

Process for the Production of Thermosetting Moulding Materials

Description

The invention relates to the process of producing moulding materials, which contain resins or resin-hardener mixtures as binders that harden on a starting temperature which is above their melting points. The most important binder of this kind is a mixture of Novolak-Hexamethylenetetramine.

There are three different ways of producing Phenol-resin moulding materials (Plastic Materials Handbook, Vol. 10, Duroplaste, 2. Edition, Hanser Publishing House 1988, Pages 211-213) : The procedure with liquid resin, where filling material is made waterproof with a resin-solution and where the humid materials are being dried and further condensed until they have reached the wanted degree of condensation. Working with humid material is undesirable in manufacturing sites, because a clean handling is difficult and the drying process requires additional energy.

During the turbo-mixing procedures, constituents of the moulding material are being homogenized in high speed mixers with short mixing times. This results in a high energy entry for the mixers which is difficult to be regulated and distributed equally. Thus, problems arise concerning the reproducibility. In particular, the degree of condensation of the pre-condensed material is not uniform. This kind of problems are smaller with the so-called melting liquid procedure. Here, pre-mixtures are being produced from grinded solid resin, hardener, as well as fillings and admixtures which are then processed on rollers or kneaders. The resin then will melt. This melting is caused by friction energy. The filling material is thus being impregnated and the resin is pre-condensated as wanted. The product is cooled down and the created material is grinded. In the course of the procedure, great portions of dust are released and the hardening material additionally has to be sieved and examined.

Therefore, it is the task of the invention to avoid these disadvantages, that is, to find an economic procedure to create thermosetting materials in only a few steps to produce an equally condensed and well reproducible substance that may be ground to any size of grain or granules without producing too much dust.

The solution is obtained in the processes according to Claims 1-10.

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A very simple production method for moulding materials is to mix the at least pre-melted resin with a previously mixed substance of filling material and/or fibres, admixtures and, if necessary, hardener. This is mixed thoroughly. Thus, a good moistening and impregnation of filling material and fibres, as well as a homogeneous mixture, will be achieved. The friction energy is low because the rise in temperature of the mixture is mainly equivalent to the cooling of the melted resins. In particular, this is favourable if the melting mass which is being created when cooling the resin, is used immediately.

Surprisingly, this process does not produce sticky material or brittle lumps but trickling tiny granules which can be crushed to the wanted size while hardly creating any dust. This simple procedure allows to reduce several operation steps. The process of mixing is milder than with the aforementioned procedures. In particular, long fibres are hardly strained, that means the produced material according to the invention has a better impact strength.

In the simple version of this procedure, the mixing process is regulated by keeping the temperature within the mixing device as well as the temperature of the produced material below the starting temperature of the hardening reaction.

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According to the standard of technology, the resins usually are prepared for a higher hardening degree to adapt to the flow of the moulding materials to the equivalent processing machines. This is especially the case for materials based on phenol resins. This also happens with the simple invention procedure. It has to be completed that way so that the temperatures in the mixing device and therefore the temperature of the created moulding materials are higher than the starting temperature when hardening sets in. The mixing has to be continued until the wanted degree of hardening is reached. Then the mixing process will be stopped and the created moulding materials will be cooled down below the starting temperature of the hardening reaction as fast as possible. The results here are also trickling granules with uniform sizes and well reproducible hardening degrees.

The composition of the thermosetting material is equivalent to the conventional moulding materials based on thermosetting binders, that means they are composed of binders which harden if exposed to heat, common fillings (e.g. chalk, clays, titandioxide, lithopone, silicium dioxide or heavy feldspar) and/or fibres (like cellulose-, wood-, glass- synthetic fibres and, if necessary, admixtures, for example, pigments, hardening accelerators, stabilizers, as well as lubrication and separation preparations). On one hand, binders are self-hardening resins or resin-mixtures or resin-hardener-mixtures. In this case, it is important that the hardening temperature of the binders is above their melting point. The adequate types of resins are the phenol-, carbamide-, and melamine resins, as well as

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equivalent mixed condensates, but also the unsaturated polyester, polyamide, polydiallylphtalate or epoxide resins. Preferred binders are Novolak-resin and hexamethylenetetramine (Hexa) as hardeners, whereas in particular, Novolak-resin is the most convenient which is a mixture of Novolak with different chemical structures (Novolak based on phenol and/or bisphenol) and/or different condensation degrees.

In a high speed mixing machine, resins - which are at least partially melted - are added to a pre-mixture of filling and additives and mixed thoroughly. It is also possible to use a resin-mixture that consists of melted resin and an unmelted resin of up to 40% of its weight in powder form.

As far as the resin requires a hardener, several possible solutions exist: The hardener is pre-mixed with filling material and/or fibres and additives and then, being a part of the pre-mixture, will be mixed with the melted resin, or, the hardener will be melted together with the resin or rather dissolved in the melted resin fluid. The binder melted substance thus created will be mixed with the pre-mixture of fillings and/or fibres and admixtures. But it is preferred to mix the fillings and/or the fibres as well as the additives first. Then the melted resin fluid is added to this composition and the product will be mixed with the hardener in liquid or solid state.

This procedure, except for the pre-mixing of the resins, is carried out in the same mixing device. Appropriate are

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high speed mixing machines which can regulate the temperature of the mixing materials, for example, high speed intensive mixers with peripheral speeds $V_u > 5$ m/s, multi-wave dissolver, turbo or high performance centrifuges.

The mixture of solid components filling material and/or fibres as well as additives and hardener is done within 0,5-30 minutes. It has to be regulated that way so that the temperature of the pre-mixture remains within the wanted range. If necessary, the mixing machine has to be cooled.

The temperature limits of the pre-mixture depend on the wanted procedure: If the moulding material is produced the way that the components are only mixed together without hardening of the resin, then the pre-mixture temperature should remain below 70 °C, preferably below 50 °C, before adding the resin. But if the resin is to be partially hardened to a certain degree within the moulding material inside the mixing machine, then the temperature of the pre-mixture has to remain below 100°C (preferably below 70°C), before adding the hardener.

Without interrupting the mixing procedure, resin or melted resin is added to the pre-mixture. The temperature of the mixture results mainly from the thermal energy of the melt. If no partial hardening reaction of the resin is wanted, the temperature within the mixing machine has to remain below the starting temperature of the hardening reaction.



But if the resin within the forming material should have a higher degree of hardening, then the temperature within the mixing machine has to be above the starting temperature of the hardening reaction. This can be achieved and controlled by the following measures : increasing the pre-mixture temperature and/or the melted resin, increasing the spinning speed in the mixing aggregates, increasing the mixing time, increasing the friction of the mixture. The latter can be done by simply adding thixotropic substances like bentonites, highly dispersable silicic acid or ash. A simple way to increase the friction of such a mixture is to add up to 4% of weight in 4% of water. As soon as the starting temperature in the mixer is exceeded, a hardening reaction will take place. This can be directly measured by the higher energy consumption of the mixer. After having reached the degree of energy consumption which is equivalent to the hardening degree of the resin, the mixing process will be stopped and the created forming material cooled as far as possible below the starting temperature. A simple method is to quickly empty the moulding material through a lid at the base into a bin.

Examples

Example 1

A mixing machine (contents 300 l) with a centrifuge mechanism with a fixed number of revolutions of 155 revs/min ($V_u = 5,26 \text{ m s}^{-1}$) is filled with :

32, 0 kg Aluminium oxidhydrate
11, 0 kg Fibreglass

17,0 kg Chalk
0,6 kg Peroxide Composition
0,6 kg Titandioxide
2,0 kg Calcium stearate
0,1 kg Colour Paste
0,3 kg Lubricating Fluid

and mixed thoroughly for 30 seconds. The pre-mixture is homogeneous and has a temperature of about 30°C. While constantly keeping the mixing temperature at the same level, 16 kg of melted polyester resin at a temperature of 130°C are added within 5 minutes. (Viscosity at 150°C: 3.000 cP).

While keeping the mixing speed constantly on the same level, the mixing will continue for 5 minutes. The created material with a temperature of 50°C is let out into a bin through a lid at the base of the mixer.

The inside wall of the mixer is clean and all mixing tools are shiny. The created material is homogeneous and trickles with only little dust. The single parts have an average size of 1-2 mm.

Example 2

In a mixing machine (contents 300 l) with a centrifuge mechanism with variable revolutions and a whirling device with fixed revolutions of 3000 per minute, a moulding material is created in the following variation :

Raw Material :

15,5 kg Wood Powder
10,5 kg Chalk
10,5 kg Kaolin
2,0 kg Magnesium oxide
0,5 kg Ash
4,0 kg Hexa
0,1 kg Wax
2,0 kg Water

are mixed in the mixing machine at 200 revolutions per minute for 25 minutes. The pre-mixture has a temperature of about 60°C.

25 kg of melted phenol-resins (160°C) are added within 2 minutes while stirring continuously. The temperature exceeds 100°C and the hardening reaction starts. After about 5 minutes, the energy consumption increases from about 11 amperes to 35 amperes. The wanted hardening level is reached.

The mixer is then stopped and the material is quickly discharged through a lid at the bottom into a bin.

After having cooled down, the trickling product is ground and sieved to become homogeneous granules. There is hardly any development of dust in this process. Furthermore, the proportion of tiny granules which cannot be exploited is very small.

With this created substance, high quality spraying and press-parts are produced.



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Patent Claims

1. Process of producing moulding materials from binders, fillings and/or fibres and, if necessary, additives, in which the binders are resins or resin-hardener mixture that harden on a starting temperature which is above the melting points of the resins, characterised in that, a high speed mixing machine is used in which fillings and additives, as well as, if necessary, hardeners, are mixed beforehand and to this pre-mixture a resin or binder mixture, which at least partly exists in melted form, is added and thoroughly mixed and the temperature within the mixing machine remains below the starting temperature of the hardening reaction.
2. Process of producing moulding materials from binders, fillings and/or fibres and, if necessary, additives, in which the binders are resins or resin-hardener mixture that hardens over a starting temperature which is above the melting point of the resins, characterised in that, a high speed mixing machine is used in which fillings and additives, as well as, if necessary, hardeners, are being mixed beforehand and to this pre-mixture a resin or binder mixture, which

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at least partly exists in melted form, is added and thoroughly mixed and the temperature within the mixing machine exceeds the starting temperature of the hardening reaction, so that, the binder hardens and the hardening can be stopped when the wanted hardening degree is reached when the mixing procedure is terminated and the moulding material is cooled down below the starting temperature as fast as possible.

3. Process according to Claim 1 or 2, characterised in that, the fillings and/or fibres as well as the additives are mixed beforehand and then the hardener is added and mixed together.
4. Process according to Claim 1, characterised in that, the temperature of the pre-mixture, before adding the melted resin, is below 70 °C.
5. Process according to Claim 2, characterised in that, the temperature of the pre-mixture, before adding the melted-resin, is below 100 °C.
6. Process according to Claims 2 to 5, characterised in that, as a binder, Novolak-resin and Hexamethylene-tetramine are used.
7. Process according to Claim 6, characterised in that, the Novolak-resin to be used is of a mixture of Novolaks of different chemical structures and/or different degrees of condensation.

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8. Process according to Claim 2, characterised in that, the increase in temperature of the mixture above the starting temperature is effected by friction heat.
9. Process according to Claim 8, characterised in that, water is added to the mixture to increase friction.
10. Process according to Claims 1 to 9, characterised in that, the cooling of the moulding material is effected by quickly emptying it into a bin.

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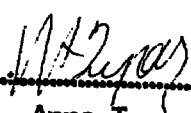
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Process for the Production of Thermosetting Moulding Materials

Summary

During the process according to the invention, moulding material is produced on the basis of thermosetting binders, that is, the binders are mixed in melted form with the fillings and additives. A hardening reaction is achieved by increasing the temperature of the mixture during the mixing process above the starting temperature of the hardening reaction. After having reached the wanted hardening degree the temperature is dropped abruptly.

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Patent Claims

1. Process of producing moulding materials from binders, fillings and additives and optionally fibres,
in which the binders are resins or resin-hardener mixture that harden on a starting temperature which is above the melting points of the resins, characterised in that, a high speed mixing machine is used in which fillings and additives, as well as, if necessary, hardeners, are mixed beforehand and to this pre-mixture a resin or binder mixture, which at least partly exists in melted form, is added and thoroughly mixed and the temperature within the mixing machine remains below the starting temperature of the hardening reaction.
2. Process of producing moulding materials from binders, fillings and additives and optionally fibres,
in which the binders are resins or resin-hardener mixture that hardens over a starting temperature which is above the melting point of the resins, characterised in that, a high speed mixing machine is used in which fillings and additives, as well as, if necessary, hardeners, are being mixed beforehand and to this pre-mixture a resin or binder mixture, which

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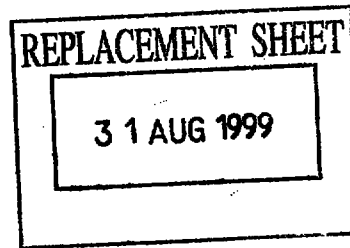
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at least partly exists in melted form, is added and thoroughly mixed and the temperature within the mixing machine exceeds the starting temperature of the hardening reaction, so that, the binder hardens and the hardening can be stopped when the wanted hardening degree is reached when the mixing procedure is terminated and the moulding material is cooled down below the starting temperature as fast as possible.

3. Process according to Claim 1 or 2, characterised in that, the fillings and additives and optionally fibres are mixed beforehand and then the hardener is added and mixed together.
4. Process according to Claim 1, characterised in that, the temperature of the pre-mixture, before adding the melted resin, is below 70 °C.
5. Process according to Claim 2, characterised in that, the temperature of the pre-mixture, before adding the melted-resin, is below 100 °C.
6. Process according to Claims 2 to 5, characterised in that, as a binder, Novolak-resin and Hexamethylene-tetramine are used.
7. Process according to Claim 6, characterised in that, the Novolak-resin to be used is of a mixture of Novolaks of different chemical structures and/or different degrees of condensation.

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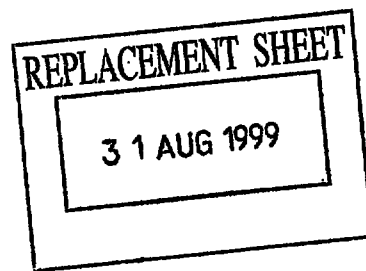
A very simple production method for moulding materials is to mix the at least pre-melted resin with a previously mixed substance of binders, fillings and additives and optionally fibres.

This is mixed thoroughly. Thus, a good moistening and impregnation of filling material and fibres, as well as a homogeneous mixture, will be achieved. The friction energy is low because the rise in temperature of the mixture is mainly equivalent to the cooling of the melted resins. In particular, this is favourable if the melting mass which is being created when cooling the resin, is used immediately.

Surprisingly, this process does not produce sticky material or brittle lumps but trickling tiny granules which can be crushed to the wanted size while hardly creating any dust. This simple procedure allows to reduce several operation steps. The process of mixing is milder than with the aforementioned procedures. In particular, long fibres are hardly strained, that means the produced material according to the invention has a better impact strength.

In the simple version of this procedure, the mixing process is regulated by keeping the temperature within the mixing device as well as the temperature of the produced material below the starting temperature of the hardening reaction.

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According to the standard of technology, the resins usually are prepared for a higher hardening degree to adapt to the flow of the moulding materials to the equivalent processing machines. This is especially the case for materials based on phenol resins. This also happens with the simple invention procedure. It has to be completed that way so that the temperatures in the mixing device and therefore the temperature of the created moulding materials are higher than the starting temperature when hardening sets in. The mixing has to be continued until the wanted degree of hardening is reached. Then the mixing process will be stopped and the created moulding materials will be cooled down below the starting temperature of the hardening reaction as fast as possible. The results here are also trickling granules with uniform sizes and well reproducible hardening degrees.

The composition of the thermosetting material is equivalent to the conventional moulding materials based on thermosetting binders, that means they are composed of binders which harden if exposed to heat, common fillings (e.g. chalk, clays, titandioxide, lithopone, silicium dioxide or heavy feldspar) and ___ fibres (like cellulose-, wood-, glass- synthetic fibres and, if necessary, admixtures, for example, pigments, hardening accelerators, stabilizers, as well as lubrication and separation preparations). On one hand, binders are self-hardening resins or resin-mixtures or resin-hardener-mixtures. In this case, it is important that the hardening temperature of the binders is above their melting point. The adequate types of resins are the phenol-, carbamide-, and melamine resins, as well as

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equivalent mixed condensates, but also the unsaturated polyester, polyamide, polydiallylphtalate or epoxide resins. Preferred binders are Novolak-resin and hexamethylenetetramine (Hexa) as hardeners, whereas in particular, Novolak-resin is the most convenient which is a mixture of Novolak with different chemical structures (Novolak based on phenol and/or bisphenol) and/or different condensation degrees.

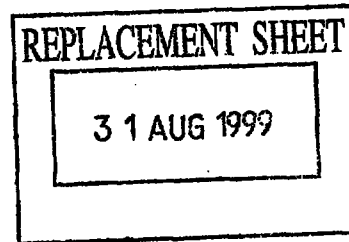
In a high speed mixing machine, resins - which are at least partially melted - are added to a pre-mixture of filling and additives and mixed thoroughly. It is also possible to use a resin-mixture that consists of melted resin and an unmelted resin of up to 40% of its weight in powder form.

As far as the resin requires a hardener, several possible solutions exist: The hardener is pre-mixed with filling material and/or fibres and additives and then, being a part of the pre-mixture, will be mixed with the melted resin, or, the hardener will be melted together with the resin or rather dissolved in the melted resin fluid. The binder melted substance thus created will be mixed with the pre-mixture of fillings and ___ fibres and admixtures. But it is preferred to mix the fillings and ___ the fibres as well as the additives first. Then the melted resin fluid is added to this composition and the product will be mixed with the hardener in liquid or solid state.

This procedure, except for the pre-mixing of the resins, is carried out in the same mixing device. Appropriate are

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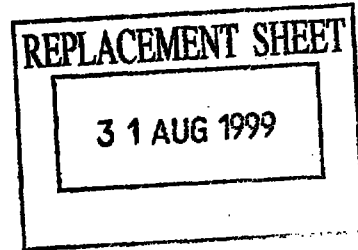


high speed mixing machines which can regulate the temperature of the mixing materials, for example, high speed intensive mixers with peripheral speeds $V_u > 5$ m/s, multi-wave dissolver, turbo or high performance centrifuges.

The mixture of solid components binders, fillings and additives and optionally fibres is done within 0,5-30 minutes. It has to be regulated that way so that the temperature of the pre-mixture remains within the wanted range. If necessary, the mixing machine has to be cooled.

The temperature limits of the pre-mixture depend on the wanted procedure: If the moulding material is produced the way that the components are only mixed together without hardening of the resin, then the pre-mixture temperature should remain below 70 °C, preferably below 50 °C, before adding the resin. But if the resin is to be partially hardened to a certain degree within the moulding material inside the mixing machine, then the temperature of the pre-mixture has to remain below 100°C (preferably below 70°C), before adding the hardener.

Without interrupting the mixing procedure, resin or melted resin is added to the pre-mixture. The temperature of the mixture results mainly from the thermal energy of the melt. If no partial hardening reaction of the resin is wanted, the temperature within the mixing machine has to remain below the starting temperature of the hardening reaction.

**Patent Claims**

1. Process of producing moulding materials from binders, fillings and additives and optionally fibres,
in which the binders are resins or resin-hardener mixture that harden on a starting temperature which is above the melting points of the resins, characterised in that, a high speed mixing machine is used in which fillings and additives, as well as, if necessary, hardeners, are mixed beforehand and to this pre-mixture a resin or binder mixture, which at least partly exists in melted form, is added and thoroughly mixed and the temperature within the mixing machine remains below the starting temperature of the hardening reaction.
2. Process of producing moulding materials from binders, fillings and additives and optionally fibres,
in which the binders are resins or resin-hardener mixture that hardens over a starting temperature which is above the melting point of the resins, characterised in that, a high speed mixing machine is used in which fillings and additives, as well as, if necessary, hardeners, are being mixed beforehand and to this pre-mixture a resin or binder mixture, which



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at least partly exists in melted form, is added and thoroughly mixed and the temperature within the mixing machine exceeds the starting temperature of the hardening reaction, so that, the binder hardens and the hardening can be stopped when the wanted hardening degree is reached when the mixing procedure is terminated and the moulding material is cooled down below the starting temperature as fast as possible.

3. Process according to Claim 1 or 2, characterised in that, the fillings and additives and optionally fibres are mixed beforehand and then the hardener is added and mixed together.
4. Process according to Claim 1, characterised in that, the temperature of the pre-mixture, before adding the melted resin, is below 70 °C.
5. Process according to Claim 2, characterised in that, the temperature of the pre-mixture, before adding the melted-resin, is below 100 °C.
6. Process according to Claims 2 to 5, characterised in that, as a binder, Novolak-resin and Hexamethylene-tetramine are used.
7. Process according to Claim 6, characterised in that, the Novolak-resin to be used is of a mixture of Novolaks of different chemical structures and/or different degrees of condensation.



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8. Process according to Claim 2, characterised in that, the increase in temperature of the mixture above the starting temperature is effected by friction heat.
9. Process according to Claim 8, characterised in that, water is added to the mixture to increase friction.
10. Process according to Claims 1 to 9, characterised in that, the cooling of the moulding material is effected by quickly emptying it into a bin.