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I-42100 Reggio Emilia(IT)**(54) **Porous mould materials, their production and their use for forming ceramic castings.**

(57) The invention relates to porous, water-absorbent plastics mould material for use in the forming of ceramic castings from ceramic moulding materials. According to the invention they contain short fibres of length 1-6 mm in a quantity of up to 4 weight% with respect to the weight of the plastics content, as filler.

The invention also relates to a process for producing these mould materials and their use in the forming of ceramic castings.

Shrinkage and mechanical properties are considerably improved by the addition of short fibres, even in a very small added quantity. By producing the mould materials from water-in-oil emulsions the permeability of the mould materials can be adjusted within a wide range by controlling the degree of dispersion of the emulsion, so that both pressure-less and pressurized ceramic body formation and controlled release of the ceramic body from the mould by compressed air without the use of an aid become possible.

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The invention relates to porous mould materials and moulds, their production and their use for forming ceramic castings from ceramic materials ranging from liquid to plastic consistency by casting, pressure casting, rotation and pressing.

As is well known, such moulds have up to the present time been advantageously produced from plaster of Paris, which allows simple mould production by casting and because of its absorption properties it presupposes that a sufficiently firm ceramic body will be formed. The water taken from the ceramic material by the mould material is removed by drying after one or more casting operations.

In order to shorten the drying process or economize on the drying, plaster of Paris moulds are also used as pressure casting moulds and press moulds. In these, the plaster of Paris moulds are provided with a channel system extending over the inner mould surface, and through which vacuum and compressed air can be fed into the mould. Compressed air releases the casting from the surface, by which water taken up from the mould is blown out. Vacuum serves to retain the casting in a part of the mould until it is desired to release it.

Various systems have already been described for producing the compressed air and vacuum channels in the mould. It is known to use fabric-covered spiral hoses and flexible cords, which are cast in and are pulled out after hardening. In both cases devices are required to which the hoses and cords are fixed and maintained spaced apart over the mould inner surface. Finally, the possibility has also been described of producing such moulds in two layers, one being finely porous, for example of plaster of Paris, and the other being coarsely porous, this being placed against the finely porous layer and serving directly for feeding vacuum and compressed air.

The moulding process can be considerably accelerated by using pressure. However, plaster of Paris is not a suitable material for this method, and hence a suitable replacement has been sought. Various processes are known for producing porous moulds from plastics instead of plaster of Paris, the following methods having been described for achieving the required porosity:

For example the required moulds can be produced from open-pore hardened polyurethane foam by machining. The cost involved is however relatively high. In addition the material tends to fracture under high pressure-stressing because of its brittleness. Moulds of hardened polyurethane foam are therefore not really suitable as mould material for producing ceramic castings.

CH 490 960 A describes a process in which highly filled resins such as epoxy resins, phenolic resins and furan resins, are used as the binder in the production of mould materials. Glass micro-heads or powdered quartz are used as the filler. The quantity of resin is determined such that it only wets the filler particles, so that open pores result in the free intermediate spaces.

Various difficulties are however associated with this procedure. The resin proportion is so small that the resultant mixtures are not flowable, and instead have to be rammed or forced into the required mould. In addition, the attainable pore volume is only small (10-20 vol%) and cannot be easily adjusted. The inorganic fillers make the machine-finishing of such moulds more difficult because of their large quantity.

DE 19 28 026 A describes the production of porous moulds from water-in-oil emulsions which in addition to water and monomers contain swellable fine-grain polymer particles. Such a polymerization system consists for example of polymethylacrylate (PMA), methylmethacrylate (MMA) and water in the weight ratio of 1:1:1. According to this state of the art, after adding hardeners and accelerators, the pourable emulsions are cast into a corresponding mould and hardened. When hardening sets in, the emulsion becomes unstable because of the removal of the monomer and the swelling of the polymer part. The phases show coalescence, and relatively coarse pores form having a diameter of 10-40 μm . This means that a high pressure of about 15-40 bar is necessary for ceramic body formation using such mould materials. Mould materials produced by this process are therefore only suitable for pressure casting. The cost of mould production and additional machining is high because of the acting pressure during use and the special polymer beads required for production, so that this conventional method is suitable only for special industrial production of porous mould materials as a substitute for plaster of Paris.

EP 165 952 A describes the production of porous mould materials having the properties typical of plaster of Paris, by which ceramic bodies can be produced from ceramic materials in a short time without the use of pressure. To achieve a suction action effective for the ceramic body formation, the emulsion to be used for producing the mould materials is adjusted to a determined degree of dispersion, and in particular to a viscosity within the range of 1600-5000 cP, particularly by adjusting the stirring or mixing conditions and the duration of mixing. With these conventional mould materials the ceramic body formation rate is higher the higher the emulsion viscosity set during the production of the water-in-oil emulsion. Compared with plaster of Paris, with these known mould materials the ceramic body formation rate can be increased by adding substances such as calcium sulphate dihydrate, sodium disilicate or disodium tetraborate as regulators for the resultant porosity. By applying pressure to such moulds the ceramic body

formation time can be additionally shortened using a pressure in the range of up to about 3 bar gauge. However, the added pore-width regulator substances have the drawback of leading to considerable shrinkage, which is extremely unfavourable in the production of castings from ceramic materials, in which particular dimensional accuracy is required throughout.

5 According to EP 165 952 A the porous plastics mould materials are produced from hardenable water-in-oil emulsions corresponding to DE 19 28 026 A, however no special polymer powder for making the emulsions unstable is used.

Although in DE 19 28 026 A the produced pressure casting moulds are dewatered with compressed air after each casting and the ceramic bodies formed can be released from the mould with compressed air, in
10 EP 165 952 A the produced mould materials cannot be treated in the same way. The increased resistance to flow due to the smaller pore width hinders dewatering and ceramic body release using pressure. Instead the ceramic bodies of such mould materials are released by virtue of the shrinkage arising during dewatering. For this reason the advantages connected with the fine porosity of this material cannot be fully utilized technically in the desired manner. The shrinking-out of the ceramic body from the mould requires
15 time. What is to be aimed at is an accelerated ceramic body formation under slight pressure, with the release of the ceramic body from the mould with compressed air set to the required time.

The mould material of EP 165 952 A behaves in this respect as plaster of Paris, which likewise does not allow release of the casting with compressed air on account of its fine porosity. In this case this is aided by producing additional porosity in the plaster of Paris mould. Compressed air is blown in through a
20 channel system provided in the mould and penetrates by pressure through the mould. This produces a coarse pore system through which the compressed air can escape. In this way a permeability is achieved which makes it possible to release the ceramic body with compressed air.

The object of the invention is to provide plastics-based porous mould materials which can be produced with little or no shrinkage and which are suitable for both pressure-less and pressurized forming of ceramic
25 castings. The corresponding process for producing ceramic castings using these mould materials and suitable processable compositions will also be defined.

This object is attained in accordance with the main claim. The subsidiary claims relate to advantageous embodiments of the inventive concept.

The porous, open-pore water absorbent mould materials of the invention consist of a hardened, filler-
30 containing plastics material and have a water-fillable pore volume of at least 10% of the total volume. They are characterised by containing, as filler, short fibres having a length of 1-6 mm and in a quantity of up to 4 weight% with respect to the weight of the plastics content excluding additives.

The basic concept of the present invention is that by adding even very small quantities of short fibres a considerable reduction in shrinkage can be achieved, which in view of the current state of the art is
35 surprising, and in particular the effectiveness of even very small quantities of added short fibres.

According to an advantageous embodiment, the mould materials contain between 0.5 and 10 weight% of short fibres with respect to the weight of the plastics content excluding additives. If plastics filler particles are added to the polymerization system for producing the plastics matrix, these are to be considered as
40 additives and not to be taken as part of the weight of the actual plastics content.

Particularly advantageous is a short-fibre content in the range of 1-1.5 weight% with respect to the emulsion.

According to the invention, short fibres of textile materials, carbon and/or glass are particularly preferred as fillers, and especially glass staple fibres.

In addition to the primary short fibres which serve to reduce shrinkage, the mould materials according
45 to the invention can also contain further fillers, which can be of granular, spherical or spheroidal shape. Suitable such additional fillers are for example glass micro-beads, ceramic micro-beads, hollow glass micro-beads, hollow ceramic micro-beads and/or granulated polymers from powder form to fine granular form, in particular those which are only difficultly soluble or only swellable in the polymerization system used for producing the mould materials.

50 These further fillers can be contained in a quantity of up to 15 weight% with respect to the total dry weight.

The plastics material consists advantageously of a homopolymer or a copolymer of monomer units deriving from styrene, α -methylstyrene, allyl phthalate, acrylic esters, in particular methylacrylate or ethylacrylate, and/or methacrylic esters, in particular methylmethacrylate or ethylmethacrylate, or contains
55 such monomer units.

The plastics material can be advantageously cross-linked with a multi-functional crosslinking agent such as divinylbenzene or a diacrylate or dimethylacrylate. It can also contain in-polymerized or grafted homopolymer blocks.

Particularly advantageous properties are obtained if the plastics material contains polymer blocks deriving from an unsaturated polyester.

The pore size of the mould materials is advantageously in the range from 0.1 to 0.5 μ and is adjustable.

The mould materials of the invention can be produced by any desired emulsion polymerization process, it being particularly advantageous to carry out the following process steps:

A) Production of a water-in-oil emulsion (W/O emulsion) with an oil phase consisting of one or more polymerizable liquid monomers using emulsifiers and a water content corresponding to the desired pore volume; and

B) Polymerization of the oil phase of the water-in-oil emulsion in the presence of a polymerization initiator in a mould; and if necessary

C) Removing the water from the mould material obtained;

this advantageous process being characterised according to the invention in that short fibres of a length of 1-6 mm are added to the polymerization system in a quantity of up to 4 weight%, with respect to the weight of the polymerizable part of the emulsion excluding additives.

In accordance with EP 165 952 A, for achieving a desired permeability or water suck-off action of the mould material it is advantageous to set the degree of dispersion of the water phase of the W/O emulsion by mixing to achieve a viscosity within the range of 1600-5000 cP in step A, particularly by adjusting the mixing time and/or the mixing intensity.

The further fillers are added to the polymerization system, in particular to the W/O emulsion, preferably in a quantity of up to 35 vol% with respect to the polymerization system including the water. (Vers. 7).

According to the invention it is further advantageous to use W/O emulsions with an oil phase in which a polyester resin, in particular an unsaturated polyester resin, and/or a liquid prepolymer predominantly of methylmethacrylate are dissolved in a quantity of 40-70 weight%.

Advantageously, calcium sulphate dihydrate, sodium disilicate and/or disodium tetraborate can be added to the W/O emulsion as permeability regulator. Although in accordance with the aforesaid state of the art the addition of this regulator further unfavourably increases the shrinkage of the mould materials, this shrinkage is restricted by the addition of short fibres according to the invention, so that the advantageous effects of the permeability regulator can be fully utilized. These regulators are advantageously added in a quantity of between about 2 and 12 weight% with respect to the weight of the polymerizable part of the emulsion.

The polymerizable liquid monomer or monomers are advantageously used according to the invention in a quantity of between 30 and 78 weight% with respect to the weight of the emulsion.

Powdered polymers swellable in the oil phase of the emulsion, polymethylmethacrylate-polymer beads, barite and/or ground quartz can be used as further fillers.

The surface of the mould materials or the outer surfaces of the corresponding moulds can be sealed by applying aqueous synthetic resin solutions, in order to direct the pressure in a determined direction (onto the inner surface of the mould) and to prevent the pressure medium (compressed air, water) from leaking out. Melamine resins, for example melamine-urea-formaldehyde resins, epoxy resins or film-forming synthetic resin dispersions are suitable for this purpose.

The use of glass fibres or glass beads treated with an adhesive, particularly by silanizing, is to be preferred because of their better adhesion to the matrix which surrounds them.

The moulds used for producing ceramic castings can be formed from the mould materials according to the invention either by machining, in particular by turning, milling and/or drilling, or by direct casting in a mould. In this latter case the procedure is as follows:

A) Production of a water-in-oil emulsion (W/O emulsion) with an oil phase consisting of one or more polymerizable liquid monomers using emulsifiers and a water content corresponding to the desired pore volume; and

B) Polymerization of the oil phase of the water-in-oil emulsion in the presence of a polymerization initiator in a mould; and if necessary

C) Removing the water from the mould material obtained,

wherein in step B a mould is used corresponding to the negative shape of the mould for producing the casting. In accordance with the invention, short fibres as heretofore defined are added to the polymerization system.

The method of the invention for producing ceramic castings from water-containing ceramic moulding materials from liquid to plastic consistency using moulds formed from a mould material produced by polymerization of a water-in-oil emulsion of a porous, open-pore, water-absorbent and hardened plastics with a pore volume of at least 10% of the total volume can be carried out by pouring, loading or forcing the ceramic moulding material into the mould, possibly applying pressure in excess of atmospheric to the

mould, and particularly a pressure of up to about 5 bar gauge, to if necessary empty the residual liquid slip from the mould and to release the formed ceramic body from the mould after sufficient dewatering. For this purpose a mould formed from a mould material as heretofore defined is used.

The release from the mould is simplified if, before pouring the moulding material into a mould formed from the mould material according to the invention, powdered plaster of Paris or an aqueous plaster of Paris suspension with a plaster of Paris content of at least 1 weight% is applied to the mould, for example by spraying.

An advantageous machinable composition suitable for use in the aforescribed method for producing mould materials comprises:

I) a styrene-containing polyester casting resin which in addition to styrene contains copolymerizable acrylates and/or methacrylates, or a liquid prepolymer of predominantly methylmethacrylate, containing copolymerizable acrylates and/or methacrylates,

II) emulsifiers and possibly surface active substances as required for forming a W/O emulsion, and if appropriate

III) calcium sulphate dihydrate, sodium disilicate and/or disodium tetraborate decahydrate in a quantity of between 2 and 15 weight% with respect to the weight of component I;

This machinable composition containing, according to the invention, short fibres of length 1-6 mm in a quantity of up to 4 weight%.

The use of short fibres in accordance with the invention considerably reduces shrinkage, as can be seen from the ensuing experimental part. Again, as stated heretofore, the permeability of the mould materials towards gases and liquids can be controlled such that under pressurization by compressed air or by suction, the liquid taken up from the mould can be squeezed out or forced from the mould surface towards the rear, to be sucked off, the ceramic body being easy to loosen with compressed air, which in known manner is fed via a channel system located in the vicinity of the inner mould surface. In addition, the mould materials according to the invention are also suitable for pressure-less ceramic body formation. The ceramic body formation can be further accelerated by pressurization with a low pressure of up to about 5 bar gauge.

The reduction in shrinkage achieved in accordance with the invention presupposes that the predominantly open pore volume obtained with the W/O emulsion is not altered when the product is hardened. In addition the corresponding emulsions must be easily pourable.

Tests with fillers such as glass micro-beads, fly ash, powdered quartz and powdered polymers showed that in this manner even with a high quantity of 10-20 vol% with respect to the emulsion volume, the shrinkage can only be reduced by about 10%. These fillers can be easily mixed into the polymerization system, but in order to achieve a clear shrinkage reduction very high filler additions of up to 50 vol% with respect to the emulsion volume are required. The addition of such a high filler quantity is difficult to achieve because of the viscosity increase related to it. In addition the resulting material is difficult to cast, and the corresponding emulsions are unstable.

The use of glass fibres, carbon fibres and other fibrous materials is known in the working of casting resins. Mechanical strength is considerably improved by such additives, however, to this end, fibre lengths of 10-50 mm and quantities of 10-30 weight% with respect to the synthetic resin content are required. In addition, in traditional ceramic resin systems the influence of such fibre additions on shrinkage is only slight. Mixing fibres of such lengths into water-in-resin emulsions can however only be achieved by the fibre injection moulding process, which is out of the question for moulds with wall thicknesses of around 15-50 mm.

On the basis of the available experience with conventional casting resin systems, in no way could it be expected that the shrinkage of porous mould parts made of hardenable W/O emulsions could be modified by adding fillers and reinforcement materials. Even more surprising is it that by mixing them with short fibres (staple fibres) of length 1-6 mm, in particular of glass, in the improbably small quantity of up to 4 weight% and preferably of between about 0.5 and 2.5 weight%, with respect to the weight of the plastics content excluding additives, a significant reduction in shrinkage of well over 60% and up to somewhat over 90% can be achieved.

According to the invention the short fibres are mixed into the emulsion during its preparation as a casting material. It has been further shown that the mixing of fibres with the emulsion achieves the best effect if the fibres remain uniformly distributed within the emulsion until a sufficiently high viscosity is reached.

This uniform working-in of the fibres is simplified by adding spherical fillers such as glass micro-beads or ceramic micro-beads. Moreover, by this means the shrinkage can be additionally reduced by some ten percent.

Sedimentation of the fibres in the emulsion can be opposed by using light-weight fillers such as hollow glass micro-beads or hollow ceramic micro-beads, and by employing a higher emulsion viscosity.

Preferred are glass staple fibres and fillers provided with an adhesive layer for better adhesion to the hardenable part of the emulsion.

In addition to or instead of inorganic fillers, polymers from fine-grain to powder consistency can be used. These should only be surface-soluble and must not destabilize the emulsion. As the particle size and the solubility of the polymers in the monomer part of the emulsion influence the viscosity, the viscosity variation of the hardenable part must be measured. As a rule of thumb it can be stated that a mixture of polymers and the hardenable part of the emulsion in the ratio of 1:1 should show a clear viscosity increase of about 20% only after about 10-15 minutes.

In addition to reducing the shrinkage, the addition of short fibres also results in a considerable improvement in impact resistance and notch impact strength, which can be increased by nearly 100%. The bending strength of the mould material is also increased, the invention achieving particular advantages also in this respect.

The reduction in shrinkability achieved by the invention occurs both in porous mould materials produced in accordance with EP 165 952 A and in mould materials produced using the polymer-monomer system, for example in accordance with DE 19 28 026. With this latter process a shrinkage of about 1% can be reckoned for a 1:1 ratio of polymerizable matter to polymer. If only 1-1.5 weight% of glass fibres (length 3 mm) with respect to the weight of the plastics content is added, this shrinkage is reduced to about 0.1%. In this respect, the polymer quantity can be reduced without influencing shrinkage.

According to EP 165 952 A, moulds of porous plastics can be produced by which considerably quicker ceramic body formation without pressure or under a low pressure of about 0.5-5 bar gauge can be achieved. This effect is particularly due to the small pore width of about 0.1 to 0.2 μm achievable by this process. However at the same time the permeability of the mould to gases and liquids is considerably reduced. It is therefore not possible to release the casting from the mould by the use of compressed air; the ceramic body loosens by shrinkage. The release is expedited by the aforesaid spraying of a plaster of Paris suspension before filling the mould with slip, so that the ceramic body can be removed as in the case of a plaster of Paris mould, but after a shorter drying time.

An important aspect of the invention is that by using this procedure the permeability is so increased that the ceramic body formation is quicker either without pressure or with the use of a small pressure of up to 5 bar, after which it can be released with compressed air. Within the framework of the invention, in accordance with the procedure of EP 165 925 A, mould materials usable, either without pressure or with a pressure of up to 6 bar, to form a ceramic body which can be released from the mould by compressed air are produced in which the water-in-oil emulsion either with or without the addition of a dispersing agent is adjusted to a degree of dispersion or a corresponding viscosity such that after moulding and hardening, pore widths of between 1 and 5 μm are achieved. Depending on the application, pore widths of about 0.1-0.2 μm can also be achieved.

Advantageously, the aforesaid compounds for accelerating the ceramic body formation, with which the pore diameter can be regulated, and in particular disodium tetraborate decahydrate, are used in a quantity of up to 4.5 weight% with respect to the hardenable content of the W/O emulsion, for which equally advantageously an unsaturated ester dissolved in styrene and methylacrylate as monomers is used.

Either without pressure or under a pressure of up to 6 bar, the mould materials produced in this manner form within a few minutes a ceramic body which can be loosened with compressed air and removed from the mould,

This result could not be predicted, because plaster of Paris with a more or less similar pore diameter does not possess the necessary permeability (permeability to compressed air) for releasing the ceramic body. As already stated, additional coarse pores have to be produced to alter the pore structure.

Different pore sizes and hence different permeabilities to gases and liquids are achievable depending on the quantity of regulating agent or agents in the water-in-oil emulsion. Using a quantity of merely up to about 3.5 weight%, with respect to the hardenable content of the emulsion, a sufficient permeability is achieved to allow the finished ceramic body to be released from the mould wall under a compressed air pressure from about 1.5 to 3 bar.

A pressure from about 3 to 5 bar is sufficient for forming the ceramic body. In contrast to plaster of Paris, additional coarse pore formation is not required, and compared with conventional pressure-casting moulds formed with the polymer-monomer system, the pores according to the procedure of the invention are up to about ten percent smaller. The release procedure for the ceramic body is hence easier to control. The considerable water discharge from the mould connected with the release of the ceramic body is minimal according to the invention. In addition the danger of clogging due to penetration of particles from

the slip is reduced because of the finer porosity.

The low pressure required for ceramic body formation means that expensive devices such as pressure-casting presses or strengthening of the moulds can be dispensed with. Hence moulds can be produced at considerably less cost and inserted for example into the moulding bank.

5 The invention is described hereinafter in terms of examples and comparison examples.

The possibility of adjusting the pore size using a regulator which itself causes the shrinkage to increase, and the suppressing of this effect by adding 2.5% of glass fibres to the emulsion can be seen from the results of the examples, which are listed in Table 1.

10 Examples 2 and 3 show the possible reduction in shrinkage attained according to the invention by adding 1.3 weight% of glass fibres, with respect to the W/O emulsion, when a polymer-monomer system is used. Example 1 is a comparison example in which the mould material is produced without the addition of glass fibres.

Examples 4-7 demonstrate the reduction in shrinkage achieved by adding glass fibres but without adding the regulator.

15 Examples 8-12 relate to shrinkage with the addition of a regulator in a quantity of 2.6 weight%, with respect to the weight of the emulsion.

Examples 13 and 14 show the low shrinkage achieved by the addition of the regulator in a quantity of 6.5 weight%, with respect to the resin, both without and with the addition of the polymer II. The water content of the emulsion was 47%.

20 Examples 15 and 16 show for an emulsion with a water content of 35% the reduction in shrinkage and the differing permeability for regulator additions of 6.5 weight% and 2.6 weight%.

The 16 examples of the following table are classified in 5 groups according to the water content of the emulsion, the permeability and the pore radius.

At a permeability of reference value 80 the mould material does not enable a ceramic body to be
25 formed without pressure. The corresponding mould is however well suitable for use in forming a ceramic body at a very high pressure of 15-50 bar. At the given permeability values of 12 to 16 the ceramic body formation is slower, however the water can be forced out through the mould and the ceramic body can be released with compressed air after its formation. At permeabilities between 0 and about 5, release of the ceramic body with pressure is hardly or no longer possible. The rate of ceramic body formation is in this
30 case considerably higher. It cannot be additionally accelerated using pressure. In such cases the ceramic body can only be released from the mould by shrinkage.

Example No.	1	2	3	4	5	6	7
Parts by wt	9	9	9	: 9	9	9	9 :
components:							
1 resin	100	100	100	: 100	100	100	100 :
2 accel.	1	1	1	: 1	1	1	1 :
3a polymer I	100	100	100	: 0	0	0	0 :
3b polymer II	0	0	0	: 0	0	0	10 :
4 regulator	0	0	0	: 0	0	0	0 :

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5	water	100	100	100	:	81	83	101	110	:
6	gf.	0	4	4	:	0	2.5	0	2.5	:
7	gc.	0	0	25	:	0	0	25	25	:
8	BPO	2.5	2.5	2.5	:	3	3	3	3	:
9	Sa.	302.5	307.5	332.5	:	184	189	229	251	:
10	% gf.	0	1.3	1.2	:	0	1.3	0	1	:
11	vol% gc.	0	0	2.9	:	0	0	4.2	3.8	:
12	% water	33	32.5	30	:	44	44	44	44	:
13	% shrinkage	1	0.2	0.05	:	1.9	0.35	1.6	0.1	:
14	pore rad. μ m	17	17	17	:	2	2	2	2	:
15	permeability	80	80	80	:	15	15	15	15	:

20	Ex.No.	8	9	10	11	12	13	14	15	16
	p.b.w.	9	9	9	9	9	9	9	9	9
	comp:									
25	1	100	100	100	100	100	100	100	100	100
	2	1	1	1	1	1	1	1	1	1
	3a	0	0	0	0	0	0	0	0	0
	3b	0	0	0	10	0	0	10	10	0
30	4	2.5	2.6	2.6	2.6	6.5	6.5	6.5	6.5	2.6
	5	85	85	103	113	86	100	108.6	66	72.6
	6	0	2.5	0	2.5	0	2.5	2.5	2.5	2.5
35	7	0	0	25	25	0	0	0	0	25
	8	3	3	3	3	3	3	3	3	3
	9	191	194	234	256	196	212.5	231	188	207
40	10	0	1.3	0	1	0	1.2	1.1	1.3	1.2
	11	0	0	4.1	3.7	0	0	0	0	4.6
	12	44	44	44	44	44	47	47	35	35
	13	2.2	0.3	2	0.1	2.8	0.4	0.2	0.2	0.2
45	14	0.6	0.6	0.6	0.6	0.1	0.1	0.1	0.15	1.5
	15	12	12	12	12	3	0	0	3	16

50 Description of components used:

1 resin:
 Unsaturated polyester, dissolved in a mixture of styrene and methylmethacrylate in a weight ratio of 1:2;
 55 solids content about 50%, W/O emulsifier 2%.
 2 accel:
 Dimethyl-p-toluidine, 10% conc.
 3a polymer I:

Polymethylmethacrylate bead polymer, bead size about 40 μm . When mixed in a 1:1 ratio with methylmethacrylate (MMA) it reaches a viscosity of over 10,000 mPa.s in 5 minutes at 20 °C. Polymer I is used when the polymer-monomer system is used for producing open pores (pore size about 35 μm).

3b polymer II:

5 Polymethylmethacrylate copolymer, bead size about 250 μm . When mixed in a 1:1 ratio with MMA it reaches a viscosity of over 10,000 mPa.s in about 25 minutes at 20 °C. Emulsion instability is not produced with polymer II.

4 regulator:

Disodium tetraborate decahydrate

10 5 water:

Tap water

6 gf:

Glass staple fibres dressed with an adhesive; length 3 mm.

7 gc:

15 Glass micro-beads, average particle size 150 μm .

8 BPO:

Benzoylperoxide, 50% conc.

Explanation of results:

20

9 Sa:

Total material weight.

10 % gf:

Weight% of glass fibres (length 3 mm), with respect to the emulsion weight.

25

11 vol% gc:

Vol% of glass micro-beads, with respect to the emulsion weight.

12 % water:

Weight% water in the emulsion, with respect to the emulsion weight.

13 % shrinkage:

30

Shrinkage of the porous mould after drying.

14 pore radius μm :

Average pore radius, measured by Hg porosimeter.

15 permeability:

35

Permeability of the mould material to water; the determined reference value corresponds to that weight of water in grams which under a pressure of 2 bar penetrates per minute through a 100 cm² area of the mould material with a wall thickness of 1.5 cm.

Examples 1-16 were carried out as follows:

40

EXAMPLES 1-3

Components 1 and 2 and components 3a and 5 were mixed separately. The polymer-water mixture was then stirred into the resin over a time of 2-4 minutes. The viscosity rose rapidly. The benzoyl peroxide and in Examples 2 and 3 also the glass micro-beads were mixed in with the last quarter. Finally, the glass fibres were sprinkled in. After a short stirring time of about 2 minutes the emulsion was cast into a crucible. After 45 60 minutes the emulsion had hardened and the crucible could be removed from the mould. The crucible obtained, which was full of water and had a wall thickness of 15 mm, was firstly weighed in its wet state and was then dewatered with compressed air at a pressure of 2 bar. It was then weighed again, the weight difference corresponding to the weight of water forced out. The water quantity per minute for a surface area of 100 cm² and a wall thickness of 15 mm was then calculated, this representing the respective permeability 50 reference value.

After the crucible was dry, the shrinkage at the upper diameter of the crucible mould was measured and the percentage shrinkage on the inner diameter of the casting mould used was calculated.

The pore radii were determined with a Hg porosimeter.

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EXAMPLES 4-16

In Examples 4-16 the sequence of mixing steps for the individual components was the same as in

Examples 1-3. However it can if necessary be altered. For example the hardener and accelerator can be interchanged.

Components 1, 2, 4 and 7 were mixed with the resin. Components 3a and 3b were mixed with component 5 (water) and then mixed with the premixed components 1, 2, 4 and 7 under stirring, by which a water-in-oil emulsion was obtained. After setting the viscosity of this water-in-oil emulsion at a value between 1500 and 3000 mPa.s, as account had to be taken of the strong viscosity rise on adding the glass fibres, the glass fibres were sprinkled in and the peroxide mixed in. After a short period of mixing of about 2 minutes the emulsion was cast into a mould and left therein to harden under cold conditions. After 40-60 minutes the mould could be opened. Porous moulded articles were obtained containing the water of the emulsion.

The determination of the shrinkage, permeability and pore radius was carried out as in Examples 1-3.

The test results given in the above table can be summarized as follows:

1. By adding a small amount of short fibres, in particular glass fibres, of a length up to 6 mm in a quantity of up to 4 weight%, with respect to the weight of the plastics content of the emulsion excluding additions, shrinkage is considerably reduced in the case of mould materials produced from water-in-oil emulsions. This effect is surprising in that during the hardening no expansion of the emulsion takes place, and in the case of casting resins with added short glass fibres no reduction in shrinkage is determined.

2. The pore radius of the hardened porous mould material can at little cost be adjusted to values between 0.5 and 5 μm by adding regulators in a quantity of between 0 and 3.2 weight% with respect to the hardenable content of the emulsion. Within this pore range the mould materials possess sufficient absorption capacity to be able to form a ceramic body from ceramic materials without the application of pressure. Ceramic body formation can be accelerated by applying a relatively low pressure of up to 6 bar. A fully sufficient permeability to liquid is also achieved to be able to force the water out of the mould by low pressure and release from it a ceramic body formed in the mould, using compressed air. The facility is hence available for considerably accelerating the production of castings from ceramic materials with simple moulds, for better controlling the release of the casting from the mould, and for substantially eliminating water run-out from the mould.

The advantages deriving from the invention can be briefly summarized as follows:

The shrinkage and the mechanical properties of mould materials produced from W/O emulsions with hardenable compounds in the oil phase are considerably improved by the addition of short fibres according to the invention, and in particular glass fibres, in very small quantities.

By adjusting the permeability of the mould materials to within a range in which pressure-less ceramic body formation, its acceleration by the use of pressure up to about 6 bar, and the controlled release of the ceramic body from the mould by means of compressed air without additional aids are possible, mould materials produced in accordance with the basic process of EP 165 952 A can also be used for pressure-casting in the the low pressure range of up to about 6 bar, and for pressing.

Claims

1. Porous, open-pore, water-absorbent mould materials consisting of a hardened, filler-containing plastics material having a water-fillable pore volume of at least 10% of the total volume, for moulds for forming ceramic castings from water-containing moulding materials from liquid to plastic consistency, characterised by containing, as filler, short fibres having a length of 1-6 mm and in a quantity of up to 4 weight% with respect to weight of the plastics content excluding additives.
2. Mould materials as claimed in claim 1, characterised by containing between 0.5 and 2.5 weight% of short fibres, with respect to the weight of the plastics content excluding additives.
3. Mould materials as claimed in claims 1 and 2, characterised by containing between 1 and 1.5 weight% of short fibres, with respect to the emulsion.
4. Mould materials as claimed in claims 1 to 3, characterised in that the fillers are short fibres of textile materials, carbon and/or glass.
5. Mould materials as claimed in claims 1 to 4, characterised in the the filler consists of glass staple fibres.

6. Mould materials as claimed in claims 1 to 5, characterised by containing granular or spherical or spheroidal fillers as further fillers.
- 5 7. Mould materials as claimed in claim 6, characterised by containing glass micro-beads, ceramic micro-beads, hollow glass micro-beads, hollow ceramic micro-beads and/or granulated polymers from powder form to fine granular form as further fillers.
8. Mould materials as claimed in claims 6 and 7, characterised by containing further fillers in a quantity of between 0 and 50 weight%, with respect to the total dry weight.
- 10 9. Mould materials as claimed in claims 1 to 8, characterised in that the plastics material consists of a homopolymer or a copolymer of monomer units deriving from styrene, α -methylstyrene, allyl phthalate, acrylic esters, in particular methylacrylate or ethylacrylate, and/or methacrylic esters, in particular methylmethacrylate or ethylmethacrylate, or contains such monomer units.
- 15 10. Mould materials as claimed in claim 9, characterised in that the plastics material is cross-linked with a multi-functional crosslinking agent such as in particular divinylbenzene or a diacrylate or dimethylacrylate.
- 20 11. Mould materials as claimed in claims 8 and 9, characterised in that the plastics material contains in-polymerized or grafted homopolymer blocks.
12. Mould materials as claimed in claim 11, characterised in that the plastics material contains polymer blocks deriving from an unsaturated polyester.
- 25 13. Mould materials as claimed in claims 1 to 12, characterised by a pore size in the range from 0.1 to 0.5 μ .
14. Mould materials as claimed in claim 13, characterised by a pore size in the range from 0.1 to 0.2 μ .
- 30 15. A process for producing the mould materials claimed in claims 1 to 14 by:
 - A) producing a water-in-oil emulsion (W/O emulsion) with an oil phase consisting of one or more polymerizable liquid monomers using emulsifiers and a water content corresponding to the desired pore volume; and
 - 35 B) polymerizing the oil phase of the water-in-oil emulsion in the presence of a polymerization initiator in a mould; and if necessary
 - C) removing the water from the mould material obtained, characterised in that short fibres of length 1-6 mm are added to the polymerization system in a quantity of up to 4 weight% with respect to the weight of the polymerizable part of the emulsion excluding additives.
- 40 16. A process as claimed in claim 15, characterised by raising the degree of dispersion of the water phase of the W/O emulsion by mixing to achieve a viscosity within the range of 1600-5000 cP in step A, in particular by adjusting the mixing time and/or the mixing intensity.
- 45 17. A process as claimed in claims 15 and 16, characterised in that the short fibres are added in a quantity of between 0.5 and 2.5 weight%, with respect to the weight of the polymerizable part of the emulsion.
18. A process as claimed in claims 15 and 16, characterised in that the short fibres are added in a quantity of between 1 and 1.5 weight%, with respect to the weight of the polymerizable part of the emulsion.
- 50 19. A process as claimed in claims 15 to 18, characterised in that short fibres of textile materials, carbon and/or glass are added as fillers.
20. A process as claimed in claims 15 to 19, characterised in that glass staple fibres are added as fillers.
- 55 21. A process as claimed in claims 15 to 20, characterised in that granular or spherical or spheroidal fillers are added to the polymerization system as further fillers.

22. A process as claimed in claim 21, characterised in that glass micro-beads, ceramic micro-beads, hollow glass micro-beads, hollow ceramic micro-beads and/or granulated polymers from powder form to fine granular form and difficultly soluble in the polymerization system are added to the polymerization system as further fillers.
- 5 23. A process as claimed in claims 21 and 22, characterised in that the further fillers are added to the polymerization system in a quantity of up to 15 weight%, with respect to the polymerization system including water.
- 10 24. A process as claimed in claims 15 to 23, characterised by using a W/O emulsion with an oil phase in which a polyester resin or a liquid prepolymer predominantly of methylmethacrylate are dissolved in a quantity of 40-70 weight%.
- 15 25. A process as claimed in claims 15 to 24, characterised by using a W/O emulsion containing calcium sulphate dihydrate, sodium disilicate and/or disodium tetraborate as permeability regulator.
- 20 26. A process as claimed in claim 25, characterised by using a W/O emulsion containing calcium sulphate dihydrate, sodium disilicate and/or disodium tetraborate in a quantity of between about 2 and 12 weight%, with respect to the weight of the polymerizable part of the emulsion.
- 25 27. A process as claimed in claims 15 to 26, characterised by using styrene, methylstyrene, allylphthalate, acrylic esters and/or methacrylic esters as polymerizable monomers.
28. A process as claimed in claims 15 to 27, characterised by using styrene and/or methyl methacrylate as polymerizable monomers.
- 30 29. A process as claimed in claims 15 to 28, characterised by adding a multi-functional crosslinking agent such as in particular divinylbenzene or a diacrylate or dimethacrylate to the polymerization system.
- 35 30. A process as claimed in claims 15 to 29, characterised by using the polymerizable liquid monomers in a quantity of between 30 and 78 weight%, with respect to the weight of the emulsion.
31. A process as claimed in claims 15 to 30, characterised by using powdered polymers swellable in the oil phase of the emulsion, polymethylmethacrylate-polymer beads, barite and/or ground quartz as further fillers.
32. A process as claimed in claims 15 to 31, characterised by applying aqueous synthetic resin solutions to the surface of the mould materials after step B or C.
- 40 33. A process as claimed in claims 15 to 32, characterised by applying melamine-urea-formaldehyde resins, epoxy resins or film-forming synthetic resin dispersions to the surface of the mould materials after step B or C.
- 45 34. A process as claimed in claims 15 to 33, characterised by using glass fibres treated with an adhesive, and in particular silanized.
35. Mould materials in accordance with claims 1 to 14, obtainable by the processes claimed in claims 15 to 34.
- 50 36. A method for producing moulds for forming ceramic castings from water-containing moulding materials from liquid to plastic consistency by machining, in particular by turning, milling and/or drilling, characterised by using a mould material in accordance with one of claims 1 to 14 and claim 35.
- 55 37. A method for producing moulds for forming ceramic castings from water-containing moulding materials from liquid to plastic consistency by:
- A) producing a water-in-oil emulsion (W/O emulsion) with an oil phase consisting of one or more polymerizable liquid monomers using emulsifiers and a water content corresponding to the desired pore volume; and

B) polymerizing the oil phase of the water-in-oil emulsion in the presence of a polymerization initiator in a mould; and if necessary

C) removing the water from the mould material obtained, wherein in step B a mould is used corresponding to the negative shape of the mould for producing the casting, characterised by adding short fibres of length 1-6 mm to the polymerization system in a quantity of up to 4 weight% with respect to the weight of the polymerizable part of the emulsion excluding additives.

38. A method as claimed in claim 37, characterised by the characteristics of claims 16 to 34.

39. Moulds for forming ceramic castings from water-containing moulding materials from liquid to plastic consistency, characterised by consisting of a mould material as claimed in one of claims 1 to 14 and claim 35.

40. A method for producing ceramic castings from water-containing moulding materials from liquid to plastic consistency using moulds formed from a mould material produced by polymerization of a water-in-oil emulsion of a porous, open-pore, water-absorbent and hardened plastics material with a pore volume of at least 10% of the total volume by pouring, loading or forcing the ceramic moulding materials into the mould, possibly applying pressure in excess of atmospheric to the mould, and particularly a pressure of up to 5 bar gauge, possibly after emptying the mould, and releasing the formed ceramic body from the mould after sufficient dewatering, characterised by using a mould formed from a mould material in accordance with one of claims 1 to 14 and claim 35.

41. A method as claimed in claim 40, characterised in that powdered plaster of Paris or an aqueous plaster of Paris suspension with a plaster of Paris content of at least 1 weight% is applied to the mould before casting.

42. The use of the mould materials claimed in claim 1 to 14 and claim 35 for the moulds claimed in claim 39 for producing ceramic castings by casting, pressure-casting or pressing.

43. The use of short fibres of textile materials, carbon or glass and in particular glass staple fibres for reducing the shrinkage of plastics moulds for forming ceramic castings.

44. A machinable composition for use in the method claimed in claims 15 to 34, 37 and 38, consisting of:
I) a styrene-containing polyester casting resin which in addition to styrene contains copolymerizable acrylates and/or methacrylates, or a liquid prepolymer of predominantly methylmethacrylate, containing copolymerizable acrylates and/or methacrylates,
II) emulsifiers and possibly surface active substances as required for forming a W/O emulsion, and if appropriate
III) calcium sulphate dihydrate, sodium disilicate and/or disodium tetraborate decahydrate in a quantity of between 2 and 15 weight% with respect to the weight of component I, characterised by containing short fibres of textile materials, carbon or glass with a length of between 2 and 6 mm and in a quantity of up to 4 weight% as fillers.

45. A machinable composition as claimed in claim 44, characterised by containing glass staple fibres as filler.



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EUROPEAN SEARCH REPORT

Application Number

EP 92 20 1457

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN vol. 13, no. 305 (M-849)(3653) 13 July 1989 & JP-A-1 095 003 (TOSHIBA CORP.) 13 April 1989 * abstract * ---	1-5, 15, 35-37, 39, 40, 42, 43	B28B1/26
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 290 (C-731)(4233) 22 June 1990 & JP-A-2 092 850 (TOKAI RUBBER IND. LTD.) 3 April 1990 * abstract * ---	1	
X	US-A-4 307 867 (SHANNON) * column 2, paragraph 1; claims 1-3 * ---	1-5, 15, 35-37, 39, 40, 42, 43	
A	FR-A-2 457 753 (INVENTA A.G.) * claims *	21	
D, A	FR-A-2 022 594 (G. WILL) * the whole document * -----	1, 15, 37, 44	TECHNICAL FIELDS SEARCHED (Int. Cl.5) B28B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 26 AUGUST 1992	Examiner LASSON Cedric
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