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(54) Title: WATER-REDISPERSIBLE POLYMER POWDER COMPRISING A TRIESTER

(57) Abstract: The present invention relates to a water-redispersible polymer powder comprising a water-insoluble polymer and a triester, wherein the triester is a triester of glycerol with a C₁-to C₅-carboxylic acid and/or a triester of a C₁-to C₅-alcohol with a tri-carboxylic acid. Furthermore, processes to make said water- redispersible polymer powder are disclosed. One process comprises the making of a powder i) comprising the triester and a water-soluble polymer, wherein the powder i) is mixed with a polymer powder PP comprising a water- insoluble polymer. The intermediate powder i) is claimed as well. The polymer powder of the invention can be used in powder adhesives, wallpaper adhesives or dry mortars.



WATER-REDISPERSIBLE POLYMER POWDER COMPRISING A TRIESTER

The present invention relates to a water-redispersible polymer powder comprising a water-insoluble polymer and a triester, to a process to prepare the water-redispersible polymer powder, to powder adhesives, wallpaper adhesives, and mortars comprising the water-redispersible polymer powder and a filler and/or a mineral binder, as well as the use of the water-redispersible powder therein.

Water-redispersible polymer powders, also called RPPs in the context of this invention, are commonly used as additives in building material compositions to improve their performance, e.g. with respect to adhesion, cohesion, and flexibility of the cured building material composition.

Such RPPs are typically obtained by emulsion polymerizing one or more olefinically unsaturated monomers in the presence of an initiator and a colloidal stabilizer to form an aqueous dispersion, which – in a second step – is dried to form a polymer powder. Due to the colloidal stabilization, water-redispersible polymer powders can be obtained of which the particles are stable and do not film-form. Upon redispersion of the RPP, a dispersion is reconstituted and the dispersion particles may well film-form. However, due to the colloidal stabilization, the degree of film formation of such (re)dispersions is limited.

In order to overcome this disadvantage and to improve film formation, the glass transition temperature T_g of the polymer in the RPP is often reduced by either adjusting the monomer composition or by adding coalescing agents. Changing the monomer composition also changes the polymer characteristics, which in many cases is not desired. Adding coalescing agents most typically improves the film formation of aqueous dispersions or aqueous redispersions. However, when coalescing agents are used when making a RPP, the same effect is observed, i.e. the coalescence of adjacent dispersion particles, i.e. latex particles, in the intermediate dispersion, resulting in powder blocking in the

process to make the RPP. Therefore, great care has to be taken to optimize the film formation effect of the redispersion, but not to adversely affect the RPP process and the ageing behaviour of the polymer powders. That is why only small amounts of coalescing agents are added, which, consequently, can
5 provide only a limited increase in film formation.

In addition, when coalescing agents are added to polymer powders which are used in building material compositions, care must also be taken to avoid the addition of volatile organic components (VOC) having a boiling point at ambient
10 pressure of 200°C or below for environmental acceptability. Furthermore, the coalescing agents may have a low compatibility with the polymer and thus show less coalescing behaviour than expected. Further, they may also migrate out of the polymer with time. Additionally, it was found that coalescing agents which provide good coalescence tend to worsen the product performance of the
15 polymer powder, e.g. leading to decreased storability of the polymer powder, and/or they have an adverse effect in the final application, i.e. when the polymer powders are employed in mortars, the coalescing agents influence the mortar workability, the air pore stabilization and/or the smoothness of the mortar in a negative way.

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US 2010/0240817 discloses aqueous polymer dispersions which include plasticizers such as triesters of glycerol. These dispersions are useful as e.g. aqueous coatings, films, and inks. Water-redispersible polymer powders are not mentioned and the specifics of the stabilization systems of said polymer
25 dispersions are not disclosed.

WO 2008/054277 discloses a polymer binder and a coalescing agent which comprises triesters of glycerol with C₃- to C₅- carboxylic acids. These binders are used in waterborne paint, adhesive, and sealants. Water-redispersible
30 polymer powders are not mentioned and the specifics of the stabilization systems of said polymer dispersions are not disclosed.

WO 2007/062771 discloses polyvinyl ester dispersions having a minimum film formation temperature of 10°C or lower and comprising a cross-linking agent and a film-forming agent from the group of esters of aliphatic monocarboxylic acids and at least a trivalent aliphatic alcohol and/or the ester of at least
5 trivalent aliphatic carboxylic acid and monovalent alcohols. The polyvinyl ester dispersions may be stabilized by a protective colloid such as polyvinyl alcohol and the cross-linking agent is preferably N-methylolacrylamide, which is added up to 10 wt.%, based on the employed monomer amount. The polyvinyl ester dispersions are used as adhesives, coating agents, and binders. However, this
10 reference is silent about water-redispersible polymer powders. As a matter of fact, the cross-linking agents would trigger cross-linking reactions upon forming a powder, which would render the powder no longer redispersible in water.

The object of the present invention is to provide a water-redispersible polymer
15 powder (RPP) with improved film formation capabilities and which has to overcome the drawbacks of the prior art, in particular a reduced block resistance and/or a worsened mortar workability when coalescing agents are added. Furthermore, the coalescing agent itself must not alter mineral mortar properties, e.g. it must not act as a hydrophobizing agent and/or influence the
20 water absorption of cured mortar.

It has surprisingly been found that the problem can be solved with a water-redispersible polymer powder comprising

- a) One or more water-insoluble polymers and
- b) One or more triesters selected from triesters of glycerol with one
25 or more C₁- to C₅-carboxylic acids and triesters of one or more C₁- to C₅-alcohols with one or more tricarboxylic acids.

It was a surprise to find that these triesters are coalescing agents with an excellent compatibility with water-insoluble polymers and that they provide a
30 well-rounded performance profile for e.g. cementitious mortars. Thus, they do not elute out of the polymer, but remain trapped inside and thus continue to perform. The water-redispersible polymer powder of the invention exhibits an

excellent block resistance, i.e. essentially the same block resistance as the same polymer powder without the triester. Although e.g. 10 percent by weight (wt.%) of these triesters will greatly facilitate the film formation of the water-redispersed polymer powder, it was not foreseeable that such an amount has
5 no effect on film formation in the polymer powder itself and thus there is no caking of the powder. Also the redispersion properties, i.e. the speed of redispersion and the redispersion back to primary particles from the initial dispersion, surprisingly are not adversely affected. Furthermore, when redispersed and film-formed, the polymer according to the invention possesses
10 a higher flexibility than the same polymer powder without the triester. In addition to all this, the triesters have a boiling point at standard pressure of well above 200°C, and thus provide an RPP which fulfils the requirement of having a low amount of volatile organic components. Moreover, the triesters of the invention do not alter the mortar properties, in particular they do not act as
15 hydrophobizing agent nor affect the water absorption of the cured mortar.

The invention further provides processes of making the RPP of the invention. One embodiment comprises the steps of (i) emulsion polymerizing one or more olefinically unsaturated monomers in the presence of an initiator and a colloidal
20 stabilizer and thus forming an aqueous dispersion, (ii) adding a triester in accordance with the invention, and thereafter (iii) drying the mixture obtained. However, it was found that these triesters may be added before, during and/or after the emulsion polymerization of said olefinically unsaturated monomers.

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Another embodiment comprises a process step (i) and a process step (ii), wherein in process step (i) the triester is mixed with a dissolved water-soluble polymer and the mixture is dried to form a powder i), and wherein in process
30 step (ii) the powder i) is mixed with a polymer powder PP comprising a water-insoluble polymer. The polymer powder PP is a water-redispersible polymer powder with or without a coalescing agent. The polymer powder PP may be

commercially available. Preferably, the polymer powder PP does not contain a triester of the invention.

Claimed also are the powder i) and the mixture of powder i) and the polymer powder PP obtainable according to above processes.

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Thus, the making of the polymer powder of the invention is surprisingly flexible and allows the skilled person to design specific products which are optimized for individual applications and needs. When working with water as solvent, the processes are environmentally friendly and thus eco-efficient. When making use
10 of process step (i), and thus mixing the triester of the invention with a water-soluble polymer in a solvent or solvent mixture and drying the same, a powder i) is formed which itself can be mixed with a polymer powder PP, which comprises a water-insoluble polymer, but not said triester. Thus, basically any polymer powder which is redispersible in water and which optionally, and preferably,
15 does not contain the triester, can be taken and mixed with the powder i) – and this even in any ratio. Hence, the ratio of triester to polymer powder PP may be adjusted to levels far beyond what would form a block-resistant polymer powder. Thus, it is very advantageous that the polymer powder of the invention can be made in an efficient manner in good yield using common and well-
20 established techniques, including e.g. emulsion and suspension polymerization, spray drying, and mixing techniques. Hence, there is no need for complex procedures or equipment.

The invention in addition provides the use of the polymer powder of the
25 invention in powder adhesives, wallpaper adhesives, and dry mortars. Claimed are dry mortars comprising a filler, the RPP of the invention, and, optionally, a mineral binder, wherein the RPP amounts to 0.1 to 70 wt.%, based on the total amount of dry mortar. Furthermore, the invention provides powder adhesive or wallpaper adhesive comprising a polysaccharide and the RPP of the invention,
30 wherein the RPP amounts to 1 to 75 wt.%, based on the total amount of powder adhesive or wallpaper adhesive.

Claimed also are processes to make the dry mortars, powder adhesives, and wallpaper adhesives according to the invention. The dry mortars according to the invention are made in one embodiment by mixing the RPP of the invention with filler and optionally with mineral binder. In another embodiment, the powder
5 i) of the invention is mixed with filler, polymer powder PP, and, optionally, with mineral binder and further optional materials. The powder adhesives and wallpaper adhesives according to the invention are made in one embodiment by mixing the RPP of the invention with a polysaccharide. In another embodiment, the powder i) of the invention is mixed with polysaccharide and polymer powder
10 PP. Further optional materials may be added as well. The skilled person is well aware of such further materials and of suitable mixing devices and procedures and no special precautions are required.

Furthermore, it was unexpected to find that powder adhesives, wallpaper
15 adhesives, and dry mortars can be formulated which possess all of the advantages of the RPP of the invention, including an excellent wettability, i.e. the RPP wets and disperses fast when getting into contact with water. In particular the high block resistance of the RPP of the invention improves – or at least maintains – the block resistance of powder adhesives and wallpaper
20 adhesives in comparison with RPPs of the state of the art. Additionally, the high compatibility of the triester with the water-insoluble polymers is of great advantage for powder adhesives and wallpaper adhesives, since it is not eluted, which is in contrast to other conventional agents. Therefore, there is less risk of harming, for example, the adhesive properties of applied and hardened powder
25 adhesives and wallpaper adhesives.

Additionally, the RPP of the invention provides mortars comprising e.g. cement with an excellent mortar workability, with good air pore stability, and thus with a smooth and even mortar surface. It also was found that the other characteristics
30 of the mortars remained about the same, and in particular the hydrophobicity of the mortar surface and the water absorption of the mortar matrix did not change. And even more unexpectedly, the water-redispersible polymer powders of the

invention provide an increased wettability of ceramic tiles when laid into e.g. cementitious mortars at various time intervals. And when ceramic tiles are laid into a mortar 30 minutes after the mortar is applied, adhesion strengths are distinctly higher than with conventional coalescing agents. The same applies
5 when compared to a commercially used polymer powder having a low enough glass transition temperature T_g . These features are real assets of the dry mortars according to the present invention.

It is noted that US 2004/0048961 discloses a dispersion powder composition
10 based on water-insoluble polymers with low water absorption. It comprises at least one carboxylic ester whose acid component has at least 6 carbon atoms and whose alcohol component is a polyhydroxy compound such as glycerol. The carboxylic esters are demonstrated to act as and are stated to be hydrophobizing agents. As such they increase the water repellency of the
15 mortar and reduce the water absorption of the mortar matrix. However, they do not act as coalescing agents and thus they have no influence on the film formation of the (re)dispersion particles.

US 2004/0019141 discloses a hydrophobically modified polymer composition
20 comprising a polymer in the form of an aqueous polymer dispersion or a water-redispersible polymer powder prepared therefrom, wherein the polymer composition further comprises a component a) being an organosilicon compound and a component b) being one or more fatty compounds, including C_8 - C_{22} fatty acid triesters of glycerol. The components a) and b) are
25 demonstrated to act as and are stated to be hydrophobizing components. Again, they do not act as coalescing agents and thus they have no influence on the film formation of the (re)dispersion particles.

It is noted that hydrophobizing agents and coalescing agents are distinctly
30 different classes of compounds. Hydrophobizing agents affect the properties of the mortar matrix, but have no significant effect on the coalescence of dispersion particles, i.e. film formation is not affected. Hydrophobizing agents

based on fatty acid esters comprise a long-chain, most typically a C₁₂- to C₁₈-chain, alkyl or alkylene group. Such fatty acid esters are therefore basically not water-soluble. Thus, when incorporated into an aqueous environment at neutral pH, they remain water-insoluble and thus they are able to diffuse into dispersion
5 particles. However, in an alkaline environment the fatty acids hydrolyze and thus liberate the long-chain fatty acid and its anion, respectively, which then provide the hydrophobizing effect. Due to the fact that the hydrophobizing agents are in separate domains and not diffused into dispersion particles, their hydrolysis occurs fast, which is an essential factor in providing efficient
10 hydrophobization.

By contrast, the triester according to the invention is a triester of glycerol with C₁- to C₅-carboxylic acids and/or a triester of a C₁- to C₅-alcohol with a tricarboxylic acid. Hence, it does not contain long-chain hydrophobic groups and
15 thus the triester of the invention does not liberate long-chain fatty acids or their anions under alkaline conditions and thus does not provide any hydrophobizing effect. Moreover, the triester possesses a limited water solubility, allowing it when in an aqueous dispersion to diffuse into the dispersion particles, where it preferably stays. Thus, even if said triesters should hydrolyze in an alkaline
20 environment, this process would occur more slowly, since said triesters would first need to diffuse out of the particles.

In conclusion, the hydrophobizing agents cannot act as coalescing agents to aid film formation and the triesters of the invention cannot act as hydrophobizing
25 agents.

The water-redispersible polymer powder

In this specification the term water-redispersible polymer powder, RPP for short,
30 according to the invention comprises one or more types of water-insoluble polymers and a specific triester. The term RPP stands for a powder wherein the water-insoluble polymer is preferably in the form of particles obtained from e.g.

emulsion or suspension polymerization. These particles are also called primary particles, dispersion particles or latex particles, which are all synonymous terms. The water-redispersible polymer powder comprises a multitude of primary particles which do not film-form or coalesce as long as they are part of the polymer powder, when stored under ambient conditions. Hence, the polymer powders are designed such that the primary particles keep their shape after they are dried, optionally with suitable adjuvants.

It has now surprisingly been found that this is even the case when the triester of the invention is present in higher amounts of more than 1 wt.%, or even 10 wt.% or more, based on the solids content of the water-insoluble polymer, even though said triester facilitates the coalescence of the primary particles when they are dispersed or redispersed in a medium such as water. Thus, drying can be done while avoiding film formation. Nevertheless, upon mixing the polymer powder with water, the polymer powder redisperses back to the primary particles, which then subsequently show the desired film formation.

In one preferred embodiment, the RPP comprises

- a) 30 wt.% or more, preferably 50 wt.% or more, more preferably 60 wt.% or more, and up to 99 wt.%, preferably up to 95 wt.%, more preferably up to 90 wt.% of water-insoluble polymer,
- b) 1 wt. % or more, preferably 2 wt.% or more, more preferably 3 wt.% or more, and up to 50 wt.%, preferably up to 40 wt.%, and more preferably up to 25 wt.% of said triester,
- c) 0 wt.% or more, preferably 2 wt.% or more, more preferably 3 wt.% or more, and up to 50 wt.%, preferably up to 35 wt.%, more preferably up to 20 wt.% of water-soluble polymer,
- d) 0 wt.% or more, preferably 3 wt.% or more, more preferably 5 wt.% or more, and up to 30 wt.%, preferably up to 25 wt.% of one or more anticaking agents, and
- e) 0 to 25 wt.%, preferably 0 to 20 wt.%, more preferably 0 to 15 wt.%, of one or more components ii), wherein component ii) is selected from the group of hydrophobic and/or oleophobic additives, rheology control additives, thickeners,

polysaccharides and derivatives thereof, additives to control the hydration and/or setting of mineral binders, surface-active additives, pigments, fibres, corrosion protection additives, pH-adjusting additives, additives for the reduction of shrinkage and/or efflorescence, wherein the sum of the components adds up to 100 wt.%. The component ii) materials are well known to the skilled person, who also is best suited to make the best selection.

It is noted that the term water-redispersible polymer powder relates to the polymer powder according to the present invention, while the polymer powder PP may comprise the same water-insoluble polymer as the polymer powder according to the invention, but without a triester of the invention. Thus the polymer powder PP may also be redispersible in water and may comprise the same types and amounts of water-soluble polymer, anticaking agents, and component ii).

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The water-insoluble polymer

The water-insoluble polymer is preferably in the form of an aqueous dispersion or suspension when used for making an RPP of the invention. In a preferred embodiment, such aqueous dispersions or suspensions have a solids content of about 30 to 70 wt.%, preferably of about 40 to 60 wt.%, and a Brookfield viscosity, measured at 23°C and 20 rpm according to DIN 53019, of about 100 to 30,000 mPa's, preferably about 500 to 20,000 mPa's. The mean particle size is about from 0.1 µm, preferably from about 0.2 µm, to about 20.0 µm, preferably to about 10.0 µm, while the dispersion may also have smaller and/or larger emulsion or suspension particles. The particle size is measured by means of light scattering and indicated as volumetric mean. Processes to make the water-insoluble polymer are well established and known to the person skilled in the art. The solubility of the polymer in demineralized water is less than 1 g/l, preferably less than 0.1 g/l, at 20°C and a pH of 7.

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The monomer selection and the selection of the weight fractions of the comonomers are made so that in general the resulting glass transition

temperature of the polymerizate, T_g , is between -20°C and $+70^{\circ}\text{C}$, preferably between -10°C and $+50^{\circ}\text{C}$. The glass transition temperature, T_g , of the polymers can be determined in a known manner by means of differential scanning calorimetry (DSC), in which case the midpoint temperature in accordance with ASTM D3418-82 has to be taken into account. The T_g can also be calculated approximately in advance using the Fox equation (T. G. Fox, *Bull. Am. Physics Soc.* 1, 3, page 123 (1956)), as follows: $1/T_g = x_1/T_{g1} + x_2/T_{g2} + \dots + x_n/T_{gn}$, wherein x_n represents the mass fraction (% by weight/100) of the monomer n and T_{gn} is the glass transition temperature, in Kelvins, of the homopolymer of the monomer n . T_g values for homopolymers are listed in e.g. *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, Vol. A21 (1992), p. 169.

In yet another preferred embodiment, it is advantageous that the water-insoluble polymer – before addition of the triester – has a minimum film formation temperature (MFFT) of at or below 50°C , more preferably at or below 30°C , wherein the MFFT is determined in accordance with DIN 53787.

The water-insoluble polymer in the RPP of the invention is preferably a water-insoluble polymer obtained by a colloiddally stabilized dispersion polymerization. More specifically, the water-insoluble polymer is preferably obtained by emulsion polymerizing one or more olefinically unsaturated monomers, preferably selected from the group of vinyl esters, (meth)acrylic esters, vinyl aromatic compounds, vinyl halides, and olefins, in the presence of an initiator, a colloidal stabilizer, and, optionally, surfactants. The colloidal stabilizer preferably is a protective colloid. Protective colloids are normally water-soluble polymer compounds which are employed for conducting an emulsion polymerization and then for stabilizing the finely dispersed polymer particles. Protective colloids, owing to their structure, are in part incorporated into the polymer as it forms in the course of emulsion polymerization. In this case one speaks of a graft polymerization. As a result, dispersions stabilized by protective colloids are

often much more stable to mechanical loads than emulsifier-stabilized dispersions.

Thus, the water-insoluble polymer can be obtained by radical polymerization of one or more olefinically unsaturated monomers in an aqueous medium in the presence of a free radical initiator and a water-soluble polymer, i.e. colloidal stabilizer. The skilled person knows how to select suitable free radical initiators as well as colloidal stabilizers.

Suitable vinyl esters are one or more monomers from the group of vinyl esters of branched or unbranched carboxylic acids having 1 to 20 carbon atoms. Preferred vinyl esters are vinyl acetate, vinyl esters of one or more branched or straight-chain alkylcarboxylic acids having 3 to 15 C atoms, in particular vinyl propionate, vinyl butyrate, vinyl 2-ethylhexanoate, vinyl laurate, 1-methylvinyl acetate, vinyl pivalate, vinyl versatate having 9, 10 or 11 carbons (i.e. VeoVa 9/ 10/ 11), vinyl decanoate, vinyl stearate, vinyl pyrrolidone, wherein VeoVa 9/ 10/ 11 are the vinyl esters of branched C₉- to C₁₁-carboxylic acids, and mixtures thereof.

Furthermore, it is also possible to copolymerize vinyl monomers derived from biomonomers. Suitable biomonomers are disclosed in EP-A-2 702 544, EP-A-2 075 322, EP-A-2 075 322, and WO 2011/141400; the contents thereof are incorporated herein by reference. Non-limiting examples include biomonomers containing an ester of a polyol and at least one fatty acid, the polyol having 2 to 10 hydroxy groups, and the biomonomer containing at least one vinyl group. They are preferably used in an amount of about 0.5 to 80 wt.%, in particular about 5 to 50 wt.%, based on the total amount of olefinically unsaturated monomers.

Suitable (meth)acrylic ester monomers are the linear, cyclic or branched C₁- to C₂₀-alkyl esters. Preferred C₁- to C₁₂-alkyl groups of (meth-)acrylic acid esters are methyl, ethyl, propyl, n-butyl, i-butyl, t-butyl, hexyl, cyclohexyl, 2-ethylhexyl,

lauryl, stearyl, norbornyl, polyalkylene oxide and/or polyalkylene glycol groups, in particular methyl, butyl, 2-ethylhexyl groups. Preferred methacrylic esters or acrylic esters are methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, n-butyl acrylate, i-butyl
5 acrylate, n-butyl methacrylate, i-butyl methacrylate, 2-ethylhexyl acrylate, (5-ethyl-1,3-dioxan-5-yl) methyl (meth)acrylate, ethyldiglycol (meth)acrylate, stearyl acrylate, stearyl methacrylate, and norbornyl acrylate. Methyl methacrylate, n-butyl acrylate, 2-ethylhexyl acrylate, stearyl (meth)acrylate, and norbornyl acrylate are particularly preferred.

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From the group of vinyl aromatic compounds styrene, styrene derivatives, such as α -methylstyrene, ortho-chlorostyrene or vinyl toluene, vinyl pyridine, as well as vinyl esters of benzoic acid and p-tert-butylbenzoic acid are preferred, with styrene being particularly preferred.

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From the group of vinyl halides it is common to use vinyl chloride, though vinylidene chloride is also an option.

From the group of olefins ethylene, propylene, isoprene, and butadiene are
20 typically used.

It is noted that some of the olefinically unsaturated monomers may also comprise at least one functional group which is different from the olefinically unsaturated group. According to the invention, these monomers are called
25 functional monomers.

Such functional monomers can be added typically in an amount of 0 to 20 wt.%, preferably of 0 to 10 wt.%, and in particular of 0 to 5 wt.%, based on the total amount of olefinically unsaturated monomers. The functional group is preferably
30 selected from the group of alkoxysilane, silanol, glycidyl, epoxy, epihalohydrin, nitrile, carboxyl, amine, ammonium, amide, imide, isocyanate, hydroxyl, thiol, keto, carbonyl, carboxylic anhydride, sulfonic acid groups, and salts thereof.

The person skilled in the art is well aware of suitable monomers comprising such functional groups. Non-limiting examples are (meth)acrylamide, monocarboxylic and dicarboxylic acids and their anhydrides, such as acrylic acid, methacrylic acid, maleic anhydride, and acrylamidoglycolic acid, hydroxyethyl (meth)acrylate, 2-aminoethyl(meth)acrylate, and 2-aminoethyl(meth)acrylate hydrochloride, N,N-[(3-chloro-2-hydroxypropyl)-3-dimethylammonium propyl]-(meth)acrylamide chloride, N-[3-dimethylamino]-propyl]-(meth)acrylamide hydrochloride, glycidyl (meth)acrylate, and (3-chloro-2-hydroxypropyl)dimethyl[3-(2-methyl-1-oxoallyl)amino]propyl)ammonium chloride, (meth)acryloxypropyl trialkoxy silane, vinyltrialkoxo silane, acetoacetoxyethyl(meth)acrylate (AAEA and AAEMA), vinylsulfonic acid and 2-acrylamido-2-methylpropane sulfonic acid, α,α -dimethyl-m-propenyl benzylisocyanate (tradename: TMI[®] from Cytec). Furthermore, it is also possible to employ one or more macromonomers, i.e. a reaction product of a component (i) having at least one olefinically unsaturated group and at least one hydroxyl, amine and/or thiol group, a component (ii) being a di- or trisocyanate, and a component (iii) having at least two terminal groups selected from hydroxyl, amine and/or thiol groups. Such macromonomers are described in *Macromolecules* 2005, 38, 4183-4192 as well as in PCT/EP2012/061626, the contents of the latter being incorporated herein by reference.

In one embodiment, the water-insoluble polymer is a homopolymer of vinyl acetate or a copolymer of essentially ethylene-vinyl acetate, ethylene-vinyl acetate-vinyl ester, ethylene-vinyl acetate-(meth)acrylate, ethylene-vinyl acetate-vinyl chloride, ethylene-vinyl ester-vinyl chloride, vinyl acetate-vinyl ester, vinyl acetate-vinyl ester-(meth)acrylate, vinyl ester-(meth)acrylate, all-(meth)acrylate, styrene-acrylate and/or styrene-butadiene, wherein the vinyl ester is a vinyl ester of one or more branched or straight-chain alkylcarboxylic acids having 3 to 15 C atoms. Preferred vinyl esters are vinyl laurate and/or vinyl versatate, wherein vinyl versatate is a vinyl ester of a branched C₃- to C₁₅-carboxylic acid, in particular a vinyl ester of a branched C₉- to C₁₁-carboxylic acid, wherein the copolymers comprise 0-20 wt.%, preferably of 0-10 wt.%, and

in particular of 0-5 wt.%, based on the total amount of olefinically unsaturated monomers, one or more functional monomers.

5 In a preferred embodiment, the water-insoluble polymer is a homopolymer of vinyl acetate or a copolymer of ethylene-vinyl acetate having an ethylene content of up to 25 wt.%, preferably up to 15 wt.%, and in particular up to 10 wt.%, based on the water-insoluble polymer.

10 In another preferred embodiment, the water-insoluble polymer does not contain crosslinkers, in particular not added crosslinkers or crosslinking monomers, e.g. N-alkylol groups such as N-methylol groups. Thus, copolymerized olefinically unsaturated monomers preferably do not comprise N-methylol (meth)acrylamide and/or derivatives thereof. Therefore, the water-insoluble polymer is not a crosslinkable dispersion in the sense of WO 2007/062771.

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The triester

20 The triester that is used in accordance with the invention comprises at least one triester of glycerol with one or more C₁- to C₅-carboxylic acids, preferably one or more C₁- to C₃-carboxylic acids, and/or a triester of one or more C₁- to C₅-alcohols, preferably one or more C₁- to C₃-alcohols, with one or more tricarboxylic acids. The triester may be part of a mixture, e.g. with diester and/or monoester of glycerol with one or more carboxylic acids, and/or a diester and/or monoester of one or more alcohols with a tricarboxylic acid. Also other esters
25 and/or partial esters may be included in the triester.

The C₁- to C₅-carboxylic acid may be formic acid, acetic acid, propanoic acid, hydroxy propionic acid, butanoic acid, butyric acid and/or pentanoic acid, wherein the preferred C₁- to C₃-carboxylic acid is formic acid, acetic acid,
30 propanoic acid and/or hydroxy propionic acid.

In a preferred embodiment, the C₁- to C₅-ester of glycerol is glycerol triformate, i.e. triformin, glycerol triacetate, i.e. triacetin, glycerol tripropionate, i.e. tripropionin, glycerol tributyrates, glycerol trivalerate, or mixtures thereof, wherein the C₁- to C₃-ester of glycerol is selected from glycerol triformate, i.e. triformin, glycerol triacetate, i.e. triacetin, glycerol tripropionate, i.e. tripropionin, and mixtures thereof, wherein said C₁- to C₃-esters of glycerol are most preferred. It is noted that the term "mixtures thereof" includes all mixtures of two or more of the mentioned compounds.

10 In another preferred embodiment, the tricarboxylic acid is selected from the group of citric acid, iso-citric acid, aconitic acid, propane-1,2,3-tricarboxylic acid, trimesic acid, and mixtures thereof, and the C₁- to C₅-alcohol is selected from methanol, ethanol, n-propanol, i-propanol, n-butanol, t-butanol, i-butanol, pentanol, such as pentane-1-ol, pentane-2-ol, pentane-3-ol, 2-methyl-butane-1-ol, 2,2-dimethyl-propane-1-ol, and mixtures thereof, wherein the preferred C₁- to C₃-alcohol is methanol, ethanol, propanol, and mixtures thereof.

In a preferred embodiment, the triester has a water solubility of 1 g/l or higher, preferably 10 g/l or higher, measured in distilled water at a pH of 7 and 20°C.

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In one preferred embodiment, the triester is combined with the water-redispersible polymer powder in an amount of 1 to 50 wt.%, preferably 2 to 30 wt.%, and in particular 5 to 20 wt.%, based on the total amount of water-redispersible polymer powder. These ranges are particularly suitable for the polymer powders obtained by the steps of (i) emulsion polymerizing monomers and thus forming an aqueous dispersion, (ii) adding the triester, and thereafter (iii) drying the mixture obtained.

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In another preferred embodiment, the triester is present in the water-redispersible polymer powder in an amount of 1 to 75 wt.%, preferably 2 to 50 wt.%, and in particular 5 to 30 wt.%, based on the total amount of water-redispersible polymer powder. These ranges are particularly suitable for the

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polymer powders obtained by process step (i) wherein the triester is mixed in a solvent or solvent mixture, which is preferably water or an aqueous mixture, with a water-soluble polymer and dried to form a powder i), and wherein in process step (ii) the powder i) is mixed with a polymer powder PP comprising a water-insoluble polymer.

It was found that it is often advantageous for the ratio of the triester to the water-insoluble polymer to be adjusted such that their combination has a minimum film formation temperature MFFT at or below 10°C, more preferably at or below 5°C, wherein the MFFT is determined in accordance with DIN 53787.

The water-soluble polymer

The water-soluble polymer can be used to make the water-redispersible polymer powder according to the invention and is preferably mixed – at least partially - with the water-insoluble polymer and/or the triester before drying said mixture. Furthermore, the water-soluble polymer can be used to make the powder i) according to the invention. Additionally, the water-soluble polymer can be used as colloidal stabilizer when making the water-insoluble polymer, e.g. by emulsion polymerizing one or more olefinically unsaturated monomers in the presence of an initiator and a colloidal stabilizer. The same or a different water-soluble polymer can be used or a mixture of different water-soluble polymers may be employed. The term water-soluble polymer is used in this invention as synonym for the terms water-soluble colloid and protective colloid. Such water-soluble polymers are readily available and well known to the person skilled in the art. Water-soluble polymer means that the solubility of the polymer in distilled water with a pH of 7 and at a temperature of 20°C is 1 g/l or more, preferably 4 g/l or more.

When the water-soluble polymer is used as colloidal stabilizer in e.g. emulsion polymerization, the amount of stabilizer, based on the sum of the monomers employed, is typically about 2 to 20 wt.%, preferably about 3 to 15 wt.%, and in particular about 4 to 12 wt.%.

The water-soluble polymer may be a synthetic polymer or a natural or synthetically made biopolymer, wherein the latter may be synthetically modified.

5 Representative synthetic water-soluble polymers which can be used according to the invention include polyvinyl pyrrolidones and/or polyvinyl acetals with a molecular weight of 2,000 to 400,000, fully or partially saponified polyvinyl alcohols and the derivatives thereof, which can be modified for instance with amino groups, acetoacetoxy groups, carboxylic acid groups and/or alkyl groups,
10 with a degree of hydrolysis of preferably about 70 to 100 mol.%, in particular of about 80 to 98 mol.%, and a Höppler viscosity in 4% aqueous solution of preferably 1 to 100 mPa's, in particular of about 3 to 50 mPa's (measured at 20°C in accordance with DIN 53015), as well as melamine formaldehyde sulfonates, naphthaline formaldehyde sulfonates, polymerizates of propylene
15 oxide and/or ethylene oxide, including also the copolymerizates and block copolymerizates thereof, styrene-maleic acid and/or vinyl ether-maleic acid copolymerizates.

Preferred synthetic protective colloids are partially saponified, optionally
20 modified polyvinyl alcohols with a degree of hydrolysis of 80 to 98 mol.% and a Höppler viscosity as 4% aqueous solution of 1 to 50 mPa's and/or polyvinyl pyrrolidone.

Representative natural and/or synthetically prepared biopolymers, i.e. water-
25 soluble polymers, can be chosen from the group of biopolymers such as polysaccharides and polysaccharide ethers, for instance cellulose ethers such as hydroxyalkyl-cellulose and/or alkyl-hydroxyalkyl-cellulose, in which case the alkyl group may be the same or different and preferably is a C₁- to C₆-group, in particular a methyl, ethyl, n-propyl and/or i-propyl group, carboxymethyl
30 cellulose, starch and starch ethers (amylose and/or amylopectin and/or the derivatives thereof), guar ethers, dextrans, agar-agar, gum arabic, carob seed grain, pectin, gum tragacanth and/or alginates. Often it is advantageous when

these are soluble in cold and/or alkaline water. The polysaccharides can, but do not need to be, chemically modified, for instance with carboxymethyl, carboxyethyl, hydroxyethyl, hydroxypropyl, methyl, ethyl, propyl, sulfate, phosphate and/or long-chain alkyl groups. As synthetic polysaccharides can be
5 used for instance anionic, non-ionic or cationic heteropolysaccharides, in particular xanthan gum, welan gum and/or diutan gum. Preferred peptides and/or proteins to be used are for instance gelatin, casein and/or soy protein.

Preferred biopolymers are dextrins, cellulose ethers, carboxymethyl cellulose,
10 starch, starch ethers, casein, soy-protein, gelatin, as well as hydroxyalkyl-cellulose and/or alkyl-hydroxyalkyl-cellulose, in which case the alkyl group may be the same or different and preferably is a C₁- to C₆-group, in particular a methyl, ethyl, n-propyl and/or i-propyl group.

15 The one or more water-soluble polymers are preferably added as an aqueous solution before the drying step and/or as a powder during and/or after the drying of the polymer powder.

The anticaking agent

20 The one or more anticaking (antiblocking) agents can be added before, during and/or after the drying step. Non-limiting examples of antiblocking agents include calcium and/or magnesium carbonate, talc, gypsum, silica, kaolins, silicates, and latent hydraulic binders such as pozzolanes, metakaolin, burnt shale, diatomaceous earth, moler, rice husk ash, air cooled slag, calcium
25 metasilicate and/or volcanic slag, volcanic tuff, trass, fly ash, silica fume, fumed silica, microsilica, blast-furnace slag and/or silica dust. They preferably have a particle size in the range from 10 nm to 100 microns, preferably 50 nm to 50 microns.

30 The component ii)

The one or more components ii) can be added before, during and/or after the drying step. When the component ii) is in liquid form, the preferred addition is

before the drying step and when the component ii) is in solid form, it can be added before, during and/or after the drying step.

The person skilled in the art is well aware of these types of components ii) and
5 is able to make the best selection with respect to type and amount.

However, to avoid any misunderstanding, hydrophobic additives are understood to be components which render the building material composition hydrophobic and thus repel water. Furthermore, they often reduce the water absorption
10 capacity of the building material composition. Preferred are paraffins, organosilanes such as alkyl alkoxy silanes, the alkyl group preferably being a C₁- to C₄-alkyl group and the alkoxy group preferably being a C₁- to C₄-alkoxy group, siloxanes, silicones, metal soaps, fatty acids and/or fatty acid esters, a rosin or a rosin derivative which might contain a resin.

15 Oleophobic additives are typically based on fluorine compounds and thus reduce the dirt pick-up of building material compositions containing the same. Such compositions are also known to have "easy-to-clean" properties.

20 Rheology control additives include, besides thickeners, casein, superplasticizers, in particular polycarboxylates, melamine formaldehyde condensates, and naphthaline formaldehyde condensates.

Thickeners include polysaccharide ethers, in particular cellulose and guar
25 ethers substituted with alkyl and/or hydroxyalkyl groups, in particular with the alkyl group being a methyl, ethyl and/or propyl group and the hydroxyalkyl group being a hydroxyethyl and/or hydroxypropyl group, starches, dextrans, modified or unmodified, fully or partially hydrolyzed polyvinyl alcohols, polyalkylene oxides, agar-agar, carob seed grains, pectins, poly(meth)acrylates
30 and/or (meth)acrylate thickeners, poly(meth)acrylamides, polyurethanes, associative thickeners, inorganic thickeners, e.g. layered silica, gelatin, peptides and/or soy protein.

Additives to control the hydration and/or setting of mineral setting systems include setting accelerators, solidification accelerators and/or setting retarders.

- 5 Surface-active additives include air-entraining agents, foam stabilizers, defoamers, wetting agents, anti-foaming agents, tensides, polyalkylene oxides and polyalkylene glycols, with the alkylene group typically being a C₂- and/or C₃-group and including their copolymerizates and block copolymerizates.
- 10 Furthermore, pigments, fibres, e.g. cellulose fibres, film-coalescing agents and plasticizers, corrosion protection additives, pH-adjusting additives having an acidic or alkaline reaction with water, in particular oxides and/or hydroxides of alkali and/or alkaline earth salts, preservative agents such as biocides, herbicides, algicides and/or fungicides, anti-foaming agents, anti-oxidants,
- 15 preservatives against oxidation, heat, ozone, light, fatigue and/or hydrolysis, additives for the reduction of shrinkage, sedimentation, bleeding and/or efflorescence such as for instance compounds based on natural resins, in particular colophony and/or the derivatives thereof, as well as quarternary organic ammonium compounds may be added.

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The powder i)

- In powder i) the weight ratio of the triester to the water-soluble polymer is typically 10 to 90, preferably 20 to 80, and in particular 30 to 70. The powder i) may further comprise one or more anticaking agents in an amount of 0 to 100
- 25 wt.%, preferably 0 to 50 wt.%, based on the sum of the triester and the water-soluble polymer and/or one or more components ii) in an amount of 0 to 100 wt.%, preferably 0 to 50 wt.%, based on the sum of the triester and the water-soluble polymer.

30 Process to make the water-redispersible polymer powder

The water-redispersible polymer powder according to the invention and comprising a water-insoluble polymer and a triester can be made by different

processes using existing technologies and equipment well known to the person skilled in the art.

In one preferred embodiment, the process comprises (i) emulsion polymerizing
5 one or more olefinically unsaturated monomers in the presence of an initiator
and a colloidal stabilizer, (ii) adding the triester, and (iii) drying the mixture
obtained. There are no specific restrictions with respect to the temperature of
adding the triester, which is preferably done between around 20°C and around
100°C. Furthermore, the triester can be added to the emulsion polymerizate
10 before, during and/or after the emulsion polymerization of olefinically
unsaturated monomers. The triester can be added to the emulsion polymerizate
as such and/or is mixed in a solvent or solvent mixture, which is preferably
water or an aqueous mixture, with a water-soluble polymer first and added as
the obtained mixture.

15 The process of emulsion polymerizing one or more olefinically unsaturated
monomers in the presence of an initiator and a colloidal stabilizer, as well as
suitable initiators and colloidal stabilizers, is well known to the person skilled in
the art. A particularly preferred colloidal stabilizer takes the form of partially
20 saponified - and optionally modified - polyvinyl alcohols having a degree of
hydrolysis of 80 to 98 mol.% and a Höppler viscosity as 4% aqueous solution of
1 to 50 mPa's at 20°C.

In another preferred embodiment, the process comprises a process step (i) and
25 a process step (ii), wherein in process step (i) the triester is mixed with a water-
soluble polymer in a solvent or solvent mixture and dried to form a powder i),
and wherein in process step (ii) the powder i) is mixed with a polymer powder
PP comprising a water-insoluble polymer. The preferred solvent is water and
the preferred solvent mixture is a mixture with water. The obtained powder i)
30 can be mixed with a polymer powder PP using conventional means well known
to the skilled person. The polymer powder PP is a water-redispersible polymer

powder with or without a coalescing agent which may be commercially available and comprises one or more water-insoluble powders.

In yet another embodiment, it is also possible to combine the powder i) with the water-redispersible polymer powder in any ratio, preferably of between 10 and 90 and 90 and 10 wt.% and based on the amount of triester in the powder i) to the water-insoluble polymer content of the water-redispersible polymer powder.

When the powder i) comprises anticaking agents and/or components ii), they can be added before, during and/or after the drying step using mixing techniques well known to the skilled person.

Drying can take place using conventional drying procedures. It may be advantageous to add up to 2 wt.% of an antifoaming agent, based on the water-insoluble polymer, before the drying.

Preferred drying means are spray drying, including pulse combustion spray drying, freeze drying, fluidized bed drying, drum drying or flash drying, in which case spray drying is particularly preferred and the spraying can take place for instance by means of a spraying wheel such as a rotating disc, one-component or multi-component nozzle. If necessary, the mixture to be dried can still be diluted with water, in order to achieve a suitable viscosity for the drying. The drying temperature in principle has no real limits. In particular because of safety-related considerations, however, it should not, as a rule, exceed about 200°C, in particular about 175°C. In order to attain sufficiently efficient drying, temperatures of the inlet air of about 110°C or higher, in particular of about 120°C or higher, are preferred. The exit temperature is generally chosen in the range from 45°C to 120°C, preferably from 60°C to 100°C.

The mean particle size of the polymer powder after drying in one embodiment amounts to at least about 10 µm or more, preferably about 30 µm or more, in particular about 50 µm or more. In addition, it is often useful when the mean particle size is at most about 2 mm or less, preferably about 1 mm or less, in

particular about 0.5 mm or less, and the polymer powder is easily pourable as well as block and storage stable. The particle size of the polymer powder particles is preferably measured by means of light scattering, in which case the volumetric mean is also decisive.

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The water-redispersible polymer powder may be used in dry mortars, powder adhesives, and wallpaper adhesives.

The dry mortar

10 The dry mortar according to the invention comprises a filler, the polymer powder of the invention, and, optionally, a mineral binder. In one preferred embodiment, the water-insoluble polymer of the polymer powder is a vinyl acetate homopolymer or an ethylene-vinyl acetate copolymer.

15 In another preferred embodiment, the dry mortar of the invention contains no or less than 5 wt.% of mineral binder, preferably less than 3 wt.%, with the mineral binder preferably being cement, gypsum, calcium oxide, calcium hydroxide and/or pozzolanic compounds. Within this embodiment, the polymer powder amounts typically range between 10 and 70 wt.%, preferably between 20 and
20 60 wt.%, in particular between 25 and 50 wt.%, based on the total amount of dry mortar. The dry mortar of this embodiment may further comprise 20 to 90 wt.%, preferably 30 to 80 wt.%, and in particular 40 to 75 wt.%, of mineral fillers and/or pigments, and further optional materials such as 0 to 10 wt.%, preferably 0.1 to 5 wt.%, of thickeners, 0 to 5 wt.% defoamers, in particular powder
25 defoamers, 0 to 2 wt.% wetting agents, 0 to 2 wt.% polysaccharide ether, e.g. cellulose ether and/or guar ether, 0 to 2 wt.% superplasticizer and/or 0 to 5 wt.% further adjuvants, wherein the ingredients add up to 100 wt.% of the total dry building material composition formulation. This type of dry mortar may also be considered to be a powder coating composition or a powder paint.

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In another preferred embodiment, the polymer powder of the invention is used in dry mortars which are based on one or more mineral binders. Mineral binders

are - in the meaning of the invention – understood to be binders which as a rule are in powder form and in particular consist of at least a) one hydraulically setting binder, b) one latent hydraulic binder and/or c) one non-hydraulic binder which reacts under the influence of air and water. Within this embodiment, the
5 polymer powder amounts typically range between 0.1 and 30 wt.%, preferably between 0.2 and 20 wt.%, in particular between 0.4 and 15 wt.%, based on the total amount of dry mortar.

The dry mortar of this embodiment may further comprise about 10 wt.% or more
10 of a mineral binder. When the mineral binder is cement, the amount of cement is about 10 to 60 wt.%, preferably about 12 to 50 wt.%, in particular about 15 to 45 wt.% of cement, based on the total amount of dry mortar. Furthermore, the dry mortar may further comprise 20 to about 90 wt.%, preferably 30 to 80 wt.%, and in particular 40 to 75 wt.%, of mineral fillers, and further optional materials
15 such as 0 to 10 wt.%, preferably 0.1 to 5 wt.%, of thickeners, 0 to 5 wt.% defoamers, in particular powder defoamers, 0 to 2 wt.% wetting agents, 0 to 2 wt.% polysaccharide ether, e.g. cellulose ether and/or guar ether, 0 to 2 wt.% superplasticizer and/or 0 to 5 wt.% further adjuvants, wherein the ingredients add up to 100 wt.% of the total dry building material composition formulation.

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When the mineral binder is gypsum, the amount of gypsum is about 30 to 99.9 wt.%, preferably about 40 to 99 wt.%, in particular about 45 to 98 wt.% of gypsum, based on the total amount of dry mortar. Furthermore, the dry mortar may further comprise 0 to about 60 wt.%, preferably 0-50 wt.%, and in particular
25 0 to 45 wt.%, of mineral fillers, and further optional materials such as 0 to 10 wt.%, preferably 0.1 to 5 wt.%, of thickeners, 0 to 5 wt.% defoamers, in particular powder defoamers, 0 to 2 wt.% wetting agents, 0 to 2 wt.% polysaccharide ether, e.g. cellulose ether and/or guar ether, 0 to 2 wt.% superplasticizer and/or 0 to 5 wt.% further adjuvants, wherein the ingredients
30 add up to 100 wt.% of the total dry building material composition formulation.

As hydraulically setting binders can be used cement, in particular Ordinary Portland Cement, for instance in accordance with EN 196 CEM I, II, III, IV, and V, high-alumina cement and/or gypsum, by which are meant in the meaning of this invention in particular calcium sulfate in the form of α - and/or β -semihydrate and/or anhydrite of form I, II and/or III. As latent hydraulic binders pozzolanes such as metakaolin, calcium metasilicate and/or volcanic slag, volcanic tuff, trass, fly ash, acid blast-furnace slag and/or silica dust can be used, which react hydraulically in combination with a calcium source such as calcium hydroxide and/or cement. As non-hydraulic binder can be used in particular lime, mostly in the form of calcium hydroxide and/or calcium oxide. Preferred above all are pure Portland cement-based construction material compounds, a mixture of Portland cement, high-alumina cement, and calcium sulfate, as well as gypsum-based building compositions, with it being possible in each case, if so desired, to also add latent hydraulic and/or non-hydraulic binders.

Suitable mineral fillers, also known under the term aggregates, include quartzitic and/or carbonatic sands and/or powders such as for instance quartz sand and/or limestone powder, carbonates, silicates, chalks, layered silicates, precipitated silicas, light-weight fillers such as for instance hollow microspheres of glass, aluminosilicates, silica, aluminium-silica, calcium-silicate hydrate, silicon dioxide, aluminium-silicate, magnesium-silicate, aluminium-silicate hydrate, calcium-aluminium-silicate, calcium-silicate hydrate, calcium-metasilicate, aluminium-iron-magnesium-silicate, clays such as bentonite and/or volcanic slag, as well as pozzolanes such as metakaolin and/or latently hydraulic components, in which case the fillers and/or light-weight fillers can also have a natural or artificially generated colour.

Dry mortars according to the inventions can be formulated as a coating or composite mortar used for thermal insulation (ETICS), sealing applications, flexible waterproofing membranes, plasters, renders, repair mortar, tile grouts, adhesive mortars, ceramic tile adhesive mortars (CTA), parquet adhesive and plywood adhesive mortars, primers, coatings for concrete and mineral-bonded

surfaces, self-leveling floor screeds, powder paints and/or smoothing and/or toweling compounds.

The dry mortar of the invention, when mixed with water, can be applied
5 basically on any substrate suitable to be covered with a mortar. Non-limiting examples of such substrates are concrete, self-leveling compounds, screeds, gypsum board, plasters, gypsum or cement-based putties, bricks, wood, cement fibreboards, ceramic tiles, expanded polystyrene and/or skim coats.

10 The powder adhesive or wallpaper adhesive

The powder adhesive and wallpaper adhesive according to the invention
comprise a polysaccharide and the RPP of the invention, wherein the
polysaccharide may be synthetically modified. In one preferred embodiment, the
water-insoluble polymer of the polymer powder is a vinyl acetate homopolymer
15 or an ethylene-vinyl acetate copolymer.

Preferred powder adhesives or wallpaper adhesives may comprise 1 to 75
wt.%, preferably 5 to 60 wt.%, in particular 10 to 50 wt.%, based on the total
amount of powder adhesives or wallpaper adhesives, of water-redispersible
20 polymer powder according to the invention. The remainder is made up by the
polysaccharide and, optionally, one or more water-soluble polymers which differ
from a polysaccharide in an amount of 0 to 30 wt.%, preferably 0 to 20 wt.%, in
particular 0 to 10 wt.%, one or more fillers in an amount of 0 to 60 wt.%,
preferably 0 to 40 wt.%, in particular 0 to 20 wt.%, as well as 0 to 10 wt.%,
25 preferably 0.1 to 5 wt.%, thickeners, in particular synthetic thickeners, 0 to 5
wt.% defoamers, in particular powder defoamers, 0 to 2 wt.% wetting agents
and/or 0 to 5 wt.% further adjuvants, wherein the ingredients add up to 100
wt.% of the total dry powder adhesive or wallpaper adhesive. The same types of
fillers may be used as for dry mortars.

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In one preferred embodiment, the polysaccharide is starch, starch ether,
dextrin, carboxymethyl cellulose, as well as cellulose ethers and/or guar ethers

modified with alkyl and/or hydroxyalkyl groups, wherein the alkyl groups are C₁- to C₂₀-alkyl groups, in particular C₁- to C₂-alkyl groups, and the hydroxyalkyl groups are C₂- to C₃-hydroxyalkyl groups, in particular ethoxy and/or propoxy groups.

5

The powder adhesive or wallpaper adhesive of the invention, when mixed with water, can be applied basically on any substrate suitable to be covered with the same or another substrate. Non-limiting examples of such substrates are concrete, self-leveling compounds, screeds, gypsum board, plasters, gypsum or
10 cement-based putties, bricks, wood, cement fibreboards, ceramic tiles, expanded polystyrene, skim coats, wallpaper, paper, cardboard, gypsum board and/or cured gypsum mortar.

The invention is further elucidated with reference to the following examples.
15 Unless indicated otherwise, the tests are carried out at a temperature of 23°C and a relative humidity of 50%.

Examples

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Example 1: Preparation of water-redispersible polymer powder P1
300 g, based on its solids content, of an aqueous vinyl acetate homopolymer dispersion stabilized with a partly hydrolyzed polyvinyl alcohol were mixed at room temperature with 17.6 g, based on its solids content, of a 25 wt.%
25 aqueous solution of polyvinyl alcohol having a degree of hydrolysis of 88 mol.-% and a Höppler viscosity as 4 wt.% solution of 4 mPas in a 1 l vessel, equipped with a propeller stirrer, with a stirring speed of 200 rpm. After a mixing time of 15 min, 11.8 wt.%, based on the solids content of the vinyl acetate dispersion, of triacetin (supplier: Eastman™), which has a water solubility in distilled water
30 at pH 7 and 20°C of 64 g/l, were slowly added while stirring. After further stirring for 15 min, the obtained mixture was diluted with water to a solids content of 25 wt.% and spray dried without further additives through conventional spray

drying with an inlet temperature of 125°C, to form a white, free-flowing powder with good yield, in which process no significant fouling occurred in the spraying tower. Finally, 0.5 wt.% of a commercially available silica and 9 wt.% of a commercially available carbonate, both amounts based on the final powder including the silica and carbonate, were added and mixed with the spray dried powder.

The obtained powder redisperses readily in water upon slight stirring. The redispersion upon drying at 23°C and 50% relative humidity forms a flexible and transparent film. The 50 wt.% aqueous redispersion has an MFFT of 0°C, determined in accordance with DIN 53787.

Example 2: Preparation of water-redispersible polymer powder P2

A) Preparation of water-redispersible polymer powder P2a:

To 100 g of a 20% aqueous polyvinyl alcohol solution with a degree of hydrolysis of 88 mol.-% and a Höppler viscosity as 4% solution of 4 mPas at 20°C in a 500 ml glass vessel with a propeller stirrer with a stirring speed of 200 rpm, were added slowly at room temperature 20 g of triacetin, which were allowed to emulsify completely. The obtained emulsion was subsequently dried without further additives by means of conventional spray drying at an initial temperature of 125°C to a white, free-flowing, and readily water-redispersible powder in good yield, in which process no significant fouling occurred in the spraying tower.

B) Preparation of water-redispersible polymer powder P2b:

Example 1 was repeated with 300 g, based on its solids content, aqueous vinyl acetate homopolymer dispersion and 15.8 g, based on its solids content, of a 25 wt.% aqueous solution of polyvinyl alcohol having a degree of hydrolysis of 88 mol.-% and a Höppler viscosity as 4 wt.% solution of 4 mPas at 20°C, with no triacetin and no further additions being added after spray drying .

C) Preparation of water-redispersible polymer powder P2:

20 g powder P2a, 90 g powder P2b, 11 g of a commercially available silica, and 0.6 g of a commercially available carbonate were homogeneously mixed together in a 500 ml vessel using a 60 mm propeller stirrer at a rate of 800 rpm, resulting in a white, free-flowing, and readily water-redispersible powder having
 5 an MFFT of 0°C, determined in accordance with DIN 53787. The obtained powder P2 performed the same as powder P1 in all tests.

Example 3 (Comparison): Preparation of powders C-P3 to C-P6

The procedure of Example 1 was repeated by making the variations as
 10 indicated in Table 1. The obtained powders were redispersed in water to obtain a 50 wt.% aqueous redispersion, with which the MFFT was measured, determined in accordance with DIN 53787, and a film of the obtained redispersion was made by applying a 1 mm thick redispersion layer onto a polyethylene foil and allowing it to dry for 1 day at 23°C and 50% relative
 15 humidity.

Table 1: Composition of powder P1 and comparison powders C-P3 to C-P6 as well as MFFT and film properties of a 50 wt.% aqueous redispersion.

20

Powder	Polymer Dispersion	Coalescing agent	MFFT ^{e)} [°C]	Film
P1	PVA ^{a)}	Triacetin	0	Flexible
P2	PVA ^{a)}	Triacetin	0	Flexible
C-P3	PVA ^{a)}	Dalpad C instead of triacetin	2	Flexible
C-P4	PVA ^{a)}	Texanol instead of triacetin	0	Flexible
C-P5	PVA ^{a)}	None ^{c)}	13	Brittle
C-P6	EVA ^{b)}	None ^{d)}	1	Flexible

a) The same vinyl acetate homopolymer dispersion (PVA) was used as in Example 1.

- b) EVA stands for an aqueous ethylene-vinyl acetate copolymer dispersion (EVA) with 10 wt% of ethylene and 90 wt.% vinyl acetate, based on the total amount of monomers employed, stabilized with a partly hydrolyzed polyvinyl alcohol.
- 5 c) The omitted amount of triacetin was replaced by the same amount of the vinyl acetate homopolymer dispersion (PVA), based on its solids content.
- d) The amount of ethylene-vinyl acetate copolymer dispersion (EVA) used, based on its solids content, is the same as for Example C-P5.
- 10 e) Measured with a 50 wt.% aqueous redispersion and determined in accordance with DIN 53787 and recorded in °C.

Example 4: Determination of the block resistance of the powders

The block resistance of the obtained powder was determined as follows:

50 ml of each of the powders P1 and C-P3 to C-P6, respectively, was placed

15 into a metal tube with a diameter of 3 cm, loaded with a weight of 1.4 kg, and placed in a drying cabinet at 50°C for 24 hrs. After cooling to room temperature, the powder was removed from the metal tube. Due to the harsh storing conditions, the powder blocked to form a cylinder. The block resistance of the powder was assessed by how easily the blocked powder cylinder can be

20 destroyed to form free-flowing powder again.

Table 2: Assessment of block resistance

Powder	Assessment of block resistance
P1	Only a slight pressure is required to form free-flowing powder again
C-P3	Medium pressure is required, some clumps remain
C-P4	Only a slight pressure is required to form free-flowing powder again
C-P5	Only a slight pressure is required to form free-flowing powder again
C-P6	Only a slight pressure is required to form free-flowing powder again

Example 5: Testing performance of water-redispersible powders in a cementitious mortar

A) Preparation of dry mortar master batch TM-1

5 kg of a cement-based dry mortar master batch TM-1 were prepared, consisting of 350 parts by weight of a commercially available Portland cement CEM I 52.5, 405 parts by weight of a quartz sand (0.1 - 0.3 mm), 225 parts by weight of a commercially available calcium carbonate (Durcal 65), and 5 parts by weight of a commercially available cellulose ether (methylhydroxyethyl cellulose), with a viscosity of 11,000-16,000 mPas (Brookfield RV viscosity measured at 20 rpm as a 2 wt.% solution in water at 20°C), in which process the components were mixed in a 10 l vessel with a FESTOOL RW1000 EQ stirrer until a homogeneous dry mortar master batch was obtained.

B) Preparation of the ready mortar mixture:

15 194 g of TM-1 and 6 g of the powder as indicated in Tables 3 to 5 were mixed together in a 500 ml vessel and mixed homogeneously using a 60 mm propeller stirrer at a rate of 800 rpm. Afterwards, 50 g of water were added slowly while stirring. Subsequently, the respective mixtures were stirred for 60 seconds. After a maturing time of 3 minutes the mortar was briefly stirred again by hand and applied. It is noted that all powders could be readily mixed with the other mortar constituents.

C) Assessment of the mortar workability:

The ready mortar mixture was applied with a spatula onto a cement fibreboard having a water absorption of lower than 20 wt.% to form a wedge. The mortar surface was visually evaluated as follows:

Table 3: Assessment of the mortar workability

Mortar with Powder No.	Assessment of the mortar workability
P1	Smooth – no open air pores
C-P3	Uneven – many open air pores
C-P4	Uneven – many open air pores
C-P5	Smooth – no open air pores
C-P6	Smooth – no open air pores

- 5 D) Determination of skin formation and open time of the mortar with stoneware tiles

The ready mortar mixture was applied according to European Standard EN 1348. A thin layer of the mortar was applied to a concrete slab substrate with a straight edge trowel, followed by a thicker layer of mortar combed with a
 10 notched trowel having 6 mm x 6 mm notches at 12 mm centres. The trowel should be held at an angle of approximately 60° to the substrate.

With intervals of 5 minutes, a stoneware tile (5 x 5 cm) was placed on the mortar and loaded with a weight of 1 kg for 30 seconds. 5 minutes after the last
 15 tile was placed on the mortar, all tiles were removed again and placed upside-down next to the concrete slab. The wettability of vitrified tiles was assessed visually by determining the surface area of the tiles covered by mortar.

Table 4: Determination of wettability of stoneware tiles laid into the mortar at intervals of 5 minutes

Powder	Surface covered by mortar (%) of tiles laid at different times						
	0 min	5 min	10 min	15 min	20 min	25 min	30 min
P1	95	55	45	25	20	10	5
C-P3	90	40	20	15	10	10	5
C-P4	98	50	30	25	20	10	0
C-P5	95	50	35	20	15	10	5
C-P6	95	45	30	15	5	2	0

5

E) Determination of adhesion strength with vitrified tiles, laid into the mortar 30 minutes after the ready mortar mixture has been applied.

10 The ready mortar mixture was applied according to European Standard EN 1348. A thin layer of the adhesive was applied to a concrete slab substrate with a straight edge trowel, followed by a thicker layer of adhesive combed with a notched trowel having 6 mm x 6 mm notches at 12 mm centres. The trowel should be held at an angle of approximately 60° to the substrate.

15 After 30 minutes 6 vitrified tiles (5 x 5 cm) were placed on the applied mortar and each tile was loaded with a weight of 2 kg for 30 seconds. The so prepared samples were stored for 28 days at standard conditions (23°C/50% r.h.) before testing the adhesion strength. One day before testing, pull-head plates were bonded to the tiles with a high-strength epoxy adhesive. The specimens were
20 subjected to a direct pull tensile force test in a tensile testing machine capable of applying the load to the pull-head plate at a rate of 250 +/- 50 N/s through a suitable fitting that does not exert any bending force.

The individual tensile adhesion strength was determined using the following formula:

$$A_s = L/A$$

With:

- 5 A_s : Individual tensile adhesion strength in newtons per square millimeter
 L: Total load in newtons
 A: Bonding area in square millimeters (the total bonding area per tile is 2,500 mm²)

- 10 Table 5: Determination of adhesion strength to the mortar of vitrified tiles laid into the mortar 30 minutes after application of the ready mortar mixture, and measured after 28 days stored at standard conditions (23°C and 50% relative humidity).

Powder	P1	C-P3	C-P4	C-P5	C-P6
Adhesion [N/mm ²]	0.39	0.29	0.25	0.47	0.34

15

- The Examples demonstrate impressively that when a triester according to the invention, i.e. a triester of glycerol with a C₁- to C₅-carboxylic acid and/or a triester of a C₁- to C₅-alcohol with a tricarboxylic acid, such as e.g. triacetin, is used as coalescing agent, a superior overall performance is obtained. This is in contrast with coalescing agents known for use in this industry. Comparison powder C-P5, containing the polyvinyl acetate homopolymers without any coalescing agent, forms a very brittle film due to its high MFFT of +13°C (Table 1). When Dalpad C is used instead of triacetin (comparison powder C-P3), the powder loses its block resistance and significantly reduces the mortar workability. The latter is also true for comparison powder C-P4 containing Texanol as coalescing agent (Tables 2 and 3). Furthermore, the adhesion strength of vitrified tiles laid in the mortar 30 minutes after its application (as described in Example 5 e)) is worsened when using the comparison powders C-P3 and C-P4, which contain another coalescing agent, as well as when using
- 20
- 25

the comparison powder C-P6, which is based on an ethylene-vinyl acetate copolymer dispersion (Table 5). Additionally, the wettability of stoneware tiles remains highest for tiles laid into the mortar at each interval when using the mortar containing the powder of the invention (P1). However, when using the
5 comparison powders, the wettability decreases faster, in particular when using the powder C-P6, which is based on an ethylene-vinyl acetate copolymer dispersion.

It is noted that there are no limitations to the present invention. Thus, all
10 dispersions suitable for making water-redispersible polymer powders by spray drying can be used. Therefore, it is also possible to add a triester of glycerol or tricarboxylic acid to copolymers, e.g. to ethylene-vinyl acetate copolymers or (meth)acrylate copolymers. Additionally, water-redispersible polymer powders according to the invention can also be obtained by blending a dispersion
15 containing such a triester with a dispersion without triester or even without any coalescing agent.

Claims

1. Water-redispersible polymer powder comprising
 - a) one or more water-insoluble polymers, and
 - b) one or more triesters, wherein the triesters are selected from triester of glycerol with one or more C₁- to C₅-carboxylic acids and triesters of one or more C₁- to C₅-alcohols with one or more tricarboxylic acids.
2. Powder of claim 1, wherein the water-insoluble polymer is obtained by emulsion polymerizing one or more olefinically unsaturated monomers selected from the group of vinyl esters, (meth)acrylic esters, vinyl aromatic compounds, vinyl halides, and olefins in the presence of an initiator and a colloidal stabilizer.
3. Powder of claim 1 or 2, wherein the water-insoluble polymer is a homopolymer of vinyl acetate or a copolymer of ethylene and vinyl acetate having an ethylene content of up to 25 wt.%, based on the water-insoluble polymer.
4. Powder of any one of claims 1 to 3, wherein the triesters comprise or consist of one or more triesters of glycerol with one or more C₁- to C₃-carboxylic acids, preferably selected from the group of glycerol triformate, glycerol triacetate, and glycerol tripropionate.
5. Powder of any one of claims 1 to 3, wherein the triesters comprise or consist of one or more triesters of one or more C₁- to C₃-alcohols with one or more tricarboxylic acids, wherein the tricarboxylic acids are selected from the group of citric acid, iso-citric acid, aconitic acid, propane-1,2,3-tricarboxylic acid, and trimesic acid, and where the C₁- to C₃-alcohol preferably is selected from methanol, ethanol, and propanol.

6. Powder of any one of claims 1 to 5, wherein the sum of the weight of the triesters present in the water-redispersible polymer powder is from 1 wt.% to 50 wt.%, based on the total amount of water-redispersible polymer powder.
- 5 7. Powder of any one of claims 1 to 6, wherein the water-redispersible polymer powder comprises
- a) 30 to 99 wt.% of one or more water-insoluble polymers,
 - b) 1 to 50 wt. % of one or more triesters,
 - 10 c) 0 to 50 wt.% of one or more water-soluble polymers,
 - d) 0 to 30 wt.% of one or more anticaking agents, and
 - e) 0 to 25 wt.% of one or more components ii), wherein the component ii) is selected from the group of hydrophobic and/or oleophobic additives, rheology control additives, thickeners, polysaccharides and derivatives thereof, additives to control the hydration and/or setting of mineral binders, surface-active additives, pigments, fibres, corrosion protection additives, pH-adjusting additives, additives for the reduction of shrinkage and/or efflorescence,
 - 15
- 20 wherein the sum of the components adds up to 100 wt.%.
8. Process to make the powder of any one of claims 1 to 7, comprising the steps of (i) emulsion polymerizing one or more olefinically unsaturated monomers in the presence of an initiator and a colloidal stabilizer, (ii) adding the one or more triesters, and thereafter (iii) drying the mixture obtained.
- 25
9. Process to make the powder of any one of claims 1 to 7, comprising a process step (i) and a process step (ii), wherein in process step (i) the one or more triesters are mixed in water with one or more water-soluble polymers and dried to form a powder i), and wherein in process step (ii)
- 30

the powder i) is mixed with a polymer powder PP comprising one or more water-insoluble polymers.

- 5
10. Powder i) obtainable according to the process step (i) of claim 9.
11. Use of a powder of any one of claims 1 to 7 in powder adhesives, wallpaper adhesives or dry mortars.
12. Dry mortar comprising a filler, a powder of any one of claims 1 to 7, and, optionally, a mineral binder, wherein the powder amounts to 0.1 to 70 wt.%, based on the total amount of dry mortar.
- 10
13. Powder adhesive or wallpaper adhesive comprising a polysaccharide and a powder of any one of claims 1 to 7, wherein the powder amounts to 1 to 75 wt.%, based on the total amount of powder adhesives or wallpaper adhesives.
- 15
14. Process to make the dry mortar of claim 12, wherein
- a) the powder obtained according to claim 8 or 9 is mixed with the filler and the optional mineral binder, or
- 20
- b) the powder i) of claim 10 is mixed with the filler, the polymer powder PP, and the optional mineral binder.
15. Process to make the powder adhesive or wallpaper adhesive of claim 13, wherein
- 25
- a) the powder obtained according to claim 8 or 9 is mixed with the polysaccharide, or
- b) the powder i) of claim 10 is mixed with the polysaccharide and the polymer powder PP.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/071908

A. CLASSIFICATION OF SUBJECT MATTER INV. C08K5/103 C08J3/05 C09J123/08 C09J131/04 C04B24/26 C04B40/00 C04B20/10 C08L23/08 ADD. C04B103/00 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C08J C08K C09J C04B C08L Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EP0-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/240817 A1 (JOSHI MAKARAND [US] ET AL) 23 September 2010 (2010-09-23) paragraph [0003] paragraph [0016] examples 1,2 claims -----	1-15
X	WO 2008/054277 A1 (PERSTORP SPECIALTY CHEM AB [SE]; JANSSON ROBERT CHRISTIAN [FI]; BJOERN) 8 May 2008 (2008-05-08) page 2 - page 3, line 4 examples 1-3,6,7,9-12,14,15,17-19,21-23 claims -----	1-15
X	US 2004/048961 A1 (KLEIN HEINZ-PETER [DE] ET AL) 11 March 2004 (2004-03-11) example 6 ----- -/--	1-15
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 2 January 2014		Date of mailing of the international search report 10/01/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Russell, Graham

INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004/019141 A1 (BASTELBERGER THOMAS [DE] ET AL) 29 January 2004 (2004-01-29) examples 1b,2b -----	1-15

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/071908

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2010240817 A1	23-09-2010	CA 2753907 A1 CN 102356125 A EP 2408855 A1 JP 2012520928 A KR 20110129476 A US 2010240817 A1 WO 2010107583 A1	23-09-2010 15-02-2012 25-01-2012 10-09-2012 01-12-2011 23-09-2010 23-09-2010
WO 2008054277 A1	08-05-2008	EP 2064295 A1 SE 0601914 A WO 2008054277 A1	03-06-2009 19-03-2008 08-05-2008
US 2004048961 A1	11-03-2004	CN 1487016 A DE 10239441 A1 EP 1394193 A1 JP 2004083912 A US 2004048961 A1	07-04-2004 11-03-2004 03-03-2004 18-03-2004 11-03-2004
US 2004019141 A1	29-01-2004	AT 264882 T CN 1477148 A DK 1394198 T3 EP 1394198 A1 ES 2220901 T3 TR 200401783 T4 US 2004019141 A1	15-05-2004 25-02-2004 02-08-2004 03-03-2004 16-12-2004 21-10-2004 29-01-2004