a composition thus contains, in preferred form, at least one of the above-mentioned crosslinkable organosilicon compounds and additionally at least one alkoxysilane.

[0038] Furthermore, the composition can contain at least one silane having halogen-containing, preferably fluorine-containing, side chains, in particular, as at least one crosslinkable organosilicon component. This is particularly preferably an alkoxysilane having halogen-containing, in particular, fluorine-containing, side chains, particularly preferably tridecafluoro-1,1,2,2-tetrahydrooctyl-1-triethoxysilane.

[0039] A composition containing both such a silane having halogen-containing side chains and an alkylalkoxysilane is described in the examples.

[0040] Apart from the at least one crosslinkable organosilicon component, a composition which can be used can also comprise at least one further crosslinkable organic component which is not of an organosilicon nature, in particular, a polyester component.

[0041] Particularly preferably, the at least one crosslinkable organosilicon component and the at least one further crosslinkable organic component are present in combination as silicone polyester resin in the composition. Suitable silicone polyester resins are, for example, commercial polyester-modified methyl-phenyl-silicone resins which are also suitable for coating of baking molds for easier removal of bakery products from molds.

[0042] Furthermore, it is preferred that the composition comprising the at least one organosilicon component has one or more mold release agents, in particular, at least one release oil. The mold release agent is preferably a linear or branched polysiloxane, in particular, a polysiloxane of the formula  $\text{RO}—[\text{R}'_2\text{Si}—\text{O}]_n—\text{R}$ , where R and R' are, independently of one another, an alkyl radical having from 1 to 8 carbon atoms or an aromatic radical having from 6 to 20 carbon atoms.

[0043] Preferably, inorganic particles, in particular, particles having particle sizes in the range from nanometers to microns, can also be present in the composition comprising the at least one organosilicon component. The nature of the inorganic particles is not critical and all ceramic particles are fundamentally suitable. However, silicate particles are particularly preferred. It has surprisingly been found that the presence of such particles significantly increases the abrasion resistance of the release layer.

[0044] As further components, a composition comprising the at least one organosilicon component has components suitable as crosslinkers. Customary crosslinkers are known to those skilled in the art. Particular preference is in the present case given to using triethoxysilane (TEOS) or triacetoxymethylsilane.

[0045] In addition to the crosslinker or as an alternative thereto, a composition can also have a catalyst, in particular, at least one condensation catalyst. This can be, for example, an acid such as hydrochloric acid or sulfuric acid.

[0046] The abovementioned solvent is preferably an organic solvent, in particular, at least one alcohol, ether and/or ester. Nonpolar solvents such as petroleum spirit can also be used. However, the nature of the solvent is in principle not critical.

[0047] An apparatus for producing molds for foundry purposes is particularly suitable for producing mask molds and sand cores. It has at least one part which is provided with an

organosilicon layer or coating, in particular, a cured organosilicon layer or coating. The apparatus is accordingly itself preferably a mold.

[0048] The layer or coating is preferably produced from a composition containing at least one organosilicon component and preferably at least one solvent, as has been comprehensively described above.

[0049] Preferably, the layer or coating has a thickness in the range from 1  $\mu\text{m}$  to 100  $\mu\text{m}$ , in particular, from 1  $\mu\text{m}$  to 20  $\mu\text{m}$ .

[0050] The at least one part preferably consists at least partly, preferably also entirely, of metal and/or plastic.

[0051] The layer or coating is particularly preferably permanently or at least semipermanently bound to the at least one part of the mold. Preferably, the bond is so strong that the layer cannot be detached without destruction. On the surface of the at least one part, the layer or coating forms an organosilicon matrix in which inorganic particles can be embedded in preferred forms.

[0052] Further features can be derived from the examples. Here, individual features can in each case be realized either on their own or as a combination of a plurality thereof in one form. The preferred forms described serve merely for the purposes of illustration and to give a better understanding and do not constitute any restriction.

#### EXAMPLE 1

##### Production of a Composition A

[0053] In a 1000 ml flask, 500 g of a polyester-modified methyl-phenyl-polysiloxane resin admixed with a release substance (for example, a commercial polyester-modified methyl-phenyl-polysiloxane resin suitable for removal of sugar-containing bakery products from molds) and 500 g of methoxypropyl acetate as solvent (possibly colored blue with ultramarine blue extra dark) are mixed with one another and the mixture is stirred at RT for one hour. Depending on the desired layer thickness, dilution in a ratio of from 2:1 to 1:2 is possible. After stirring at RT for 4 hours, the product is ready to use and can be applied by spraying.

#### EXAMPLE 2

##### Production of a Composition B

Composition:

[0054]

Raw material	%
2-Propanol	93.8425
Silane having fluorine-containing side chains	2.49
TEOS (Dynasyl A) Tetraethoxysilane	2.035
Trimethylethoxysilane	0.5775
Hydrochloric acid 0.1 mol/l	1.055

[0055] The alcohol is placed in a 1000 ml glass flask. The silane having fluorine-containing side chains (tridecafluoro-1,1,2,2-tetrahydrooctyl-1-triethoxysilane), the TEOS and the trimethylethoxysilane are added in succession over a period of one hour from a dropping funnel while stirring vigorously. The hydrochloric acid is then added dropwise. After stirring

at room temperature for 4 hours, the hydrolysis product is ready to be used and can be applied.

### EXAMPLE 3

#### Production of a Composition C

[0056]

Raw material	%
2-Propanol	93.76
Silane having fluorine-containing side chains	2.55
Colloidal silicate dispersion	3.59
Conc. sulfuric acid	0.10

[0057] The alcohol is placed in a 100 ml glass flask. The silane having fluorine-containing side chains (tridecafluoro-1,1,2,2-tetrahydrooctyl-1-triethoxysilane) and the colloidal silicate dispersion (silicate dispersion in isopropanol having a particle size of about 13 nm and a solids content of 30%) are added in succession over a period of one hour from a dropping funnel while stirring vigorously. The sulfuric acid is then added dropwise. After stirring at RT for 4 hours, the product is ready to use and can be applied.

### EXAMPLE 4

#### Processing of Composition A

[0058] In preparation, the parts to be coated (e.g., stainless steel test plates having a size of 5 cm×15 cm as test substrates) are preferably cleaned with isopropanol. As an alternative or in addition, the parts can also be cleaned by sand blasting.

[0059] The product A from Example 1 is applied by means of a spray gun (e.g., SATA minijet 4 HVLV having a 0.8 nozzle) at 2 bar. The layer thicknesses achieved are in the range from 3 μm to 75 μm. Curing is carried out (in a drying oven) at from 150° C. to 230° C. over a period of from 1 to 4 h.

### EXAMPLE 5

#### Processing of Compositions B and C

[0060] The products B and C from Examples 2 and 3 are applied by means of a cloth (preferably cleanroom cloth, e.g., Betawype TX 2009 from Texwype) and rubbed in (polished). Thermal setting is carried out at 200° C. by means of a hot air blower over a period of from 1 to 3 minutes, preferably 90 s, or (in a drying oven) 1-4 h at 150-190° C., preferably 2 h at 190° C.

### EXAMPLE 6

[0061] In an automotive foundry, a core flask having 20 engravings was treated with the product A. Here, the critical regions (places opposite the shooting-in nozzles for the core mold material) were treated with the product. The product was applied and allowed to cure at room temperature for 24 hours. The core flask was then used in mass production. It was found that the time until critical caking of core mold material occurred could be tripled.

### EXAMPLE 7

[0062] In a foundry, the parts of a hollow model for producing exterior molds for the casting of sanitary fittings were

treated with the product A. Product A was applied in such a way that the walls of the interior cavity of the hollow model were completely coated with a thin layer of the product. The product was subsequently allowed to cure at room temperature for 24 hours. The mold was then used in mass production. Even after the hollow model had been used a number of times, no critical caking of mold material was observed.

### EXAMPLE 8

[0063] In an automotive foundry, a mold box made of metal having two engravings was treated with the product A. In the case of one engraving, the critical regions (places opposite the shooting-in nozzles for the core mold material) were treated with the product. The product was applied and allowed to cure at room temperature for 24 hours. The second engraving was covered by sticking on a Quickpad (adhesive film having a non-stick effect). The mold was then used in mass production. It was found that the time until critical caking of core mold material occurred is identical for the two methods.

1-28. (canceled)

29. A process for producing a mold comprising:

introducing a composition comprising a particulate, refractory material and a binder into a hollow model having an interior cavity which determines contours of all surfaces of the mold or a mold part, wherein the model comprises at least two separate parts to permit removal of the mold; and

applying a second composition containing at least one organosilicon component to at least one of the separable parts before use.

30. The process as claimed in claim 29, further comprising: introducing a composition comprising the particulate, refractory material and the binder through at least one feed opening into the interior cavity;

curing the binder; and

removing the mold.

31. The process as claimed in claim 29, wherein the composition comprising the organosilicon component is applied such that walls of the interior cavity are partly or completely covered with a layer of the composition.

32. The process as claimed in claim 29, wherein the composition comprising the organosilicon component is cured after introduction into the interior cavity.

33. The process as claimed in claim 32, wherein curing the composition is effected thermally.

34. The process as claimed in claim 29, wherein the particulate, refractory material is sand.

35. The process as claimed in claim 29, wherein the organosilicon component is at least one member selected from the group consisting of crosslinkable silanes, siloxanes and silicone compounds.

36. The process as claimed in claim 29, wherein the composition containing the organosilicon component comprises at least one alkoxysilane.

37. The process as claimed in claim 36, wherein the composition containing the organosilicon component comprises trimethylethoxysilane or trimethylmethoxysilane.

38. The process as claimed in claim 29, wherein the organosilicon component comprises at least one silane having halogen-containing side chains.

39. The process as claimed in claim 38, wherein the silane having halogen-containing side chains is at least one alkylalkoxysilane having fluorine-containing side chains.

40. The process as claimed in claim 39, wherein the silane having halogen-containing side chains is tridecafluoro-1,1,2,2-tetrahydrooctyl-1-triethoxysilane.

41. The process as claimed in claim 29, wherein the composition containing the organosilicon comprises at least one further crosslinkable organic component which is not an organosilicon.

42. The process as claimed in claim 41, wherein the at least one further crosslinkable organic component is a polyester component.

43. The process as claimed in claim 41, wherein the organosilicon component and the one further crosslinkable organic component are present as silicone polyester resin in the composition.

44. The process as claimed in claim 29, wherein the composition containing the organosilicon component has at least one mold release agent.

45. The process as claimed in claim 43, wherein the mold release agent is a polysiloxane of the formula  $\text{RO}—[\text{R}'_2\text{Si}—\text{O}]_n—\text{R}$ , where R and R' are each, independently of one another, an alkyl radical having from 1 to 8 carbon atoms or an aromatic radical having from 6 to 20 carbon atoms.

46. The process as claimed in claim 29, wherein the composition containing the organosilicon component has inorganic particles.

47. The process as claimed in claim 29, wherein the inorganic particles have particle sizes in the nanosize range.

48. The process as claimed in claim 46, wherein the particles are silicate particles.

49. The process as claimed in claim 29, wherein the composition containing the organosilicon component has at least one component suitable as a crosslinker.

50. The process as claimed in claim 49, wherein the crosslinker is triethoxysilane (TEOS).

51. The process as claimed in claim 29, wherein the composition containing the organosilicon component has at least one catalyst.

52. The process as claimed in claim 51, wherein the catalyst is an acid.

53. The process as claimed in claim 29, wherein the composition containing the organosilicon component has at least one organic solvent.

54. An apparatus for producing molds for foundry purposes, in particular mask molds or sand cores, comprising at least one part which is provided with an organosilicon layer or coating.

55. The apparatus as claimed in claim 54, wherein the layer or coating has a thickness in the range from 1  $\mu\text{m}$  to 100  $\mu\text{m}$ .

56. The apparatus as claimed in claim 54, wherein the layer or coating has an organosilicon matrix in which inorganic particles are embedded.

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