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(54) Titre : COMPOSITION POLYMERISABLE POUR LA FABRICATION D'ARTICLES MOULES EN PLASTIQUE
(54) Title: CURABLE CASTING COMPOSITIONS

(57) Abrégé/Abstract:
A curable casting composition for producing plastic molded articles comprising a liquid, monomeric acrylate component is proposed, and also a process for producing it, wherein the time-consuming step of producing the sirup can be dispensed with, while, on the other hand, too rapid settling and sedimentation of inorganic particles can be reliably prevented. To this end, it is proposed that the casting composition comprise in addition to a liquid, monomeric acrylate component, a proportion of a particulate plastic material, a proportion of a particulate inorganic material and, if necessary, a cross-linker. The total content of particulate plastic material and particulate inorganic material should be approximately 45 to 85 % by weight, preferably 60 to 70 % by weight of the casting composition, with a minimum content of 8 % by weight of particulate plastic material.

Abstract

A curable casting composition for producing plastic molded articles comprising a liquid, monomeric acrylate component is proposed, and also a process for producing it, wherein the time-consuming step of producing the sirup can be dispensed with, while, on the other hand, too rapid settling and sedimentation of inorganic particles can be reliably prevented. To this end, it is proposed that the casting composition comprise in addition to a liquid, monomeric acrylate component, a proportion of a particulate plastic material, a proportion of a particulate inorganic material and, if necessary, a cross-linker. The total content of particulate plastic material and particulate inorganic material should be approximately 45 to 85 % by weight, preferably 60 to 70 % by weight of the casting composition, with a minimum content of 8 % by weight of particulate plastic material.

Specification

Curable Casting Compositions

The invention relates to a curable casting composition for producing plastic molded articles with a liquid, monomeric acrylate component.

Curable casting compositions of this kind are known from a plurality of publications. By way of example, reference is made here to only German patent P 24 49 696 and the European patent applications EP-A 0 491 170, EP-A 0 218 866, EP-A 0 361 101 and EP-A 0 321 193.

What all these curable casting compositions on the basis of acrylate have in common is that owing to the low viscosity of pure acrylate monomer, components in the form of partly polymerized acrylate with typical molecular weights of 50,000 to 1,000,000 are added to increase the viscosity.

The acrylate component most frequently used in the prior art is methyl methacrylate, but, in accordance with the present invention, other acrylic acid and methacrylic acid esters with aliphatic, alicyclic or aromatic alcohols can just as well be used, as listed individually, for example, in DE-PS 24 49 656. On the whole, polymethyl methacrylate with the aforementioned molecular weight range is primarily used for producing a sirup which adjusts the viscosity of the pure methyl methacrylate of 0.5 mPa*s at 20° C to values between 10 and 250 mPa*s at room temperature. The necessary percentage by weight of the polymethyl methacrylate is approximately 5 to 25 % by weight of the sirup.

A disadvantage of this way of thickening the monomeric component is that the process for the dissolving of the polymethyl methacrylate in the monomeric methyl methacrylate

takes several hours, even at elevated temperature, and is, therefore, decisive in determining the amount of time required for producing the casting composition.

The problem with the curable casting compositions is always the sedimentation of the inorganic particulate materials contained in these casting compositions and great efforts have, therefore, been made in the past to enable the curable casting compositions to be produced as stable dispersions.

Reference is also made to the published international patent application WO92/03497 as a recent example from the patent literature. This publication discloses a dispersion of polymethyl methacrylate particles in MMA/PMMA sirup. Herein there is no suggestion that particulate inorganic material or plastic particles made from polymers filled with inorganic fillers be used.

The object of the invention is to indicate a formulation for a casting composition and a process for producing it, wherein the time-consuming step of producing the sirup can be dispensed with, while, on the other hand, too rapid settling and sedimentation of inorganic particles can be reliably prevented.

This object is accomplished in accordance with the invention with a curable casting composition of the kind described at the outset by the curable casting composition comprising in addition to a monomeric acrylate component which can be formed by one of the esters of acrylic acid and/or methacrylic acid, as described hereinabove, a proportion of a particulate plastic material and the proportion of a particulate inorganic material, the total content of particulate plastic material and inorganic material being approximately 45 to 85 % by weight of the casting composition. The proportion of the particulate plastic material should be at least approximately 8 % by weight of the casting composition, preferably between 15 and 30 % by weight. If necessary, a cross-linker is added to the curable

casting composition, where this is required in the individual case for the mechanical and thermal properties of the plastic molded article that is to be produced.

It is preferable for no polymeric acrylate proportions at all, i.e., in particular, also no PMMA proportions for thickening the monomeric component to be added to the curable casting compositions.

Surprisingly, it has been found that the monomeric acrylate or methacrylate can be thickened to such an extent by adding a particulate plastic material that the sedimentation of the further proportion of a particulate inorganic material that is added is reduced to such an extent that the dispersion remains stable within normal storing and processing times. It is preferable for the casting composition according to the invention to be used immediately after the process for producing it, but it remains usable for more than 8 hours.

A wide range of materials is available for selection of the particulate plastic material, but in view of reusability of the materials, it is preferable to resort to a particulate plastic material which, itself, is made on the basis of acrylate. This also has the advantage that the plastic material particles can be wetted without any problem by the liquid, monomeric acrylate component.

Surprisingly, such a stabilizing effect is achievable for the suspension of the inorganic material particles in the casting composition without adding any PMMA portions, and so the time-consuming step of dissolving PMMA material in the monomeric acrylate or methyl acrylate can be dispensed with entirely.

Curable casting compositions which are essentially free from dissolved PMMA portions are, therefore, preferred. This means that, in particular, the monomeric acrylate component is

essentially free from PMMA portions when the particulate organic and particulate inorganic materials are added to it.

Of course, PMMA portions which have dissolved from the particulate plastic material can occur to a more or less significant extent later, but this does not make any significant contribution towards increasing the viscosity of the casting composition and, in particular, not to the initial stabilization of the dispersion.

Surprisingly, it has also been found that the particulate plastic material can be made from a polymer material filled with an inorganic filler. This means that, in particular, materials such as those to be found in German patent P 24 49 656 and the aforementioned European publications are usable in finely ground form, in this case as particulate, in particular, granular plastic material, which opens up a wide field for the use of recycled plastic materials, in particular, also from recycled plastic sinks, counter-tops, etc.

Plastic molded articles produced in accordance with the invention and their scrap material are, of course, also suitable as starting material for producing the particulate plastic materials which can be used again in a curable casting composition according to the invention.

The filled polymer is preferably an at least partly cross-linked acrylate polymer, preferably a PMMA polymer.

The inorganic filler of the filled polymer can be selected from the series cristobalite, quartz, aluminium oxide trihydrate, calcium carbonate, mineral silicates, in particular, mica, or any mixtures of the aforementioned materials.

The proportion of inorganic fillers in the filled polymer is between 20 and 80 % by weight of the polymer, and, accordingly,

the proportion of the organic polymer matrix of the filled polymer is between 20 and 80 % by weight.

The particle size of the particulate plastic material is typically < 1 mm, and in order to keep swelling of the plastic particles and hence withdrawal of liquid, monomeric material from the casting composition within acceptable limits, the average particle diameter should be at least 10 µm. If very short storage times can be observed between production of the casting composition and processing of the casting composition, noticeable portions of fine plastic particles can, of course, also be contained in the plastic material. If, in the event of a somewhat longer standing time, the casting composition should become too high on account of the swelling effect of the plastic material particles, the viscosity can be brought into the preferred viscosity range of 1 to 5 Pa*s again by adding more monomeric acrylate component, without any disadvantages for the casting composition, its workability or indeed the products made from it. It is preferable for the particulate inorganic material that is added to the casting composition to have an average particle size in the range of 10 µm to 1 mm. Again, the materials of the series cristobalite, quartz, mineral silicates and/or aluminium oxide trihydrate or also mixtures of these are suitable as particulate inorganic materials.

Polyfunctional acrylate compounds are preferred as cross-linkers and, in particular, ethylene glycol dimethacrylate and/or trimethylolpropane trimethacrylate are used therefor.

The cross-linker is used in a proportion of up to 6 % by weight of the proportion of monomeric acrylate component.

The process according to the invention for producing a casting composition described hereinabove comprises the steps:

a) producing, in particular, grinding a particulate plastic material, often using plastic products that are to be recycled, including filled plastic materials; if necessary, screening to the desired particle size is carried out;

b) first introducing into a mixing tank a liquid, monomeric acrylate component which, if necessary, comprises a mold release agent and/or a suitable cross-linker of up to 6 % by weight;

c) adding and stirring the plastic material produced in accordance with step a) into the monomeric acrylate component, and subsequently stirring the mixture for at least approximately 20 minutes, the stirring time being inter alia dependent on the particle size of the plastic material used and the speed at which the swelling of these plastic particles takes place;

d) adding and likewise stirring the remaining constituents of the casting composition, in particular, the inorganic material, and, if necessary, pigments, catalysts, accelerators, etc.

The aforementioned process can be simplified by the materials according to steps c) and d) being added jointly to the liquid acrylate component and by stirring being carried out subsequently, again, for a minimum time of approximately 20 minutes. Here, too, as mentioned above, the stirring time depends on the particle size of the plastic material used.

The casting compositions produced in accordance with the invention are then further processed in the known casting process, i.e., introduced through a feed channel into a mold cavity and cured. The plastic molded articles can be dyed any color using normal pigments, and granite effects, etc., can,

for example, be obtained by appropriate choice of the components.

Depending on how the polymerization process is carried out, very shiny surfaces are just as obtainable as dull ones. Dull surfaces are obtained with a low starting temperature on the visible side of the molds used, whereas shiny surfaces are obtained with a high starting temperature.

The casting composition according to the invention is preferably used for producing plastic molded articles for kitchens and bathrooms, in particular, as counter-tops for kitchens, kitchen sinks, bathtubs, shower troughs, washbasins or the like.

The organic polymer matrix of the plastic particles preferably consists of cross-linked polymethyl methacrylate. Cristobalite or quartz, glass, aluminium trihydrate, calcium carbonate, mineral silicates (e.g., mica) or a mixture of the aforementioned fillers can, for example, be contained therein as inorganic filler. The particles of the plastic material typically have a particle size of < 1 mm.

They can be produced by chopping suitable polymer materials; here one can, for example, resort to using waste from the production of molded articles on the basis of PMMA (cross-linked)/filler or to recycling molded articles made from the casting composition according to the invention that are no longer usable.

When inorganic fillers such as, e.g., cristobalite, quartz, glass or mineral silicates are added to pure MMA or to a mixture of MMA and a suitable cross-linker (e.g. ethylene glycol dimethacrylate or trimethylolpropane trimethacrylate), a stable dispersion is not obtained. The filler settles quickly. It is, therefore, not possible to produce homogeneous molded articles in the casting process.

Surprisingly, it has been found that when a dispersion produced in accordance with the invention is used instead of the pure MMA or the mixture of MMA and a suitable cross-linker, the rapid sedimentation of the filler is prevented and a casting composition which can be used without any problem is obtained. The plastic particles used for producing the dispersion, therefore, have a binder-like effect and, in the production of castable, stable dispersions, enable the time-consuming step of producing a sirup from methyl methacrylate and polymethyl methacrylate to be dispensed with.

Examples

Example 1

10 kg of a plastic material (SILACRON™ 2000 of BLANCO GmbH & Co. KG) made from cross-linked polymethyl methacrylate and cristobalite are ground (average particle size 100 - 200 µm) and subsequently added to and stirred into a mixture of 17 kg methyl methacrylate, 0.125 kg mold release agent (stearic acid) and 0.32 kg of a standard cross-linker. After stirring for 20 minutes, 25 kg silanized cristobalite powder (particle size 0 - 40 µm), 0.250 kg of a peroxidic catalyst and approximately 0.5 kg of a pigment preparation are added.

The thus obtained casting composition dispersion has a viscosity at 23° C of 1000 mPa*s and can be filled into the casting mold and cured without any problem. After a further 30 minutes, the viscosity of the remaining dispersion has risen to 4000 mPa*s, but it can still be worked with without any problem.

Example 2

8 kg of a plastic material (SILACRON 2000 of BLANCO GmbH & Co. KG) made from cross-linked polymethyl methacrylate and cristobalite are ground (average particle size 200 - 300 µm) and subsequently added to and stirred into a mixture of 10 kg methyl methacrylate, 0.125 kg mold release agent (stearic acid) and 0.20 kg of a standard cross-linker. 10 kg silanized cristobalite powder (particle size 0 - 40 µm) and 4 kg quartz sand (particle size < 1 mm) are simultaneously added. After stirring for 20 minutes, 0.17 kg of a peroxidic catalyst and approximately 0.2 kg of a pigment preparation are added.

The thus obtained casting composition dispersion has a viscosity at 23° C of 1300 mPa*s and can be filled into the casting mold and cured without any problem. After a further 30 minutes the viscosity of the remaining dispersion has risen to 5000 mPa*s, but it can still be worked with without any problem.

Comparative Example 1

2.2 kg polymethyl methacrylate granulate (average particle size approximately 500 µm) (molecular weight Mw = 150 000) are added to and stirred into 10 kg methyl methacrylate. The thus obtained mixture has to be stirred at elevated temperature until the polymethyl methacrylate has dissolved completely. The dissolving process is completed after approximately 8 to 10 hours (depending on the temperature used).

0.20 kg of a standard cross-linker, 16 kg silanized cristobalite powder (particle size 0 - 40 µm), 0.125 kg mold release agent (stearic acid), 0.16 kg of a peroxidic catalyst and approximately 0.5 kg of a pigment preparation are added to and stirred into the thus produced sirup.

The thus obtained dispersion has a viscosity at 23° C of 1000 mPa*s and can be filled into the casting mold and cured without any problem.

Comparative example 2

0.20 kg of a standard cross-linker, 16 kg silanized cristobalite powder (particle size 0 - 40 µm), 0.125 kg mold release agent (stearic acid), 0.16 kg of a peroxidic catalyst and approximately 0.5 kg of a pigment preparation are added to and stirred into 13 kg methyl methacrylate.

Sedimentation of the filler occurs rapidly. A stable dispersion is not obtained.

The approximate times for producing a castable dispersion for the examples given hereinabove are summarized in the following:

	Example 1	Example 2	Comparative example 1	Comparative example 2
t (min)	35 min	40 min	500 min	*)

*) A castable dispersion was not obtainable.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A curable casting composition for producing plastic molded articles comprising a liquid, monomeric acrylate component, a proportion of a particulate plastic material, a proportion of a particulate inorganic material, wherein the total content of particulate plastic material and particulate inorganic material is approximately 45 to 85 % by weight of the casting composition, with a minimum content of 8 % by weight of particulate plastic material, said liquid, monomeric acrylate component being essentially free from a prepolymerized acrylate component, and the casting composition further comprising a cross-linker, wherein the cross-linker is present in a proportion of up to 6% by weight of the proportion of the monomeric acrylate component.

2. A casting composition as defined in claim 1, wherein the total content of particulate plastic material and particulate inorganic material is approximately 60 to 70 % by weight of the casting composition.

3. A casting composition as defined in claim 1 or 2, wherein the particulate plastic material is made from a polymer filled with an inorganic filler.

4. A casting composition as defined in claim 3, wherein the filled polymer is an at least partly cross-linked acrylate polymer.

5. A casting composition as defined in claim 3 or 4, wherein the inorganic filler comprises proportions of cristobalite, quartz, aluminium oxide trihydrate, calcium carbonate, mineral silicates or any mixtures of the aforementioned materials.

6. A casting composition as defined in any one of claims 3 to 5, wherein the polymer proportion of the plastic material is approximately 20 to approximately 80 % by weight, and the filler proportion is approximately 80 to approximately 20 % by weight.

7. A casting composition as defined in any one of claims 3 to 6, wherein the average particle size of the inorganic filler is from 1 µm to 1 mm.

8. A casting composition as defined in any one of claims 1 to 7, wherein the average particle size of the particulate inorganic material is from 1 µm to 1 mm.

9. A casting composition as defined in any one of claims 1 to 8, wherein the particulate inorganic material comprises cristobalite, quartz, glass, mineral silicates, calcium carbonate, barium sulfate and/or aluminium trihydroxide.

10. A casting composition as defined in any one of claims 1 to 9, wherein the particle size of the particulate plastic material is from 1 µm to 1 mm.

11. A casting composition as defined in any one of claims 1 to 10, wherein polyfunctional acrylate compounds are contained therein as cross-linkers.

12. A process for producing a casting composition as defined in any one of claims 1 to 11 comprising the steps:

a) producing a particulate plastic material;

b) first introducing into a mixing tank a liquid, monomeric acrylate component being essentially free from a prepolymerized acrylate component, which optionally comprises a cross-linker and/or a mold release agent;

c) adding and stirring the plastic material produced in accordance with step a) into the monomeric acrylate component, and subsequently further stirring the mixture for at least approximately 20 minutes;

d) adding and stirring the remaining constituents of the casting composition and optionally pigments, catalysts, accelerators.

13. A process as defined in claim 12, wherein the materials of steps c) and d) are added jointly to the acrylate component, and that stirring is carried out subsequently for at least approximately 20 minutes.

14. A use of the casting composition as defined in any one of claims 1 to 11 for the production of plastic molded articles for kitchens or bathrooms.

15. A use as defined in claim 14, wherein the molded articles are selected from counter-tops for kitchens, bathtubs, shower troughs or washbasins.

16. A plastic molded article produced using a casting composition according to any one of claims 1 to 11.