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(54) Title: ADDITIVE COMPOSITION FOR MORTARS, CEMENTS AND JOINT COMPOUNDS AND CEMENTITIOUS COMPOSITIONS MADE THEREFROM

(57) Abstract: An additive composition for mortars, exterior insulation finish systems, self-leveling compounds and joint compounds is disclosed. The additive composition contains a nitrogen-containing polymer and a reactive agent capable of forming a crosslinking reaction with the nitrogen-containing polymer. Small amounts of the additive composition contained in a product cannot only increase one or more properties of the product but can also minimize the use of redispersible polymers in the product.



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ADDITIVE COMPOSITION FOR MORTARS, CEMENTS
AND JOINT COMPOUNDS AND CEMENTITIOUS
COMPOSITIONS MADE THEREFROM

5 Claim for Priority

 This application is based upon United States Provisional Patent Application Serial No. 60/991,492, filed November 30, 2007, of the same title, the priority of which is hereby claimed and the disclosure of which is incorporated herein by reference.

10

Background

 Cementitious materials can include various different types of cements, compounds, mortars, joint compounds, construction adhesives, and the like. These products typically contain a binder and a filler. The
15 binder may comprise, for instance, a cement such as Portland cement or gypsum. The filler, on the other hand, may comprise a quartz sand or calcium carbonate.

 In addition to a binder and a filler, the compositions can also contain
20 various other additives. For instance, cellulose derivatives and other materials have been added to the cementitious compositions. The cellulose derivatives are added in order to improve the workability of the composition, to increase the water-retention properties of the composition, and to increase the adhesiveness and the resistance to sliding. Increasing
25 water retention, for instance, can prevent the composition from losing water prior to setting on highly absorbent substrates and allows for control of the open time and adjusting time. If the composition sets too quickly, the resulting composite may not develop the mechanical adhesion strength required to keep a tile adhesive attached on the adjacent surface
30 as well as to prevent cracks, for example. Workability is also improved due to the lubricant properties of the cellulose ethers. Cellulose

derivatives may be used with or without a polyvinyl alcohol resin in cementitious tile adhesive compositions; see Great Britain 1,490,783 of Griffith *et al.* and Great Britain 1,225,755 of Vaughn *et al.*, the disclosures of which are incorporated herein by reference. Latex and other resinous additives for cementitious compositions are also seen in the following references: European Patent Application Publication 0 649 823 which discloses the use of polyvinyl alcohol and polyvinyl acetate; United States Patent No. 7,294,194 to Reddy *et al.* which discloses various latexes for preserving elasticity; and United States Patent Application Publication No. 2001/0018881 of Futami *et al.* which advocates the use of melamine and sulfonic acid/formaldehyde condensates, naphthalene sulfonic acid condensates and amide resins in cement.

Synthetic polymer additives for mortars are frequently supplied as redispersible powders or emulsions. The redispersible polymer may comprise, for instance, an emulsion made out of polyvinyl acetate homopolymer and copolymers stabilized with polyvinyl alcohol. The redispersible polymer may improve workability, sag resistance, flexibility and tension strength under standard conditions, but also after water immersion, heat aging and freeze-thaw cycles and so forth. Exemplary redispersible powders are described in European Patent Application Publication No. 1 158 007 of Hara *et al.* and European Patent Application Publication No. 0 873 978 of Hornamen *et al.*, both of which relate to polyvinyl alcohol (PVOH) stabilized latexes. The disclosures of EP 1 158 007 and EP 0 8873 9788 are incorporated herein by reference.

Although the incorporation of cellulose derivatives, redispersible polymers and other additives has provided many advances in the art, some deficiencies still remain. For example, cellulose ethers when present in the composition can cause a considerable delay in cement

setting. Redispersible polymers, on the other hand, can be relatively expensive, thus adding cost to the final product.

In view of the above, a need currently exists for additives that can
5 further improve the properties of a cementitious composition. In particular,
a need exists for additives that can be used to control the wet properties
and the mechanical properties of a cementitious composition containing
the additives. A need also exists for additives that can reduce or eliminate
the amount of redispersible polymers in a cementitious composition
10 without adversely affecting the properties of the composition. This need is
based on both the high cost of redispersible powders, and the fact that
high levels of redispersible powders can cause an imbalance in a
cementitious composition. For example, redispersible powders can help
impart flexibility; however they typically can hinder properties like water
15 resistance.

Summary of Invention

In general, the present invention is directed to an additive
composition for cementitious compositions and to cementitious
20 compositions made therefrom. Cementitious compositions may include,
for instance, a mortar, a cement, a joint compound, exterior insulation
finishing systems, self leveling systems and the like. Specific applications
include: tile adhesives (bathroom & kitchen floor, countertop and wall);
exterior insulation finishing systems (EIFS) (adhesive system for exterior
25 wall insulation); self-leveling compounds (mortars that are poured onto a
floor for leveling and tile or carpet sub-surface); coatings; concrete repair;
façade coatings; grouts; gypsum applications; joint fillers; mineral plasters;
patch and repair mortars; rendering plaster; powder paints; sealing
slurries; thin bed mortars; and troweling compounds. In one embodiment,
30 the cementitious composition can be packaged in a dry form. In this
embodiment, water can be added prior to use.

In one embodiment, the additive composition of the present invention comprises a nitrogen-containing polymer and a reactive agent capable of forming a cross-linking reaction with the nitrogen-containing polymer. The additive composition may, optionally, contain one or more additional ingredients such as, for instance a cellulose derivative and a polyvinyl alcohol polymer. According to one embodiment, the nitrogen-containing polymer may be a copolymer of a vinyl alcohol and a vinyl amine. The reactive agent, in addition to being capable of forming a crosslinking reaction with the nitrogen-containing polymer, can for instance, also be capable of forming a crosslinking reaction with the cellulose derivative, and/or the polyvinyl alcohol. In another embodiment, for instance, the reactive agent may comprise a glyoxal, borax, or maleic anhydride copolymer, materials that are believed to form a crosslinking reaction with the nitrogen-containing polymer and, optionally, with the cellulose derivative and/or the polyvinyl alcohol. Other crosslinking agents that may be used include gluteraldehyde, succinic dialdehyde, blocked glyoxal (12% glyoxal, 33% dipropylene glycol, and water), cationic amine polymer-epichlorohydrin, polyamide epichlorohydrin, potassium zirconium carbonate, ammonium zirconium carbonate, ketone formaldehyde, styrene maleic anhydride copolymer, cyclic amide condensate, and the like.

The nitrogen-containing polymer is further described as a polymer containing primary or secondary nitrogen functional groups, such as amines, imines, amides, and the like. For instance, in various embodiments, the nitrogen-containing polymer comprises polyvinylalcohol-co-vinylamine, polyvinylalcohol-co-vinylformamide, polyvinylamine, polyvinylformamide, polyethyleneamine, polyethyleneimine, polyacrylamide, or mixtures thereof. Suitable nitrogenous polymers may thus include any one or a combination of the following nitrogen functionalities: primary amino ($--NH_2$) groups; mono-substituted

(secondary) amino groups --NHR where R is hydrocarbyl, generally either alkyl or aryl, e.g., lower alkyl or phenyl, for example, methylamino, ethylamino, isopropylamino, butylamino, cyclopropylamino, cyclohexylamino, n-hexylamino, phenylamino, benzylamino, 5 chloroethylamino, hydroxyethylamino, etc.); amides --(CO)—NR¹ R² where R¹ and R² may be the same or different and are either hydrogen or R, wherein R is as defined above (including, for example, amides wherein one of R¹ or R² is H and the other is methyl, butyl, benzyl, etc.); imines and so forth. Typical nitrogen-containing polymers may be prepared using 10 one or more of the following classes of monomers: vinylamines; vinylformamides; ethyleneamines; ethyleneimines; acrylamides; methacrylamides; acrylates and methacrylates substituted with a primary or secondary amino group optionally bound through a lower alkylene linker (e.g., aminoethyl methacrylate); caprolactams and so forth. The 15 foregoing list is intended to be illustrative and not limiting with regard to possible nitrogen-containing monomers that can be used in the preparation of suitable nitrogen-containing polymers for use with the inventive additive compositions.

20 The derivatized cellulose that may be contained within the additive composition can be any suitable cellulose ether. For instance, in one embodiment, the derivatized cellulose comprises methyl cellulose, hydroxypropyl methyl cellulose, hydroxyethyl methyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, ethyl hydroxyethyl 25 cellulose, hydroxypropyl cellulose, ethyl cellulose, or mixtures thereof.

As mentioned, the nitrogen-containing polymer may, according to an embodiment be a vinyl alcohol and vinyl amine copolymer which, if present can contain from about 2 to about 30 mole percent vinyl amine 30 functionality. For instance, the vinyl alcohol and vinyl amine copolymer may contain from about 2 mole percent to about 12 mole percent vinyl

amine. The weight ratio of nitrogen-containing polymer presenting the cementitious composition can vary depending upon the particular application and the desired result. In one embodiment, for instance, the percent addition of the nitrogen-containing polymer in the cementitious composition can be from about 0.01% to about 5%, or more preferably 0.1% to 2%.

In one embodiment, the reactive agent, such as a glyoxal, can be pre-reacted with a cellulose derivative, polyvinyl alcohol, or an inorganic compound such as clays, calcium carbonates, calcium oxides, and the like. This effectively creates a carrier system for the reactive agent that would allow for easy incorporation of both wet and dry reactive agents with the nitrogen-containing polymer and the other components of the cementitious composition, if present. The weight ratio of the reactive agent to the carrier, if present, can be from about 0.001:1 to about 0.5:1, or more preferably 0.01:1 to about 0.1:1.

In another preferred aspect of the invention, the reactive agent is pre-reacted with a carrier such as cellulose in a reversible reaction. These components can be prepared or purchased, e.g., FQ grades of BERMOCOLL™ resins available from Akzo Nobel as is discussed hereinafter.

The additive composition can be incorporated into numerous construction adhesives. In one embodiment, for instance, the additive composition can be contained in a dry cementitious composition. The cementitious composition in addition to the additive composition can contain a binder and a filler. The binder, for instance, may comprise cement, gypsum, or mixtures thereof. The filler, on the other hand, may comprise calcium carbonate particles, quartz sand, or mixtures thereof.

In one particular embodiment, the cementitious composition contains the binder in an amount from about 20 parts to about 60 parts by weight and the filler in an amount from about 40 parts to about 80 parts by weight. The nitrogen-containing polymer can be present in the
5 composition in an amount from about 0.01 parts to about 5 parts by weight, preferably from about 0.01 parts to about 2 parts by weight. According to those embodiments where a cellulose derivative is present, it may be present in the cementitious composition in an amount from about 0.01 parts to about 3 parts by weight, preferably from about 0.1 to about 1
10 part by weight.

In one particular embodiment, the cementitious composition can further contain a redispersible polymer powder. The redispersible polymer powder may comprise, for instance, polyvinyl acetate homopolymer and
15 copolymers, with or without an olefin such as ethylene that are dispersible in water. The powder may be stabilized with the nitrogen-containing polymer alone or in combination with polyvinyl alcohol polymer. The redispersible polymer powder can be present in the composition in an amount from 0 to about 16 parts by weight. In one embodiment, for
20 instance, the redispersible polymer powder is present in an amount less than about 2 parts by weight.

In addition to a redispersible polymer, various other additives and ingredients can be contained in the cementitious composition. For
25 instance, in one embodiment, the cementitious composition optionally may contain additives, such as lubricants, hydrophobic agents, fillers, pigments, setting accelerators, retardants or mixtures thereof. For example, suitable modifiers may include sodium stearate silicones, siloxanes and so forth.

30 In an alternative embodiment, the nitrogen-containing polymer may be incorporated into a redispersible polymer powder that is then added to

the cementitious composition optionally in conjunction with the derivatized cellulose and crosslinking agent. In this embodiment, for instance, the redispersible polymer may comprise a powder as described above. The powder, for instance, may include a copolymer of vinyl acetate and a
5 comonomer. The comonomer, for instance, may comprise an olefin, a vinyl ester of a carboxylic acid, vinyl chloride, styrene, or mixtures thereof. Suitable olefins that may be used include, for instance, ethylene or propylene. Vinyl esters of carboxylic acids, on the other hand, may comprise vinyl esters of alpha-branched monocarboxylic acids such as a
10 vinyl ester of versatic acid. Versatic acid is a branched carboxylic acid having ten carbon atoms. The above copolymer if present can be combined with the nitrogen-containing polymer.

In one embodiment, for instance, the redispersible polymer powder
15 containing the polyvinyl alcohol polymer may contain a vinyl acetate and a comonomer in a weight ratio of from about 60:40 to about 90:10, such as at a weight ratio of about 80:20. The polyvinyl alcohol polymer, optionally in conjunction with the nitrogen-containing polymer, may be combined with the above copolymer in order to stabilize the powder when formed into an
20 emulsion. The redispersible polymer powder may contain, in one embodiment, the polyvinyl alcohol polymer particles and/or the nitrogen-containing polymer particles in an amount from about 4% to about 18% by weight, such as in an amount of about 8% to about 12% by weight, based upon the total weight of the monomers present used to form
25 the copolymer. In addition to the vinyl acetate copolymer, the polyvinyl alcohol polymer and the nitrogen-containing polymer, the redispersible polymer may further include a defoamer, an initiator, one or more surfactants, a buffer, and any other suitable additives.

30 In one embodiment, for instance, the redispersible polymer powder may be incorporated into the cementitious composition in an amount from

about 0.5 parts to about 16 parts by weight, such as from about 1 part to about 6 parts by weight.

Other features and aspects of the present disclosure are discussed
5 in greater detail below.

Detailed Description

The invention is described in detail below with reference to numerous embodiments and examples. Such discussion is for purposes
10 of illustration only. Modifications to particular examples within the spirit and scope of the present invention, set forth in the appended claims, will be readily apparent to one of skill in the art.

Terminology used herein is given its ordinary meaning consistent
15 with the usage of such terms in the chemical and polymer arts. Unless otherwise specified, the version of a test method applied is that in effect as of January 1, 2008. %, percent, and so forth refers to percent by weight on a dry basis unless the usage or context clearly indicates otherwise. "Dry" means substantially dry, but not excluding that amount of residual
20 moisture which is bound to or sorbed by the material at equilibrium with its ordinary surroundings.

When we refer to a molar equivalent ratio of the reactive moieties of the reactive agent to nitrogen in a nitrogen-containing polymer, we are
25 referring to the use of a pair of reactive moieties capable of crosslinking. For example, 1 mol of glyoxal per mol of nitrogen is a 1:1 ratio. Likewise, for example, a 1:1 molar equivalent ratio refers to 1 mole of maleic anhydride units in a styrene maleic anhydride copolymer to 1 mole of nitrogen in the nitrogen-containing polymer in the composition. Zirconium
30 is in a 1:1 molar equivalent ratio with the nitrogen in the

nitrogen-containing polymer as a reactive agent when present in equimolar amounts and so forth.

“PPHC” refers to parts per hundred weight of inorganic binder and
5 filler in a cementitious composition on a dry basis. For example, in a
composition containing 60 parts sand, 40 parts Portland Cement and 10
parts polymer additive and water, the composition has 60 PPHC sand, 40
PPHC binder and 10 PPHC polymer irrespective of the amount of water
added.

10

In general, the present disclosure is directed to an additive
composition that is well suited for use in cementitious compositions. For
example, the additive composition can be included in various products
including a mortar, a cement, a joint compound, and the like.
15 Cementitious compositions made in accordance with the present
disclosure generally contain a binder and a filler. The binder may
comprise, for instance, a cement, such as Portland cement, and/or
gypsum. These products can be packaged in dry form. When packaged
in dry form, the cementitious composition may then be combined with
20 water and mixed to form a slurry or paste. The wetted material is then
applied to a desired area where it hardens over time. The additive
composition of the present disclosure can be added to the cementitious
composition to provide one or more benefits and advantages.

25 The additive composition, for instance, has been found, in some
applications, to improve one or more properties of the cementitious
composition. The additive composition has also been found, in certain
embodiments, to improve the properties of the resulting cement or mortar
product, such as slip and water resistance in tile adhesive. As will be
30 described in greater detail below, use of the additive composition in a
cementitious composition can, in one particular embodiment, also

minimize the amount of redispersible polymers contained in the composition without adversely impacting upon the properties of the resulting product.

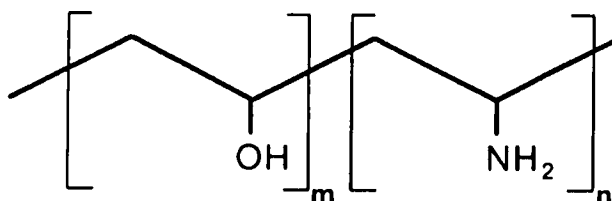
5 In general, the additive composition of the present disclosure comprises: a nitrogen-containing polymer and a reactive agent capable of forming a cross-linking reaction with the nitrogen-containing polymer. In one embodiment the nitrogen-containing polymer may be a vinyl alcohol and vinyl amine copolymer. A reactive agent is selected that forms a
10 crosslinking reaction with at least the nitrogen-containing polymer. In one particular embodiment, for instance, the reactive agent may be configured to form a crosslinking reaction with two or more of the other optional components contained in the additive composition. The
nitrogen-containing polymer can be incorporated into a cementitious
15 composition in accordance with the present disclosure either directly or, alternatively, may be used to form a redispersible polymer that is then added to the cementitious composition.

Cellulose derivatives that may optionally be included in the additive
20 composition of the present disclosure include any suitable cellulose ether. Cellulose ethers have been added to construction materials in the past in order to increase the water retention capacity of the product, to increase the stability of the product under load, to improve the working properties of the product prior to hardening, and/or to improve the mechanical adhesion
25 properties of the product.

Cellulose ethers that may be used according to the present disclosure include methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose, ethyl hydroxyethyl cellulose,
30 hydroxypropyl cellulose, ethyl cellulose, hydroxypropyl methyl cellulose, hydroxyethyl methyl cellulose and mixtures thereof. In one particular

embodiment, for instance, the cellulose ethers present within the additive composition include hydroxyethyl methyl cellulose, hydroxypropyl methyl cellulose, or mixtures thereof.

5 As described above, the nitrogen-containing polymer provided in the additive composition may be a vinyl alcohol and vinyl amine copolymer. Processes for producing vinyl alcohol and vinyl amine copolymers are disclosed, for instance, in United States Patent No. 5,300,566, which is incorporated herein by reference. Vinyl alcohol and
10 vinyl amine copolymers, for instance, can be formed by copolymerizing vinyl acetate and an N-vinyl formamide to yield a poly(vinyl acetate)-co-poly(N-vinyl formamide) which is thereafter hydrolyzed to form the copolymer. The vinyl alcohol and vinyl amine copolymer can be described as having the following structure:



15

wherein m is from about 0.80 to about 0.98 and n is from about 0.02 to about 0.30.

As shown above, the vinyl alcohol and vinyl amine copolymer
20 generally contains from about 1 mole percent to about 30 mole percent vinyl amine functionality. For example, the vinyl alcohol and vinyl amine copolymer can contain vinyl amine in an amount from about 2 mole percent to about 30 mole percent, such as from about 2 mole percent to about 12 mole percent. Vinyl alcohol and vinyl amine copolymers
25 particularly well suited for use in the present disclosure can be obtained commercially from the Celanese Corporation of Dallas, Texas. Such

copolymers are commercially sold, for instance, under the trade name CELVOL.

The various polymeric ingredients are of suitable molecular weight. Generally, polyvinyl alcohols, polyvinyl amines, and so forth useful in connection with the invention have molecular weights (number average) in the range of from 5,000 - 200,000 or so. For example, a suitable vinyl amine nitrogen-containing polymer may have a number average molecular weight of from 35,000 - 40,000 Daltons/mol corresponding to a weight average molecular weight of 55,000 - 75,000 Daltons/mol or so. Cellulose derivatives typically have higher molecular weights; generally having molecular weights (number average) in excess of 100,000 Daltons/mol as is known in the art.

The addition of a nitrogen-containing polymer, which according to one embodiment may be a vinyl alcohol and vinyl amine copolymer into a cementitious composition can provide various advantages and benefits. For example, vinyl alcohol and vinyl amine containing copolymers have enhanced cold water solubility, can improve the open time, adjustability, tensile and shear adhesion strength and compressive strength, of a resulting composition, and can be used to better control setting times for the cement or mortar product, especially when combined with a reactive agent that is capable of forming a crosslinking reaction with the nitrogen-containing polymer and other optional ingredients such as a cellulose derivative.

The reactive agent present within the additive composition can be any suitable reactive agent capable of crosslinking with the nitrogen-containing polymer. In one particular embodiment, for instance, the reactive agent may comprise a dialdehyde, such as a glyoxal or gluteraldehyde. A glyoxal or gluteraldehyde reactive agent, for example, is

capable of reacting with the nitrogen-containing polymer and, optionally with the cellulose derivatives if present. A glyoxal when reacted with a nitrogen-containing polymer may form, for instance, an imine. In addition to a glyoxal or gluteraldehyde, various other reactive agents may be used.

5 For instance, other reactive agents that may be incorporated into the formulation include borax, succinic dialdehyde, blocked glyoxal (12% glyoxal, 33% dipropylene glycol, and water), cationic amine polymer-epichlorohydrin, polyamide epichlorohydrin, potassium zirconium carbonate, ammonium zirconium carbonate, ketone formaldehyde,

10 styrene maleic anhydride copolymer, cyclic amide condensate, and the like.

When contained in a cementitious composition, the components of the additive composition of the present disclosure may be added separately to the cementitious composition or can be first blended together

15 and then added. In one embodiment, the reactive agent can be pre-reacted with a carrier prior to being incorporated into the cementitious composition. The carrier can consist of a cellulose ether, polyvinyl alcohol, starch, polyacrylamide, or other water soluble organic compound. Furthermore, the carrier can also be inorganic in nature, specifically a clay,

20 calcium carbonate, calcium oxide, and the like. The amount of reactive agent contained within the additive composition can depend upon various factors and the desired result. In those embodiments where the carrier is present, the weight ratio of the carrier to the nitrogen-containing polymer can also vary depending upon the particular application. In one particular

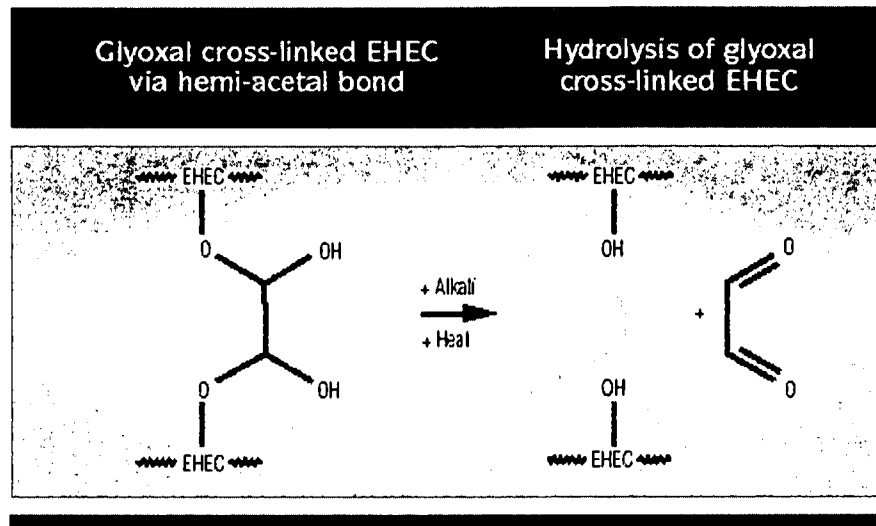
25 embodiment, for instance, the weight ratio of the nitrogen-containing polymer to the carrier can be from about 1:5 to about 5:1. For instance, the weight ratio of the nitrogen-containing polymer to the cellulose derivative can be from about 1:4 to about 4:1. In those embodiments where the additive additionally contains the cellulose derivative and the polyvinyl

30 alcohol polymer the weight ratio of the cellulose derivative to the polyvinyl alcohol polymer can also vary. In one particular embodiment, for instance,

the weight ratio of the polyvinyl alcohol polymer to the cellulose derivative can be from about 1:5 to about 5:1. For instance, the weight ratio of the polyvinyl alcohol polymer to the cellulose derivative can be from about 1:4 to about 4:1.

5

In one preferred aspect of the invention, the reactive agent is pre-reacted with a carrier such as cellulose in a reversible reaction. These components can be prepared or purchased, e.g., FQ grades of BERMOCOLL™ resins available from Akzo Nobel. The FQ grades of
10 BERMOCOLL™ cellulose ethers are powders with delayed hydration which provide exceptional handling flexibility and control of solubilization rate. This delay of hydration has been achieved by reaction with glyoxal during production. In the chemical reaction, the polymer chains of the cellulose ether become linked to the bifunctional aldehyde glyoxal, forming
15 a hemi-acetal. Cellulose ethers, crosslinked in this manner, lose their capability to hydrate but they are readily wetted out by cold water and will disperse uniformly without lumping, and with minimal agitation. In the acid pH range, and low temperature of the water, hemi-acetals are relatively stable. At higher pH values and temperatures seen in cement
20 applications, the crosslinkers are broken and the cellulose ethers dissolve spontaneously, releasing the glyoxal as a reactive agent.



In those embodiments where the additive additionally contains the cellulose derivative and the polyvinyl alcohol polymer the weight ratio of the cellulose derivative to the polyvinyl alcohol polymer can also vary. In one particular embodiment, for instance, the weight ratio of the polyvinyl alcohol polymer to the cellulose derivative can be from about 1:5 to about 5:1. For instance, the weight ratio of the polyvinyl alcohol polymer to the cellulose derivative can be from about 1:4 to about 4:1.

10

When incorporated into a mortar or cement product, the amount of the additive composition present in the product can vary. In general, however, very small amounts of the additive composition can produce the intended benefits and advantages. For instance, in general, the additive composition can be present in a cementitious composition in an amount less than about 5% by weight, such as less than about 3% by weight, such as even less than about 1% by weight, based upon the weight of the solids present.

15

The additive composition of the present invention can be incorporated into numerous different types of adhesive and construction

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products. Products that can be formulated with the additive composition include mortars, cements and joint compounds. Particular products, for instance, that can be made with the additive composition include tile adhesives, exterior insulation and finishing system adhesives, troweling
5 compositions, leveling compounds, grouts, reinforcing mortars for exterior insulation and finishing systems, wood flooring adhesives, cementing compositions useful in cementing oil, gas and water wells, patching mortars, joint fillers, plasters, and the like.

10 In one embodiment, for instance, the additive composition of the present invention may be incorporated into a cementitious composition containing a binder and a filler. The binder may comprise, for instance, any suitable cement, such as Portland cement, gypsum, an aluminate, or mixtures thereof. The binder can be present in the cementitious
15 composition in an amount from about 5% to about 80% by weight, such as from about 20% to about 50% by weight. When describing the cementitious composition, the above percentages by weight are based upon the weight percentage of dry material and thus exclude water if present in the product.

20 In general, the cementitious composition may contain any suitable filler. Fillers that may be used include, for instance, quartz sand, calcium carbonate such as limestone, talc, dolomite, aluminum silicates, mica, pumice, perlites, vermiculites, and mixtures thereof. Fillers can be present
25 in the cementitious composition in an amount from about 10% to about 90% by weight, such as from about 40% to about 90% by weight, such as from about 60% to about 80% by weight.

As described above, the additive composition of the present
30 invention may be present in the cementitious composition in relatively small amounts. The nitrogen-containing polymer may be present in the

cementitious composition in an amount from about 0.01% to about 5% by weight, such as from about 0.1% to about 1% by weight. The nitrogen-containing polymer may be added to the cementitious composition either directly or in conjunction with the redispersible polymer powder as will be described in greater detail below. In one particular embodiment, for instance, the cellulose derivative may be present in the composition in an amount from about 0.1% to about 3% by weight, such as from about 0.3% to about 0.5% by weight. In yet another embodiment, the polyvinyl alcohol polymer may be present in the cementitious composition in an amount from about 0.05% to about 5% by weight, such as from about 0.05% to about 2% by weight. The polyvinyl alcohol polymer may also be added into the cementitious composition either directly and/or in conjunction with the redispersible polymer powder.

In addition to the above ingredients, the cementitious composition may contain various other components. For instance, in one embodiment, the cementitious composition may contain a water redispersible polymer powder. Redispersible polymer powders are polymer powders which break down in water into primary particles, which are then dispersed in the water.

Suitable redispersible polymers that may be used include, for instance, those based on one or more vinyl chlorides, styrenes, vinyl esters of unbranched or branched alkylcarboxylic acids having from 1 to 15 carbon atoms, methacrylic esters and acrylic esters of alcohols having from 1 to 10 carbon atoms, vinyl-aromatics, olefins, dienes, and vinyl halides as monomers or comonomers. It is also possible to use mixtures of these polymers made using one or more of the above-described monomers.

30

Suitable vinyl esters include vinyl acetate, vinyl propionate, vinyl butyrate, vinyl 2-ethylhexanoate, vinyl laurate, 1-methylvinyl acetate, vinyl pivalate, and vinyl esters of alpha-branched monocarboxylic acids having from 5 to 11 carbon atoms, examples being VeoVa5®, VeoVa9®,
5 VeoVa10® or VeoVa11® which are commercially available from Hexion Specialty Chemicals. Suitable methacrylic esters or acrylic esters are methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, n-butyl acrylate, n-butyl methacrylate, and 2-ethylhexyl acrylate. Suitable vinyl-aromatics are styrene,
10 methylstyrene, and vinyltoluene. One example of a vinyl halide is vinyl chloride. Suitable olefins are ethylene and propylene, and suitable dienes are 1,3-butadiene and isoprene.

If desired, the polymers may also contain from 0.1 to 10% by
15 weight, based on the overall weight of the polymer, of functional comonomer units, for example ethylenically unsaturated monocarboxylic or dicarboxylic acids such as acrylic acid; ethylenically unsaturated carboxamides such as (meth)acrylamide; ethylenically unsaturated sulfonic acids and/or their salts, preferably vinylsulfonic acid;
20 polyethylenically unsaturated comonomers such as divinyl adipate, diallyl maleate, allyl methacrylate and triallyl cyanurate, and/or N-methylol(meth)acrylamides and their ethers, such as their isobutoxy or n-butoxy ethers.

25 Particular redispersible polymers that may be used include the following wherein the weight percentages provided below add up to 100% by weight, together, where appropriate, with the fraction of functional comonomer units.

30 From among the vinyl ester polymers: vinyl acetate polymers, vinyl acetate-ethylene copolymers with an ethylene content of from 1 to 60% by

weight; vinyl ester-ethylene-vinyl chloride copolymers with an ethylene content of from 1 to 40% by weight and a vinyl chloride content of from 20 to 90% by weight; vinyl acetate copolymers with from 1 to 50% by weight of one or more copolymerizable vinyl esters such as vinyl laurate, vinyl
5 pivalate, vinyl esters of an alpha-branched carboxylic acid, especially versatic acid vinyl esters, which may also contain from 1 to 40% by weight of ethylene; and vinyl acetate-acrylic ester copolymers with from 1 to 60% by weight of acrylic ester, especially methyl methacrylate, n-butyl acrylate, or 2-ethylhexyl acrylate, which may also contain from 1 to 40% by weight
10 of ethylene.

From among the (meth)acrylic ester polymers: polymers of n-butyl acrylate or 2-ethylhexyl acrylate; copolymers of methyl methacrylate with n-butyl acrylate and/or 2-ethylhexyl acrylate; and copolymers of methyl
15 methacrylate with 1,3-butadiene.

From among the vinyl chloride polymers, besides the abovementioned vinyl ester/vinyl chloride/ethylene copolymers: vinyl chloride-ethylene copolymers and vinyl chloride-acrylate copolymers.
20

Styrene polymers that may be used include: styrene-1,3-butadiene copolymers and styrene-acrylic ester copolymers such as styrene-n-butyl acrylate or styrene-2-ethylhexyl acrylate copolymers, each with a styrene content of from 10 to 70% by weight. Other styrene polymers are styrene-
25 1,3-butadiene copolymers having a styrene content of from 10 to 70% by weight and a 1,3-butadiene content of from 30 to 90% by weight, with or without the abovementioned functional comonomer units, the fractions in % by weight adding up to 100% by weight.

30 Aqueous polymer dispersions and the water-redispersible powders of the abovementioned polymers that are obtainable from them by drying

are known and are available commercially. The polymers are prepared in a conventional manner, preferably by an emulsion polymerization process. The dispersions used may be stabilized with an emulsifier or else with a protective colloid, an example being polyvinyl alcohol.

5

Polyvinyl alcohols that may be used include those that are partially (or intermediate) hydrolyzed and have a degree of hydrolysis of from about 80 to up to about 95 mole percent. Likewise, so called "fully" hydrolyzed polyvinyl alcohol having a degree of hydrolysis of more than 95% can be
10 used. The polyvinyl alcohol particles can be incorporated into the redispersible polymer in order to stabilize the composition. Polyvinyl alcohol can be incorporated into the redispersible polymer composition, for instance, in an amount from about 4% to about 20% by weight. Greater amounts of polyvinyl alcohol powders may also be added for various other
15 reasons. For instance, polyvinyl alcohol powders have been incorporated into cementitious compositions in order to improve the workability of the composition when wet and also to improve mechanical adhesion strength. In the past, redispersible polymer powders were typically present in cementitious compositions in an amount of about 0.5% to about 16% by
20 weight.

Although redispersible polyvinyl alcohol powders can provide various benefits and advantages when incorporated into a cementitious composition, unfortunately such redispersible polymers can significantly
25 affect the cost of the final product, as well as altering the balance of performance in such a composition. For example, in a cementitious tile adhesive, high levels of redispersible powders impart good flexibility, freeze-thaw resistance, and resistance to heat aging; however, those same high levels of redispersible powder tend to negatively impact
30 properties like water immersion resistance and resistance to slip on a horizontal surface.

In one embodiment of the present invention, by incorporating the additive composition of the present invention into the cementitious composition, the amount of redispersible polymer present in the composition can be drastically reduced or even negated without adversely interfering with the physical properties of the resulting product. More particularly, cementitious compositions can be formulated in accordance with the present disclosure that contain a redispersible polymer in an amount from 0% to about 16% by weight, such as less than about 2% by weight. For instance, in one embodiment, a redispersible polymer may be present in the cementitious composition in an amount less than about 1% by weight, such as less than about 0.5% by weight.

As will become apparent from the examples which follow, benefits seen include, for example, improved slip and water resistance in tile adhesives, as well as reduced cost.

In an alternative embodiment, the nitrogen-containing polymer can be incorporated into a redispersible polymer powder which is then added to the cementitious composition. For example, in one embodiment, all or a portion of the polyvinyl alcohol contained in the redispersible polymer can be replaced with a nitrogen-containing polymer. Thus, a redispersible polymer composition can be formulated in accordance with the present disclosure that contains a nitrogen-containing polymer in an amount from about 4% to about 20% by weight, such as in an amount from about 8% to about 14% by weight. Again, the nitrogen-containing polymer can be used alone or in conjunction with polyvinyl alcohol particles in the redispersible polymer composition.

In addition to the above components, the cementitious composition can contain various other ingredients and additives. For instance, the

cementitious composition may also contain defoamers, dispersing aids, antioxidants, and the like. Antioxidants that may be contained in the composition include, for instance, one or more sterically hindered phenol or hydroquinone, aromatic amine, organosulfur compound, phosphite, and
5 phosphonite antioxidants.

Other additives that may be contained in the cementitious composition include accelerators, retardants, standardizers, air pore formers, and natural or synthetic polymer fibers.

10

In one embodiment, for instance, the composition may also contain a lubricant, such as sodium stearate. The sodium stearate may be present in an amount less than about 5% by weight, such as in an amount from about 0.1% to about 2% by weight.

15

Cementitious compositions made in accordance with the present invention may be formulated so that the compositions are easily workable when combined with water, have good mechanical adhesive strength properties (as tensile, compressive and/or shear) and set properties in an
20 appropriate amount of time.

The nitrogen-containing polymer improves a wide range of properties of the cementitious composition, especially the working properties of the composition and may also increase the tensile strength
25 and mechanical adhesion properties of the product. It is believed that the optionally present components of the additive composition may work synergistically together with the nitrogen-containing polymer to improve the properties of a cementitious composition. For instance, inclusion of the cellulose derivative is believed to increase the water retention capacity
30 of the resulting composition, increase the workability of the composition when combined with water, and to improve the stability of the resulting

product under load. The polyvinyl alcohol polymer is believed to improve the working properties of a cementitious composition and, in some embodiments, to increase the tensile strength of the resulting product. The polyvinyl alcohol polymer may also improve the mechanical adhesion
5 properties of the product.

When a cementitious composition is combined with water, although unknown, it is believed that the reactive agent may undergo a crosslinking reaction with the nitrogen-containing polymer. In particular, when the
10 cementitious composition is combined with water, the pH of the composition may be alkaline which may cause the reactive agent, such as the glyoxal, to react with the nitrogen-containing polymer. Nitrogen-containing polymers undergo relatively fast crosslinking reactions. Thus, it is believed that the properties of the nitrogen-containing
15 polymer, optionally combined with the other components of the additive composition result in a better balance of attributes that when mixed with the cementitious components results in enhanced properties. In addition, all of these improvements are realized while also minimizing the amount of redispersible polymer present in the composition to achieve desired
20 physical properties.

The present disclosure may be better understood with reference to the following examples.

25 Examples

The following examples were conducted in order to demonstrate some of the advantages and benefits of the present disclosure.

The following test for cementitious tile adhesives were conducted in
30 the following examples and fall under the European Norm 12004:

Open time (minutes): EN 1346

Tensile Strength @ 5 minutes and Tensile Strength @ 10 minutes
(Nw/mm²): EN 1348

Tensile Adhesion Strength after water immersion: EN 1348

5 Tensile Strength after heat aging: EN 1348

Tensile Strength after freeze-thaw cycles: EN 1348

Deformation/Flexibility: EN 12002

Further cementitious tile adhesive tests were also conducted and
10 tested under Mexican Specifications:

Shear Resistance (kg/cm²): Test No. NMX-C-420 ONNCCE(2003)

Compressive Strength (kg/cm²): Test No. NMX-C-420 ONNCCE(2003)

15 For Joint Compounds, testing was conducted in accordance with
EN 13963.

Hardening Time: Paragraph 5.2

Determination of the absence of fissures: Paragraph 5.3

Determination of the absence of large particles: Paragraph 5.4

20 Determination of adhesion/cohesion: Paragraph 5.5

Determination of Break Load by Flex: Paragraph 5.8.2

For Exterior Insulation and Finishing Systems (EIFS), testing was
conducted in accordance with ETAG 004.

25 Water Absorption (capillarity test): Section 5.1.3.1

Freeze-thaw Behavior: Section 5.1.3.2.2

Resistance to Perforation (Perfotest): Section 5.1.3.3.2

Base Coat to Insulation Bond Strength: Section 5.1.4.1.1

Example Series 1

In this example, various cementitious tile adhesive compositions were formulated. Specifically, tile adhesive mortar formulated only with a redispersible polymer was compared to formulations containing a derivatized cellulose, a reactive agent, polyvinyl alcohol polymer, and a vinyl alcohol and vinyl amine copolymer in accordance with the present disclosure. After the tile adhesive compositions were formulated, water was added and the composition was allowed to harden.

The following table lists the ingredients used to formulate the tile adhesive compositions. Water was added to each example so that all of the samples had the same consistency. The produced samples were then tested for various properties as shown in Table 1, below.

Table 1

Tile Adhesive Ingredients	Control	Sample 1-1	Sample 1-2
Base Mortar (Cement/Filler)	97%	97%	97%
Cellulose ether-glyoxal product	0.24%	0.24%	0.24%
Re-dispersible powder	3%	0%	0%
Vinyl alcohol and vinyl amine copolymer containing 6 mole percent vinyl amine*	0%	2.76%	0%
Vinyl alcohol and vinyl amine copolymer containing 12 mole percent vinyl amine**	0%	0%	2.76%
Water	21%	33.3%	28.6%
Open Time (minutes)	25	52	22
Tensile Strength @ 5' minutes (Nw/mm ²)	2.4	2.3	2.8
Tensile strength @ 10' minutes (Nw/mm ²)	2.0	1.5	2.7
Shear resistance (kg/cm ²)	27	17	21
Compressive Strength (kg/cm ²)	40	15	21

*referred to hereinafter as VaVam 6

**referred to hereinafter as VaVam 12

The base mortar contained 80% calcium carbonate and 20% Portland cement. The cement was Portland cement type CPC 30 sold under the tradename TOLTECA by Cemex. The calcium carbonate was obtained from Derivados Macroquimicos S. A. de C. V. The cellulose
5 ether/glyoxal product was obtained from Derivados Macroquimicos S. A. de C. V and had a glyoxal content of 0.1:1. The redispersible polymer used in the examples was a polyvinyl acetate ethylene copolymer powder commercially available from Wacker Polymer Systems GmbH under the trade name VINNAPAS 5010. The polyvinyl alcohol polymer and the vinyl
10 alcohol and vinyl amine copolymers were obtained commercially from the Celanese Corporation.

As shown above, incorporating the additive composition of the present disclosure into a mortar composition allows for the reduction in
15 redispersible powder without significantly adversely affecting the physical properties. In fact, Sample 2 showed an increase in tensile strength over the control. Of particular advantage, incorporation of the additive composition into Sample 1 dramatically increased the open time of the formulation.

20

Although decreases were observed in shear resistance and compressive strength, it is believed that these decreases are due to the high water used to achieve uniform mortar consistency.

25 Example Series 2

In this example, further cementitious compositions were formulated and tested.

The following table lists the ingredients used to formulate the
30 adhesive compositions. The produced samples were then tested for various properties as shown in Table 2, below.

Table 2

Tile Adhesive	Sample 2-1	Sample 2-2	Sample 2-3	Sample 2-4	Sample 2-5	Sample 2-6	Sample 2-7
Cement (%)	14.954	14.9	14.808	14.808	28.124	26.634	28.124
Hydroxyl propyl methyl cellulose (%)	0.239	0.238	0.237	0.237	0.225	0.213	0.225
PVOH type	VaVam 12	VaVam 6	C540S	VaVam 6	VaVam 12	VaVam 12	C540S
PVOH amount (%)	0.06	0.397	0.059	0.059	0.375	0.355	0.375
Cross linker Type	BORAX	BORAX	GLYOXAL	GLYOXAL	BORAX	GLYOXAL	BORAX
Cross linker amount (%)	0.005	0.03	0.987	0.987	0.028	5.327	0.028
Calcium Carbonate (100 mesh) (%)	52	52	51	51	54	51	54
Calcium carbonate (324 mesh) (%)	32.9	32.78	32.577	32.77	16.874	15.98	16.874
Open time (min)	19	30	22	23	23	17	12
Water retention (%)	23.7	26.88	23.14	23.03	24.65	24.76	24.85
Adjustability (min)	20	25	17.5	22.5	22.5	22.5	7.5
Open time by tensile adhesion strength after 10 minutes (Nw/mm ²)	1.38	1.86	0.97	1.26	1.95	1.49	1.72
Tensile adhesion strength after water immersion (Nw/mm ²)	0.65	0.65	0.61	0.71	1.25	1.14	1.59
Tensile adhesion strength after heat aging (Nw/mm ²)	1.82	1.68	1.55	0.7	2.41	2.03	3.05
Compressive strength (kg/cm ²)	36	14	18	23	120	122	126
Shear adhesion strength (kg/cm ²)	8	8	7	11	27	32	20

Table 2 (cont'd)

Tile Adhesive	Sample 2-8	Sample 2-9	Sample 2-10	Sample 2-11	Sample 2-12	Sample 2-13	Sample 2-14
Cement (%)	26.634	28.221	14.9	14.954	28.221	14.066	14.9
Hydroxyl propyl methyl cellulose (%)	0.213	0.226	0.238	0.239	0.226	0.225	0.238
PVOH type	VaVam 6	C540S	C540S	C540S	VaVam 6	VaVam 12	VaVam 12
PVOH amount (%)	0.355	0.056	0.397	0.06	0.056	0.375	0.397
Cross linker Type	GLYOXAL	BORAX	BORAX	BORAX	BORAX	GLYOXAL	BORAX
Cross linker amount (%)	5.327	0.005	0.03	0.005	0.005	5.626	0.03
Calcium Carbonate (100 mesh) (%)	51	55	52	52	55	49	52
Calcium carbonate (324 mesh) (%)	15.98	16.932	32.78	32.9	16.932	30.945	32.78
Open time (min)	24	18	10	25	19	15	22
Water retention (%)	26.92	23.74	23.89	23.95	24.4	24.55	25
Adjustability (min)	2705	17.5	5	17.5	20	17.5	17.5
Open time by tensile adhesion strength after 10 minutes (Nw/mm ²)	1.87	1.52	1.24	1.14	1.53	1.4	1.8
Tensile adhesion strength after water immersion Nw/mm ²	1.21	1.11	0.64	0.69	1.09	0.78	0.66
Tensile adhesion strength after heat aging (Nw/mm ²)	2.23	2.75	1.17	0.85	1.8	1.23	0.94
Compressive strength (kg/cm ²)	125	175	37	35	166	29	24
Shear adhesion strength (kg/cm ²)	31	30	5	14	50	24	18

Table 2 (cont'd)

Tile Adhesive	Sample 2-15	Sample 2-16	Sample 12-7	Sample 2-18	Sample 2-19	Sample 2-20	Sample 2-21
Cement (%)	28.221	26.634	28.124	27.959	14.954	14.066	27.959
Hydroxyl propyl ethyl cellulose (%)	0.226	0.213	0.225	0.224	0.239	0.225	0.224
PVOH type	VaVam 12	C540S	VaVam 6	VaVam 12	VaVam 6	C540S	VaVam 6
PVOH amount (%)	0.056	0.355	0.375	0.056	0.06	0.375	0.056
Cross linker Type	BORAX	GLYOXAL	BORAX	GLYOXAL	BORAX	GLYOXAL	GLYOXAL
Cross linker amount (%)	0.005	5.327	0.028	0.0932	0.005	5.626	0.932
Calcium Carbonate (100 mesh) (%)	55	51	54	54	52	49	54
Calcium carbonate (324 mesh) (%)	16.932	15.98	16.874	16.775	32.9	30.945	16.775
Open time (min)	18	10	30	20	23	12	20
Water retention (%)	23.43	23.36	26.21	23.6	24.5	23.9	24.36
Adjustability (min)	20	12.5	22.5	22.5	17.5	7.5	22.5
Open time by tensile adhesion strength after 10 minutes (Nw/mm ²)	1.8	1.99	2.82	0.99	1.31	0.91	1.3
Tensile adhesion strength after water immersion (Nw/mm ²)	1.24	1.21	1.3	1.4	0.643	0.64	1.05
Tensile adhesion strength after heat aging (Nw/mm ²)	2.23	1.82	2.3	2.95	0.45	0.44	1.99
Compressive strength (kg/cm ²)	181	166	138	156	20	26	154
Shear adhesion strength (kg/cm ²)	46	35	29	28	18	7	26

Table 2 (cont'd)

Tile Adhesive	Sample 2-22	Sample 2-23	Sample 2-24
Cement (%)	27.959	14.808	14.066
Hydroxyl propyl methyl cellulose(%)	0.224	0.237	0.225
PVOH type	C540S	VaVam 12	VaVam 6
PVOH amount(%)	0.056	0.059	0.375
Cross linker Type	GLYOXAL	GLYOXAL	GLYOXAL
Cross linker amount(%)	0.932	0.987	5.626
Calcium Carbonate (100 mesh) (%)	54	51	49
Calcium carbonate (324 mesh) (%)	16.775	32.577	30.945
Open time (min)	18	19	32
Water retention (%)	23.44	23.93	27.3
Adjustability (min)	17.5	7.5	25
Open time by tensile adhesion strength after 10 minutes (Nw/mm ²)	1.65	0.66	1.75
Tensile adhesion strength after water immersion (Nw/mm ²)	1.44	0.62	0.6
Tensile adhesion strength after heat aging (Nw/mm ²)	2.26	0.04	0.78
Compressive strength (kg/cm ²)	156	18	19
Shear adhesion strength (kg/cm ²)	17	13	5

The cement was Portland cement type CPC 30 sold under the
 tradename TOLTECA by Cemex. The calcium carbonate was obtained
 from Derivados Macroquimicos S. A. de C. V. The cellulose ether/glyoxal
 product was obtained from Derivados Macroquimicos S. A. de C. V and
 had a glyoxal content of 0.1:1. The redispersible polymer used in the
 examples was a polyvinyl acetate ethylene copolymer powder
 commercially available from Wacker Polymer Systems GmbH under the
 trade name VINNAPAS 5010. The polyvinyl alcohol polymer and the vinyl

alcohol and vinyl amine copolymers were obtained commercially from the Celanese Corporation.

As shown above in the table, the compositions made according to
5 the present disclosure exhibited very favorable properties. The table also shows that the mortar adhesive attributes can be balanced inside a broad range of values.

Example Series 3

10 In this example, further cementitious compositions were formulated and tested.

The following table lists the ingredients used to formulate the adhesive compositions. The produced samples were then tested for
15 various properties as shown in Table 3, below.

Table 3

Tile Adhesive Ingredients	Control	Sample 3-1	Sample 3-2	Sample 3-3	Sample 3-4
Cement	28.74%	29.46%	29.51%	24.66%	24.36%
Hydroxyl propyl methyl cellulose	0.38%	0.39%	.39%	0.15%	.39%
Re-dispersible powder	3.83%	0.98%	0.98%	0.99%	1.95%
Copolymer vinyl Alcohol Vinyl Amine	0.00%	0.29%	0.10%	0.10%	0.10%
Polyvinyl Alcohol	0.00%	0.10%	0.10%	0.10%	0.10%
Glyoxal/HPMC	0.00%	0.03%	0.05%	0.03%	0.03%
Calcium Carbonate pass 325 mesh	67.05%	68.74%	68.86%	73.98%	73.07%
Open time (min)	43	46	44	18	35
Adjustability	45	35	57.5	12.5	17.5
Tensile strength after 5' minutes (Nw/mm ²)	1.6	1.5	1.6	1.3	1.8
Tensile strength after 15' minutes (Nw/mm ²)	2.8	2.6	1.8	1.7	2.3
Tensile Strength after water immersion (Nw/mm ²)	0.8	0.9	0.8	0.8	0.8
Tensile Strength after heat aging (Nw/mm ²)	2.0	1.4	1.3	0.9	1.2
Compressive strength (kg/cm ²)	145	112	124	152	111
Shear adhesion strength (kg/cm ²)	36	20	22	32	30

- The cement was Portland cement type CPC 30 sold under the tradename TOLTECA by Cemex. The calcium carbonate was obtained from Derivados Macroquimicos S. A. de C. V. The cellulose ether/glyoxal product was obtained from Derivados Macroquimicos S. A. de C. V. The redispersible polymer used in the examples was a polyvinyl acetate ethylene copolymer powder commercially available from Wacker Polymer Systems GmbH under the trade name VINNAPAS 5010. The polyvinyl alcohol polymer and the vinyl alcohol and vinyl amine copolymers were obtained commercially from the Celanese Corporation.

As shown in the table above, the samples made according to the present disclosure generally exhibited about the same or better properties than the Control Sample.

5 Example Series 4

In this example, further cementitious compositions were formulated and tested.

10 The following table lists the ingredients used to formulate the adhesive compositions. The produced samples were then tested for various properties as shown in Table 4, below.

Table 4

Tile Adhesive	Control	Sample 4-1	Sample 4-2	Sample 4-3	Sample 4-4	Sample 4-5	Sample 4-6
Cement (%)	28.74	28.68	29.53	29.47	29.53	29.41	29.47
Hydroxyl propyl methyl cellulose (%)	0.38	0.38	0.39	0.39	0.39	0.39	0.39
Re-dispersible powder (%)	3.83	3.82	0.98	0.98	0.98	0.98	0.98
Copolymer vinyl Alcohol Vinyl Amine (%)	0	0.1	0.1	0.29	0.1	0.29	0.1
PVOH type	-	165SF	165SF	165SF	C540S	C540S	165SF
PVOH (%)	0	0.1	0.1	0.1	0.1	0.29	0.29
Borax (%)	0	0.0019	0.0039	0.0039	0.002	0.002	0.0039
Calcium Carbonate (%)	67.05	66.92	68.89	68.76	68.9	68.63	68.76
Open Time (min)	38	33	37	35	28	39	26
Open time by tensile adhesion strength after 15 minutes (Nw/mm ²) (Adhesion Type ISO-C1)	2.07	1.83	1.46	2.02	2.24	2.32	2.12
Open time by tensile adhesion strength after 5 minutes (Nw/mm ²) (Adhesion Type ISO-C2)	2.51	2.32	2.18	2.04	2.57	1.42	2.24

Table 4 (cont'd)

Tile Adhesive	Control	Sample 4-1	Sample 4-2	Sample 4-3	Sample 4-4	Sample 4-5	Sample 4-6
Tensile adhesion strength after water immersion(Nw/mm ²) (Adhesion Type ISO-C2)	0.65	1.36	1.16	1.09	1.22	0.75	1.35
Tensile adhesion strength after heat aging(Nw/mm ²) (Adhesion Type ISO-C2)	1.9	2.43	2.17	1.95	2.1	1.34	2.26
Compressive strength(kg/cm ²)	108	116	107	89	94	106	87
Shear adhesion strength(kg/cm ²)	26	28.28	28.59	27.34	25.68	34.84	29.84
Tensile adhesion strength after 5 minutes(Nw/mm ²) (Adhesion Type ISO-C2)	2.18	2.27	2.53	2.36	1.6	2.07	2.46
Tensile adhesion strength after water immersion (Nw/mm ²) (Adhesion Type ISO-C2)	---	1.32	1.18	1.17	1.34	0.84	1.07
Tensile adhesion strength after heat aging(Nw/mm ²) (Adhesion Type ISO-C1)	2.43	1.53	1.7	2.21	2.33	1.9	2.22

Table 4 (cont'd)

Tile Adhesive	Sample 4-7	Sample 4-8	Sample 4-9	Sample 4-10	Sample 4-11	Sample 4-12
Cement (%)	29.47	29.47	29.47	29.41	29.41	29.53
Hydroxyl propyl methyl cellulose (%)	0.39	0.39	0.39	0.39	0.39	0.39
Re-dispersible powder (%)	0.98	0.98	0.98	0.98	0.98	0.98
Copolymer vinyl Alcohol Vinyl Amine (%)	0.1	0.29	0.29	0.29	0.29	0.1
PVOH type	C540S	C540S	C540S	165SF	C450S	C450S
PVOH (%)	0.29	0.1	0.1	0.29	0.29	0.1
Borax (%)	0.002	0.0039	0.002	0.002	0.0039	0.0039
Calcium Carbonate (%)	68.76	68.76	68.76	68.63	68.62	68.89
Open Time (min)	36	35	33	42	41	42
Open time by tensile adhesion strength after 15 minutes (Nw/mm ²) (Adhesion Type ISO-C2)	2.39	2.64	2.19	2.23	2.34	2.32
Open time by tensile adhesion strength after 5 minutes (Nw/mm ²) (Adhesion Type ISO-C2)	1.96	2.38	2.18	2.34	1.99	2.14
Tensile adhesion strength after water immersion (Nw/mm ²) (Adhesion Type ISO-C2)	1.01	0.96	1.34	1.26	0.88	1.27
Tensile adhesion strength after heat aging (Nw/mm ²) (Adhesion Type ISO-C2)	1.97	1.91	2.72	2.11	1.39	1.88
Compressive strength(kg/cm ²)	110	97	101	107	109	93
Shear adhesion strength(kg/cm ²)	25.48	29.08	32.81	25.62	31.19	25.21
Tensile adhesion strength after 5 minutes(Nw/mm ²) (Adhesion Type ISO-C1)	2.17	2.35	2.27	2.09	2.03	2.25
Tensile adhesion strength after water immersion (Nw/mm ²)(Adhesion Type ISO-C1)	0.92	1.2	1.14	1.28	0.78	1.35
Tensile adhesion strength after heat aging(Nw/mm ²) (Adhesion Type ISO-C1)	2.35	2.72	2.13	2.41	2.29	2.28

Table 4 (cont'd)

Tile Adhesive	Sample 4-13	Sample 4-14	Sample 4-15	Sample 4-16	Sample 4-17	Sample 4-18
Cement (%)	29.47	29.47	29.47	29.47	29.41	29.47
Hydroxyl propyl methyl cellulose (%)	0.39	0.39	0.39	0.39	0.39	0.39
Re-dispersible powder (%)	0.98	0.98	0.98	0.098	0.98	0.98
Copolymer Vinyl Alcohol Vinyl Amine (%)	0.29	0.2	0.1	0.1	0.29	0.2
PVOH type	165SF	165SF	165SF	C540S	165SF	C540S
PVOH (%)	0.1	0.2	0.29	0.29	0.29	0.2
Borax (%)	0.002	0.0029	0.002	0.0039	0.0039	0.0029
Calcium Carbonate (%)	68.76	68.76	68.76	68.76	68.62	68.76
Open Time (min)	50	37	41	33	38	37
Open time by tensile adhesion strength after 15 minutes (Nw/mm ²) (Adhesion Type ISO-C2)	2.13	1.87	1.82	2.16	2.54	2.37
Open time by tensile adhesion strength after 5 minutes (Nw/mm ²) (Adhesion Type ISO-C2)	2.02	1.61	2.16	1.83	2	1.99
Tensile adhesion strength after water immersion (Nw/mm ²) (Adhesion Type ISO-C2)	1.23	1.39	1.07	0.76	1.15	1.22
Tensile adhesion strength after heat aging (Nw/mm ²) (Adhesion Type ISO-C2)	1.81	2.1	2.03	1.54	1.5	1.9
Compressive strength(kg/cm ²)	105	92	88	102	113	126
Shear adhesion strength(kg/cm ²)	27.97	29.64	37.33	31.13	37.03	29.1
Tensile adhesion strength after 5 minutes (Nw/mm ²) (Adhesion Type ISO-C1)	2.06	1.95	2.25	2.27	2.51	2.44
Tensile adhesion strength after water immersion (Nw/mm ²) (Adhesion Type ISO-C1)	0.98	1.08	0.93	0.92	1.02	1.07
Tensile adhesion strength after heat aging(Nw/mm ²) (Adhesion Type ISO-C1)	2.18	2.4	1.91	1.91	2	1.9

The cement was Portland cement type CPC 30 sold under the tradename TOLTECA by Cemex. The calcium carbonate was obtained from Derivados Macroquimicos S. A. de C. V. The cellulose ether/glyoxal product was obtained from Derivados Macroquimicos S. A. de C. V and
5 had a glyoxal content of 0.1:1. The redispersible polymer used in the examples was a polyvinyl acetate ethylene copolymer powder commercially available from Wacker Polymer Systems GmbH under the trade name VINNAPAS 5010. The polyvinyl alcohol polymer and the vinyl alcohol and vinyl amine copolymers were obtained commercially from the
10 Celanese Corporation.

As shown in the table above, samples made according to the present disclosure exhibited very favorable properties in comparison to the Control. Sample Nos. 10 and 11 particularly demonstrated improved
15 properties.

Example Series 5 – Multifunctional Components

The various components of the inventive compositions can be added as separate components or combined as a multifunctional
20 component for ease of handling and formulation. One aspect of practicing the present invention is to incorporate the nitrogen-containing polymer into a redispersible powder composition as a stabilizer when preparing the redispersible powder emulsion. One might employ, for example, a PVOH-VAM copolymer, 6 mole % nitrogen as a stabilizer when preparing
25 a redispersible powder emulsion as described in the examples appearing immediately below.

Polyvinyl acetate based emulsion stabilized with 6 mole % nitrogen
PVOH-VAM copolymer:

30

Equipment:

A 2 liter glass reactor was equipped with a tempered water jacket, mechanical stirrer, feed lines and thermocouple.

5 Feed solutions:

Monomers: vinyl acetate (VAM) and optionally vinyl versatate (VeoVa)

52013-145: 776 g VAM and 258 g VeoVa)

52013-149: 775 g VAM and 258 g VeoVa)

10

Stabilizer blend

52013-145: 72 g Celvol 504 Polyvinyl alc.

+ 52 g Vinyl alcohol - vinyl amine copolymer, 12% in water

15

52013-149: 62 g Celvol 504 Polyvinyl alc.

+ 62 g Vinyl alcohol - vinyl amine copolymer, 11% in water

Initiator Potassium persulfate, (PPS) 3.0% w/w in water)

20

Buffer: Sodium Acetate 5% w/w in water

Surfactant: Sodium Lauryl Sulfate (SLS) 20% w/w in water

Antifoam: 116 FG (as is) (Harcros)

Redox: Hydrogen peroxide (H₂O₂)

Sodium formate salt (SFS)

25

Sample 5-1**Procedure:**

The reactor was charged with

Monomers	119 g
----------	-------

30

Stabilizer blend	915 g
------------------	-------

Antifoam	0.9 g
SLS	9.0 g

The contents were heated to 65°C with moderate (200 rpm) stirring,
5 and Initiator (19.9g) added. The temperature is raised and controlled at
80°C.

After 10 minutes of stirring, feeds were initiated and maintained.

10	Monomers	2.25 g/min	300 minutes
	Initiator:	0.18 g.min	340 minutes

At 300 min, the temperature was raised to 85°C

15 The reactor was stirred for an additional 30 minutes, then cooled to
50°C. H₂O₂ (22.2 g) and SFS (16.0g) were added to quench the
polymerization and initiator, and the system cooled to 30°C. The emulsion
was spray dried to yield Sample 52013-45.

20 Sample 5-2

Procedure:

The reactor was charged with

	Monomers	119 g
	Stabilizer blend	930 g
25	Antifoam	0.9 g
	SLS	6.75 g

The contents were heated to 65°C with moderate (200 rpm) stirring,
and Initiator (16.6g) added. The temperature is raised and controlled at
30 80°C.

After 10 minutes of stirring, feeds were initiated and maintained.

Monomers 2.25 g/min 300 minutes
Initiator: 0.18 g.min 340 minutes

5

At 300 min, the temperature was raised to 85°C.

The reactor was stirred for an additional 30 minutes, then cooled to 50°C. H₂O₂ (22.2 g) and SFS (16.0g) were added to quench the polymerization and initiator, and the system cooled to 30°C. The emulsion was spray dried to yield Sample 52013-149.

10

The powders prepared had the following assays:

15

Sample#	5-1	5-2
VAM-VeoVa copolymer	89.3%	89.3%
Polyvinyl alcohol	6.2%	5.4%
Vinyl alcohol - vinyl amine copolymer	4.5%	5.4%

20

Experiment 6-21 below used a 1:1 blend of the Sample 5-1 material and the Sample 5-2 material.

Experiment 6-22 below used the Sample 5-1 material.

Example Series 6

25

Following the procedures generally discussed above, a further series of compositions was prepared and tested. Details and results appear in Tables 5 through 12, below:

Table 5 – Ingredient Source and Description

Ingredient Name	Company Information	Brief Description
Electroland 42.5R	Cementos Molins (Spain)	42.5R rated Portland Cement
H33/H35 Blend	Quarwerke (Germany)	1 Part H33 to 4 parts H35 Blend
MO 60016P4	SE Tylose (Germany)	Hydroxypropylmethylcellulose
MOT 60000YP4	SE Tylose (Germany)	Solubility controlled Hydroxypropylmethylcellulose
MH 60001P4	SE Tylose (Germany)	Hydroxyethylmethylcellulose
MHS 60000YP4	SE Tylose (Germany)	Solubility controlled Hydroxyethylmethylcellulose
Culminal 1034	Hercules (US)	Hydroxypropylmethylcellulose
Culminal 1034R	Hercules (US)	Solubility controlled Hydroxypropylmethylcellulose
Demacol 30MN	Demacsa (Mexico)	Hydroxypropylmethylcellulose
Demacol 30MST	Demacsa (Mexico)	Solubility controlled Hydroxypropylmethylcellulose
5010N	Wacker (Germany)	VAE Redispersible Powder
5012T	Wacker (Germany)	VAE Redispersible Powder - Thixotropic modification
5044N	Wacker (Germany)	VAE Redispersible Powder - Flexible
DM117P	Elotex	VA-VeoVa Redispersible Powder
Celvol 540S	Celanese (US)	partially hydrolyzed polyvinylalcohol
Celvol 165SF	Celanese (US)	fully hydrolyzed polyvinylalcohol
Berset 2700	Bercin. Inc. (US)	cyclic amide condensate aqueous blend with glyoxal
Polycup 172	Hercules (US)	aqueous solution of a cationic amine polymer-epichlorohydrin adduct
Zirgel K	MEL Chemicals	Potassium Zirconium Carbonate

Table 5 – Ingredient Source and Description (cont'd)

Ingredient Name	Company Information	Brief Description
SMA 1000P	Sartomer (US)	Styrene-Maleic Anhydride 1:1 molar ratio
SMA 3000P	Sartomer (US)	Styrene-Maleic Anhydride 3:1 molar ratio
Hyperdrill 247RD	QMAX Solutions Inc (US)	polyacrylamide
Penford Gum 290	Penford (US)	Hydroxyethyl ether derivatized corn starch
Lupamin 9095	BASF	Polyvinylamine
Lupamin 9030	BASF	Polyvinylamine-co-vinylformamide
Polyamine B	Akzo Nobel	Polyethyleneamine
Glyoxal	Sigma-Aldrich (US)	40% aqueous solution of glyoxal
Omyacarb 8 - CL	Omya	Calcium Carbonate
Omyacarb 10 - BE	Omya	Calcium Carbonate
Caloxol PG	Omya	Calcium Oxide

Table 6 – Sample Compositions

Example	Cement		Sand		Hydroscopic/Rheology Modifier	
	Type	Amount	Type	Amount	Type	Amount
6-1a		Proprietary Spanish Mortar Producer Blend			CE Demacol 30MST	0.4
6-1b		Proprietary Spanish Mortar Producer Blend			CE Demacol 30MST	0.4
6-2	Electroland 42.5R	40	Quarzwerte H33/H35 Blend	60	CE Tylose MOT 60000YP4	0.4
6-3	Electroland 42.5R	40	Quarzwerte H33/H35 Blend	60	CE Tylose MHS 60000YP4	0.4
6-4	Electroland 42.5R	40	Quarzwerte H33/H35 Blend	60	CE Tylose MOT 60000YP4	0.4
6-5		Proprietary Spanish Mortar Producer Blend			CE Demacol 30MST	0.4
6-6	Electroland 42.5R	35	Quarzwerte H33/H35 Blend	65	CE Tylose MHS 60000YP4	0.4
6-7	Electroland 42.5R	40	Quarzwerte H33/H35 Blend	60	PAM Hyperdrill 247RD	0.4
6-8	Electroland 42.5R	40	Quarzwerte H33/H35 Blend	60	Starch Penford Gum 290	0.4
6-9		Proprietary Spanish Mortar Producer Blend			CE Demacol 30MST	0.4
6-10	Electroland 42.5R	40	Quarzwerte H33/H35 Blend	60	CE Tylose MOT 60000YP4	0.4
6-12	Electroland 42.5R	40	Quarzwerte H33/H35 Blend	60	CE Tylose MH 60001P4	0.4
6-13	Electroland 42.5R	40	Quarzwerte H33/H35 Blend	60	CE Tylose MO 60016P4	0.4
6-14	Electroland 42.5R	40	Quarzwerte H33/H35 Blend	60	CE Tylose MO 60016P4	0.4
6-15	Electroland 42.5R	40	Quarzwerte H33/H35 Blend	60	CE Tylose MO 60016P4	0.4
6-16	Electroland 42.5R	40	Quarzwerte H33/H35 Blend	60	CE Tylose MO 60016P4	0.4
6-20	Electroland 42.5R	35	Quarzwerte H33/H35 Blend	65	CE Demacol 30MN	0.4
6-21	Electroland 42.5R	35	Quarzwerte H33/H35 Blend	65	CE Demacol 30MST	0.4
6-22	Electroland 42.5R	35	Quarzwerte H33/H35 Blend	65	CE Demacol 30MST	0.4
6-23a		Proprietary Spanish Mortar Producer Blend			CE Demacol 30MST	0.4
6-23b		Proprietary Spanish Mortar Producer Blend			CE Demacol 30MST	0.4
6-23c		Proprietary Spanish Mortar Producer Blend			CE Demacol 30MST	0.4
6-24a		Proprietary Spanish Mortar Producer Blend			CE Culminal 1034	0.4
6-24b		Proprietary Spanish Mortar Producer Blend			CE Culminal 1034R	0.4
6-24c		Proprietary Spanish Mortar Producer Blend			CE Culminal 1034R	0.4
CE	Cellulose Ether					
PAM	Polyacrylamide					

Table 6 – Sample Compositions (cont'd)

Example	Cement		Sand		Hydroscopic/Rheology Modifier	
	Type	Amount	Type	Amount	Type	Amount
6-25a	Electroland 42.5R	35	Quarzwerte H33/H35 Blend	65	CE Tylose MO 60016P4	0.4
6-25b	Electroland 42.5R	35	Quarzwerte H33/H35 Blend	65	CE Tylose MHS 60000YP4	0.4
6-26a	Electroland 42.5R	35	Quarzwerte H33/H35 Blend	65	CE Tylose MH 60001P4	0.4
6-26b	Electroland 42.5R	50	Quarzwerte H33/H35 Blend	50	CE Tylose MHS 60000YP4	0.4

Example	Cement		Calcium Oxide		Sand		Hydroscopic/Rheology Modifier	
	Type	Amount	Type	Amount	Type	Amount	Type	Amount
6-18a	Electroland 52.5R	25	Caloxol	7.5	Quarzwerte H35	65	CE Tylose MH 15002P6	0.25
6-18b	Electroland 52.5R	25	Caloxol	7.5	Quarzwerte H35	65	CE Tylose MHS 60000YP4	0.25
6-18c	Electroland 52.5R	25	Caloxol	7.5	Quarzwerte H35	65	CE Tylose MHS 60000YP4	0.25
6-18d	Electroland 52.5R	25	Caloxol	7.5	Quarzwerte H35	65	CE Tylose MHS 60000YP4	0.25

Example	Cement		Calcium Oxide		Calcium Carbonate		Hydroscopic/Rheology Modifier	
	Type	Amount	Type	Amount	Type	Amount	Type	Amount
6-19a	Electroland 52.5R	19	Caloxol	2	Omyacarb Blend**	79	CE Tylose MH 10007P6	0.3
6-19b	Electroland 52.5R	19	Caloxol	2	Omyacarb Blend**	79	CE Tylose MHS 60000YP4	0.3
6-19c	Electroland 52.5R	19	Caloxol	2	Omyacarb Blend**	79	CE Tylose MHS 60000YP4	0.3
6-19d	Electroland 52.5R	19	Caloxol	2	Omyacarb Blend**	79	CE Tylose MHS 60000YP4	0.3

** Omyacarb blend is a 50:50 Blend of Omyacarb 8 and Omyacarb 10

Table 6 – Sample Compositions (cont'd)

Example	Redispersible Powder		Nitrogen Containing Polymer		Polyvinyl Alcohol		Reactive Agent	
	Type	Amount	Type	Amount	Type	Amount	Type	Amount
6-1a	Wacker 5010N	1	Polyvinylalcohol-co-vinylamine	0.4	Celvol 540S	0.2	glyoxal	
6-1b	Wacker 5010N	1	Polyvinylalcohol-co-vinylamine	0.3	Celvol 540S	0.1	glyoxal	
6-2	Wacker 5010N	2	Lupamin 9095	0.4	Celvol 540S	0.1	glyoxal	
6-3	Wacker 5010N	2	Lupamin 9030	0.4	Celvol 540S	0.1	glyoxal	
6-4	Wacker 5010N	2	Polyamine B	0.4	Celvol 540S	0.1	glyoxal	
6-5	Wacker 5010N	1	Polyvinylalcohol-co-vinylamine	0.4	Celvol 540S	0.2	glyoxal	
6-6	Wacker 5012T	0.5	Polyvinylalcohol-co-vinylamine	0.4	Celvol 540S	0.2	glyoxal	
6-7	Wacker 5010N	2	Polyvinylalcohol-co-vinylamine	0.4	Celvol 540S	0.1	glyoxal	0.016
6-8	Wacker 5010N	2	Polyvinylalcohol-co-vinylamine	0.4	Celvol 540S	0.1	glyoxal	0.016
6-9	Wacker 5010N	1	Polyvinylalcohol-co-vinylamine	0.4	Celvol 540S	0.2	glyoxal	
6-10	Wacker 5010N	2	Polyvinylalcohol-co-vinylamine	0.4	Celvol 165SF	0.1	glyoxal	
6-12	Wacker 5010N	2	Polyvinylalcohol-co-vinylamine	0.4	Celvol 540S	0.1	Berset 2700	0.018
6-13	Wacker 5010N	2	Polyvinylalcohol-co-vinylamine	0.4	Celvol 540S	0.1	Polycup 172	0.016
6-14	Wacker 5010N	2	Polyvinylalcohol-co-vinylamine	0.4	Celvol 540S	0.1	Zirgel K	0.030
6-15	Wacker 5010N	2	Polyvinylalcohol-co-vinylamine	0.4	Celvol 540S	0.1	SMA 1000P	0.028
6-16	Wacker 5010N	2	Polyvinylalcohol-co-vinylamine	0.4	Celvol 540S	0.1	SMA 3000P	0.083
6-18a	Wacker 5010N	2.0	-	-	-	-	-	-
6-18b	Wacker 5010N	0.5	Polyvinylalcohol-co-vinylamine	0.2	C540S	0.05	glyoxal	
6-18c	Wacker 5010N	0.5	Polyvinylalcohol-co-vinylamine	0.25	C540S	0.07	glyoxal	
6-18d	Wacker 5044N	0.5	Polyvinylalcohol-co-vinylamine	0.2	C540S	0.05	glyoxal	
6-19a	Wacker 5010N	1.5	-	-	-	-	-	-
6-19b	Wacker 5010N	0.5	Polyvinylalcohol-co-vinylamine	0.2	C540S	0.05	glyoxal	
6-19c	Wacker 5010N	0.5	Polyvinylalcohol-co-vinylamine	0.23	C540S	0.07	glyoxal	
6-19d	Wacker 5044N	0.5	Polyvinylalcohol-co-vinylamine	0.15	C540S	0.05	glyoxal	

Table 6 – Sample Compositions (cont'd)

Example	Redispersible Powder		Nitrogen Containing Polymer		Polyvinyl Alcohol		Reactive Agent	
	Type	Amount	Type	Amount	Type	Amount	Type	Amount
6-20	Wacker 5010N	4	-	-	-	-	-	-
6-1	CZ VA-VeoVa*	4	-	-	-	-	glyoxal	-
6-2	CZ VA-VeoVa*	2	Polyvinylalcohol-co-vinylamine	0.146	Celvol 540S	0.13	glyoxal	-
6-23a	Wacker 5010N	4	-	-	-	-	-	-
6-23b	Wacker 5010N	1	Polyvinylalcohol-co-vinylamine	0.4	Celvol 540S	0.2	glyoxal	-
6-23c	Wacker 5010N	1	Polyvinylalcohol-co-vinylamine	0.3	Celvol 540S	0.1	glyoxal	-
6-24a	Eloxtex DM117P	4	-	-	-	-	-	-
6-24b	Eloxtex DM117P	1	Polyvinylalcohol-co-vinylamine	0.4	Celvol 540S	0.2	glyoxal	-
6-24c	Eloxtex DM117P	1	Polyvinylalcohol-co-vinylamine	0.3	Celvol 540S	0.1	glyoxal	-
6-25a	Wacker 5012T	4	-	-	-	-	-	-
6-25b	Wacker 5012T	0.5	Polyvinylalcohol-co-vinylamine	0.4	Celvol 540S	0.2	glyoxal	-
6-26a	Wacker 5044T	4	-	-	-	-	-	-
6-26b	Wacker 5044T	0.5	Polyvinylalcohol-co-vinylamine	0.2	Celvol 540S	0.1	glyoxal	-

* CZ VA-VeoVa is a RP stabilized with a blend of PVOH and polyvinylalcohol-co-vinylamine

Table 7 – Comparison of Compositions with Different Nitrogen-Containing Polymers

Example #	Description of Nitrogen Containing Polymer	Cementitious Tile Adhesive Properties								
		% Water	28 Day Std. Aging	Water Immersion	Heat Aging	Freeze-Thaw	Open Time 20min	Open Time 30min	Slip	Flexibility
		(%)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(mm)	(mm)
6-1a	PVOH-VAm Copolymer	24	2.2	1.2	1.5	1.2	1.2	0.9	6.6	1.7
6-1b	PVOH-VAm Copolymer	24	1.0	0.8	1.1	1.5	1.2	0.6	0.1	1.5
6-2	Polyvinylamine Polymer	22	1.6	0.5	0.8	0.6	0.8	0.3	0.3	2.2
6-3	Polyvinyl-formamide - vinylamine Copolymer	21.5	2.0	1.0	1.6	1.3	1.0	0.5	0.3	2.3
6-4	Polyethylene - imine	23	1.7	0.8	1.6	0.8	1.3	0.8	1.2	2.0

Table 7 demonstrates the use of a variety of nitrogen containing polymers in cementitious compositions in a formulation designed for Tile Adhesives. Each of the nitrogen containing polymers tested showed positive results in adhesive properties as well as specialty properties like slip resistance, which demonstrates the versatility of this technology to work with several different types of nitrogen chemistry. Examples 1-4 also used 2 or less parts of redispersible powder, which is beneficial to cementitious mortar producers. All results in Table 7 were tested using the EN 12004 Norm.

Table 8 – Comparison of Compositions with Different Modifiers

Example #	Description of Different Rheological Modifiers and Hygroscopic Polymers	Cementitious Tile Adhesive Properties								
		% Water	28 Day Std. Aging	Water Immersion	Heat Aging	Freeze- Thaw	Open Time 20min	Open Time 30min	Slip	Flexibility
		(%)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(mm)	(mm)
		See Example #1 as a reference								
6-5	Hydroxypropylmethyl cellulose									
6-6	Hydroxyethylmethyl cellulose	23	1.7	0.8	1.2	1.3	1.3	0.8	0.2	2.5
6-7	Polyacrylamide	25	1.1	0.4	1.0	0.8	1.4	0.7	0.1	1.8
6-8	Starch	21	0.3	0.2	0.1	0.3	0.1	0	0.1	2.0
6-9	Partially Hydrolyzed. High MW PVOH									
6-10	Fully Hydrolyzed. High MW PVOH	24	1.7	0.7	1.4	1.6	1.5	1.1	3.2	3.3

Table 8 demonstrates the use of a variety of alternate polymeric ingredients in cementitious compositions in a formulation designed for Tile Adhesives. Each example in Table 8 uses the vinylalcohol-vinylamine copolymer as the nitrogen containing group with glyoxal as the reactive agent. However, the examples vary in the type of rheological or hygroscopic polymeric modifiers. The technology of the incorporating the nitrogen containing polymer with a reactive agent performs very well generally regardless of what other polymeric additives are used. Two types of cellulose derivatives are used with success: hydroxypropyl-methylcellulose and hydroxyethylmethylcellulose. Also, two types of polyvinylalcohol are used with success: partially hydrolyzed and fully hydrolyzed. Furthermore, a nitrogen containing rheological modifier like polyacrylamide also showed good properties as a tile adhesive. Starch, on the other hand, clearly imparted poor performance to the formulation.

Table 9 – Comparison of Compositions with Different Crosslinkers

Example #	Description of Reactive Agents	Cementitious Tile Adhesive Properties								
		% Water	28 Day Std. Aging	Water Immersion	Heat Aging	Freeze-Thaw	Open Time 20min	Open Time 30min	Slip	Flexibility
		(%)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(mm)	(mm)
		Examples 1-10 show the use of standard glyoxal								
6-11	Dialdehyde #1 - Pure Glyoxal									
6-12	Dialdehyde #2 - Proprietary Glyoxal Blend	22	1.7	0.6	1.1	0.8	0.6	0.3	0.3	2.2
6-13	Polyamide-Epichlorohydrin	23	2.2	1.1	1.9	1.4	1.1	0.6	0.5	2.1
6-14	Zirconium Salt	28	1.8	0.6	1.6	1.2	1.6	1.1	8.5	2.1
6-15	50:50 SMA Polymer	25	1.7	0.7	1.9	0.9	1.1	0.8	1.2	1.9
6-16	75:25 SMA Polymer	31	1.5	0.6	1.5	0.8	1.4	1.3	0.3	3.6

Table 9 demonstrates the use of a variety of reactive agents in cementitious compositions in a formulation designed for Tile Adhesive applications. Each example in Table 9 uses the vinylalcohol-vinylamine
5 copolymer as the nitrogen containing group. Despite varying the type of reactive agent, each example in Table 9 demonstrates a set of quality tile adhesive with favorable properties. This further supports the technology that claims any reactive agent capable of crosslinking with the nitrogen containing polymer works in these cementitious systems.

Table 10A – Comparisons with Difference End Uses (Exterior Insulation and Finishing Systems – EIFS)

Example #	Alternative Application - Exterior Insulation & Finishing Systems	EIFS Properties - According to ETAG 004							
		Water Demand	Water Absorption (6mm Thickness)		Freeze-thaw Behavior	Resistance to Perforation (Perfotest)	Base Coat to Insulation Bond Strength (N/mm^2)		
			%	1 hour - (kg/m^2)			24 hours - (kg/m^2)	(pass/fail)	(mm) - Category
6-18a	Control Sample	22	0.14 - pass	0.83 - pass	no failures - pass	15mm (pass) - Cat II	0.16	0.15	0.17
6-18b	Celanese Sample #1	22	0.12 - pass	0.76 - pass	no failures - pass	15mm (pass) - Cat II	0.15	0.15	0.14
6-18c	Celanese Sample #2	22	0.07 - pass	0.53 - pass	no failures - pass	12mm (pass) - Cat II	0.16	0.17	0.17
6-18d	Celanese Sample #3	22	0.11 - pass	0.62 - pass	no failures - pass	15mm (pass) - Cat II	0.14	0.15	0.17

Table 10A provides examples of typical formulations used as adhesives for Exterior Insulation and Finishing Systems (EIFS). The testing protocol follows ETAG 004. All samples 18a-18d were mixed to the same consistency using 22% water addition by weight. For a sample
5 to pass the water absorption test, it must have less than 1.0kg/m^2 water absorption after 1 hour of immersion. All samples pass this test, and all samples with the novel nitrogen-containing polymer and reactive agent perform better than the Control Sample 6-18a with only redispersible powder. Furthermore, if a sample retains less than 0.5kg/m^2 water after 24
10 hours of immersion, no Freeze-thaw testing is required. None of the samples reached the aforementioned benchmark, so all required Freeze-thaw testing; however, sample 6.18c was much improved over the control and came close to the 0.5kg/m^2 specification, and all Celanese Samples outperformed the Control. The Freeze-thaw behavior is measured on a
15 pass fail basis to be determined by the appearance of cracks and fissures. All samples passed the test. Next, all samples received a rating of Category II for the perforation test. Category II is the medium tier level for EIFS systems described by light traffic and potential for impact. Finally, the adhesion of the mortar to the insulation board was excellent for all
20 samples. In each case, there was cohesive failure within the insulation board and not on the interface between the mortar and insulation. Based on these results, all the samples with the nitrogen-containing polymer and reactive agent performed at an identical level in each test to the Control, except for water absorption, where it was superior.

Table 10B – Comparisons of Compositions with Different End Uses (Joint Filler Compounds)

Example #	Alternative Application - Joint Filling Compound	EN 13963 Properties - Jointing for Gypsum Plasterboards								
		% Water	Fire Reaction EN13501	Curing Time	Crack Test	315 micron Course Particles	200 micron Course Particles	Adhesion / Cohesion (N/mm2 and Class)	Break Load by Flexion Method	
		(%)	(rating)	(min)	(pass/fail)	%	%		First Fissure (N)	Break (N)
6-19a	Control Sample	35	Not Tested	40 - Short	pass	0.08% - pass	0.41% - pass	0.37 - Type C	139	151
6-19b	Celanese Comparison #1	40	A1	50 - Short	pass	0.11% - pass	0.32% - pass	0.34 - Type C	133	140
6-19c	Celanese Comparison #2	35	A1	35 - Short	pass	0.06% - pass	0.21% - pass	0.37 - Type C	127	132
6-19d	Celanese Comparison #3	35	A1	60 - Short	pass	0.09% - pass	0.24% - pass	0.33 - Type C	148	157

Table 10B provides examples of typical formulations used as jointing compound for plasterboards. Formulations 19a-d could be used in Bedding, Finishing, Dual-Purpose, and/or Tapeless Jointing Compounds (Type 1A-4A and 1B-4B). Example 19a, the control sample, contained a
5 typical amount of redispersible powder for this application, 1.5 PPHC. Each of the Celanese Comparison samples #1-3 which contain a reduced amount of redispersible powder and the novel nitrogen-containing reactive polymer system showed highly comparable, mostly identical, results compared to the control. Furthermore, since examples 19b-d contains
10 less than 1% organic components by weight, they do not require a Fire Reaction test and receive an automatic rating of A1.

Table 11 – Comparison of Nitrogen Containing Polymer Stabilized Redispersible Powders

Example #	Description of Redispersible Powder	Cementitious Tile Adhesive Properties								
		% Water	28 Day Std. Aging	Water Immersion	Heat Aging	Freeze-Thaw	Open Time 20min	Open Time 30min	Slip	Flexibility
		(%)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(mm)	(mm)
6-20	Commercial VAE RP	21	1.7	0.5	1.6	0.7	0.6	0.3	0.6	2.7
6-21	VA-VeoVA with PVOH-Vam stabilizer	23	1.3	0.4	0.4	1.0	0.2	0.1	0.1	2.0
6-22	Blend of VA-VeoVA with PVOH-Vam stabilizer & additional PVOH-Vam	22	1.1	0.4	0.4	0.9	0.2	0.1	0.1	1.8

Table 11 is a comparison of a commercially available vinylacetate ethylene (VAE) emulsion (Wacker 5010N) in Example 20, with novel Celanese redispersible powders stabilized with a vinylalcohol-vinylamine copolymer and a reactive agent, glyoxal, in Examples 21 and 22. Example 21 is a direct comparison to Example 20, where 4 parts of the VAE redispersible powder were replaced with 4 parts of a VA-VeoVa, nitrogen polymer stabilized redispersible powder with a reactive agent in the same general formulation. Example 22 substitutes the VA-VeoVa redispersible powder at a lower addition rate as well as includes additional vinylalcohol-vinylamine copolymer with a reactive agent. Whereas both Example 21 and 22 have some deficiencies when compared to Example 20, they also showed some novel improvements as well. For example, even the with addition of more water in Examples 21 and 22, the slip values of those formulas were far improved over the control in Example 20. This property supports our theory of a crosslinked polymer system providing specific benefits in cementitious compositions.

One aspect of novelty in this technology is the ability to reduce the overall level of polymer in a cementitious formulation by reducing the level of redispersible powder and still maintaining or even improving product performance. This would represent both a cost savings for mortar formulators and provide them with the ability to make a more balanced formulation. The following Examples 12a-d, demonstrate that novelty.

**Table 12a – Comparison #1 of Invention Compositions with Control Composition
Having Higher Redispersible Powder Content**

Example #	Control Comparison #1	Cementitious Tile Adhesive Properties								
		% Water	28 Day Std. Aging	Water Immersion	Heat Aging	Freeze-Thaw	Open Time 20min	Open Time 30min	Slip	Flexibility
		(%)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(mm)	(mm)
6-23a	Control Formulation 23a	24%	2.3	1.0	2.2	2.1	1.8	1.5	50	2.3
6-23b	Celanese Comparison 23b	24%	2.2	1.2	1.5	1.2	1.5	0.7	3.0	1.7
6-23c	Celanese Comparison 23c	24%	1.0	0.8	1.1	1.5	1.2	0.6	0.1	1.5

Table 12a compares Control Formulation 23a that contains 4 parts of Wacker 5010N redispersible powder with Examples 23b and 23c that contain only 1 part of Wacker 5010N redispersible powder in typical Tile Adhesive based formulations. Example 23b replaces the 3 parts of redispersible powder with 0.4 parts of vinylalcohol-vinylamine copolymer and 0.2 parts of polyvinylalcohol, and Example 23c uses only 0.3 parts of vinylalcohol-vinylamine copolymer and 0.1 parts of polyvinylalcohol. Example 23b meets all of the same standards (as defined by EN 12004) as the Control 23a. Example 23b also demonstrates a strong improvement in slip properties as the same water addition rate. Example 23c, which has even less polymer than 23b, meets the majority of the same standards as 23a, only failing to reach 1.0N/mm² in Water Immersion; however, Example 23c has extremely high slip resistance that would give it a superior rating than the control in that category.

Table 12b – Comparison #2 of Invention Compositions with Control Composition
Having Higher Redispersible Powder Content

Example #	Control Comparison #2	Cementitious Tile Adhesive Properties								
		% Water	28 Day Std. Aging	Water Immersion	Heat Aging	Freeze-Thaw	Open Time 20min	Open Time 30min	Slip	Flexibility
		(%)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(mm)	(mm)
6-24a	Control Formulation 24a	24%	1.8	0.7	1.3	1.8	1.2	1.0	12.2	2.2
6-24b	Celanese Comparison 24b	24%	1.1	1.0	0.9	1.2	1.2	0.9	6.6	1.5
6-24c	Celanese Comparison 24c	24%	2.0	0.6	0.8	2.0	1.1	0.8	0.8	1.6

Table 12b compares Control Formulation 24a that contains 4 parts of Elotex DM117P redispersible powder with Examples 24b and 24c that contain only 1 part of Elotex DM117P redispersible powder in typical Tile Adhesive based formulations. Example 24b replaces the 3 parts of redispersible powder with 0.4 parts of vinylalcohol-vinylamine copolymer and 0.2 parts of polyvinylalcohol, and Example 24c uses only 0.3 parts of vinylalcohol-vinylamine copolymer and 0.1 parts of polyvinylalcohol. Both Examples 24b and 24c meet the exact same standards (as defined by EN 12004) as the Control 24a sample. Also, both Celanese Comparison samples show a strong improvement in slip with the same level of water addition.

Table 12c – Comparison #3 of Invention Compositions with Control Composition
Having Higher Redispersible Powder Content

Example #	Control Comparison #3	Cementitious Tile Adhesive Properties						
		% Water	28 Day Std. Aging	Water Immersion	Heat Aging	Freeze-Thaw	Open Time 20min	Open Time 30min
		(%)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)
6-25a	Control Formulation 25a	22%	1.4	0.7	1.3	1.6	0.7	0.3
6-25b	Celanese Comparison 24b	23%	1.7	0.8	1.2	1.3	1.3	0.8
							Slip (mm)	Flexibility (mm)
							0.3	3.1
							0.2	2.5

- Table 12c compares Control Formulation 25a that contains 4 parts of Wacker 5012T redispersible powder with Examples 25b that contains only 0.5 parts of Wacker 5012T redispersible powder in typical Tile
- 5 Adhesive based formulations. Example 25b replaces the 3.5 parts of redispersible powder with 0.4 parts of vinylalcohol-vinylamine copolymer and 0.2 parts of polyvinylalcohol. Despite removing the majority of the redispersible powder, Sample 25b has the same rating (based on EN 12004) as the Control 25a. Furthermore, Sample 25b shows better 28
- 10 Day again, Water Immersion, Open Time, and Slip performance.

Table 12d – Comparison #3 of Invention Compositions with Control Composition
Having Higher Redispersible Powder Content

Example #	Control Comparison #4	Cementitious Tile Adhesive Properties								
		% Water	28 Day Std. Aging	Water Immersion	Heat Aging	Freeze-Thaw	Open Time 20min	Open Time 30min	Slip	Flexibility
		(%)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(N/mm ²)	(mm)	(mm)
6-26a	Control Formulation 25a	22%	1.2	0.9	1.3	1.7	1.2	0.8	4.7	2.4
6-26b	Celanese Comparison 26b	26%	1.5	1.2	1.0	1.4	0.9	0.6	6.6	1.8

Table 12d compares Control Formulation 26a that contains 4 parts of Wacker 5044N redispersible powder with Examples 26b that contains only 0.5 parts of Wacker 5044N redispersible powder in typical Tile
5 Adhesive based formulations. Example 26b replaces the 3.5 parts of redispersible powder with only 0.2 parts of vinylalcohol-vinylamine copolymer and 0.1 parts of polyvinylalcohol. Despite removing the majority of the redispersible powder, Sample 26b has a better rating (based on EN 12004) than the Control 26a because Sample 26b provides
10 a higher level of performance.

It is appreciated from the foregoing examples that cementitious compositions in accordance with the invention exhibit a superior balance of properties, including flexibility, open times and so forth even with low
15 levels of polymer additive. For example, the invention compositions in the adhesive exhibit surprising slip and water resistance which is a highly desirable feature for these classes of compositions.

There is thus provided in accordance with the invention the
20 improvement for cementitious compositions comprising a reactive polymeric composition including a nitrogen-containing polymer and a reactive agent capable of crosslinking with the nitrogen of the polymer *in situ* within the cementitious composition. In some cases, the nitrogen-containing polymer composition comprises an amine-functional
25 polymer, while in others, the nitrogen-containing polymer comprises an amide-functional polymer.

A suitable polymer is a vinyl alcohol and vinyl amine copolymer which contains from 2 mole percent to 30 mole percent vinyl amine, such
30 as from 2 mole percent to 12 mole percent vinyl amine. Another suitable

polymer is a vinyl amine homopolymer. Still other suitable nitrogen-containing polymers are vinylformamide-vinylamine copolymers and ethyleneimine polymers. Typically, the nitrogen-containing polymer is present in the cementitious composition in an amount of from 0.01% to 5% based on the dry weight of the cementitious composition such as where the nitrogen-containing polymer is present in the cementitious composition in an amount of from 0.1% to 2% based on the dry weight of the cementitious composition.

10 The reactive agent may comprise polyaldehydes, dialdehydes such as glyoxal; dicarboxylic anhydrides, maleic anhydride copolymers such as styrene maleic anhydride copolymer; an epichlorohydrin resin; polyacids, such as polyacrylic acid or polymethacrylic acid; polyacid esters such as polymethacrylate and polymethylmethacrylate; polyvinyl alcohol esters
15 such as polyvinyl alcohol- acetoacetic acid ester (Gohsifimer Z); or a zirconium salt. Suitable reactive agents thus include a gluteraldehyde; a succinic dialdehyde; a blocked glyoxal; a cationic amine epichlorohydrin polymer; an amide-epichlorohydrin polymer; a potassium zirconium carbonate; an ammonium zirconium carbonate; a ketone formaldehyde; a
20 styrene maleic anhydride copolymer; or a cyclic amide condensate. The dry weight ratio of reactive agent:nitrogen-containing polymer in the reactive polymeric composition is generally from 0.01 to 0.3; typically from 0.025 to 0.1. So also, the molar equivalent ratio of the reactive moieties of the reactive agent to nitrogen in the nitrogen-containing polymer is
25 generally from 1:1 to 1:500; typically the molar equivalent ratio of the reactive moieties of the reactive agent to nitrogen in the nitrogen-containing polymer is from 1:10 to 1:200; and preferably the molar equivalent ratio of the reactive moieties of the reactive agent to nitrogen in the nitrogen-containing polymer is from 1:25 to 1:75.

In one preferred aspect, the reactive agent is reversibly reacted with a carrier prior to being provided to the reactive polymeric composition. The carrier may be a cellulose derivative, polyvinyl alcohol, or an inorganic carrier selected from clays, calcium carbonate and calcium oxide. The dry weight ratio of reactive agent:carrier is generally from 0.001:1 to 0.5:1; typically dry weight ratio of reactive agent:carrier is from 0.01:1 to 0.1:1. Suitable cellulose derivatives are hydroxypropyl methyl cellulose and hydroxyethyl methyl cellulose. Still others which may be employed include methyl cellulose; hydroxyethyl cellulose; hydroxypropyl cellulose; carboxymethyl cellulose; hydroxyethyl cellulose; ethyl hydroxyethyl cellulose; ethyl cellulose or mixtures thereof. In general, dry weight ratio of the nitrogen-containing polymer to the cellulose derivative is from 1:5 to 5:1; such as where the dry weight ratio of the nitrogen-containing polymer to the cellulose derivative is from 1:4 to 4:1; or where the dry weight ratio of the nitrogen-containing polymer to the cellulose derivative is from 1:2 to 2:1.

In many cases, the reactive polymeric composition comprises a vinyl alcohol polymer or copolymer thereof as well as a cellulose derivative where the dry weight ratio of the cellulose derivative to the vinyl alcohol polymer is from 5:1 to 1:5. Typically in such cases the dry weight ratio of the cellulose derivative to the vinyl alcohol polymer is from 1:4 to 4:1 or from 1:1 to 3:1.

Generally speaking, when polyvinyl alcohol or vinyl alcohol copolymers are used, the vinyl alcohol polymer is present in an amount of from 0.05% to 1% based on the dry weight of the cementitious composition and the reactive polymeric composition is present in the cementitious composition in an amount of from 0.1% to 15% based on the dry weight of the cementitious composition. Perhaps more preferably, the reactive polymeric composition is present in the cementitious composition

in an amount of from 0.25% to 5% based on the dry weight of the cementitious composition. In some preferred cases, the reactive polymeric composition is present in the cementitious composition in an amount of from 0.5% to 2% based on the dry weight of the cementitious
5 composition.

The cementitious compositions of this invention are especially useful in connection with tile adhesive compositions, exterior insulation finishing compositions, joint filler compositions, as well as all cement
10 compositions which traditionally employ redispersible powders such as troweling compositions; thin bed mortar compositions; sealing slurry compositions; powder paint compositions; rendering plaster compositions; patch and repair mortar compositions; mineral plaster compositions; gypsum compositions; grout compositions; façade coating compositions;
15 concrete repair compositions; coatings; or self-leveling compositions.

In various applications, the reactive polymeric composition is admixed dry with the other components of the cementitious composition which are likewise dry, while in other cases the reactive polymeric
20 composition is admixed wet or dry with a wet cementitious composition if so desired. In still yet further applications of the inventive compositions, the reactive polymeric composition is admixed wet with the other components of the cementitious composition, where the other components are wet or dry.

25

In another aspect of the invention, there is provided a cementitious composition comprising an inorganic binder; an inorganic filler; a polymeric composition including a nitrogen-containing polymer and a reactive agent capable of crosslinking with the nitrogen of the polymer *in situ* within the
30 cementitious composition; and a cellulose derivative or a vinyl alcohol polymer which is also reactive with the reactive agent. Generally, the

inorganic binder comprises cement, gypsum, an aluminate or mixtures thereof, whereas the filler comprises calcium carbonate, quartz, or mixtures thereof.

5 The compositions may further include an additive, the additive comprising a lubricant, hydrophobic agent fibers, pigments or mixtures thereof. Generally, the binder is present in an amount from 20 parts to 50 parts per hundred dry weight cement (PPHC), the filler is present in an amount from 10 parts to 90 PPHC and the nitrogen-containing polymer is
10 present in an amount from 0.01 to 2 PPHC. A cellulose derivative may be present in an amount of from 0.01 to 3 PPHC and the composition further comprises a polyvinyl alcohol polymer in an amount of from 0.01 to 2 PPHC. In some embodiments, the composition contains a redispersible polymer powder, the redispersible polymer powder being present in an
15 amount from 0.1 to 15 PPHC. The redispersible polymer powder may be present in an amount from 0.2 to 8 PPHC or from 0.25 to 5 PPHC or in an amount greater than 0.2 and less than 2 PPHC. Other suitable amounts for redispersible powder is present is from 0.1 to 8 PPHC; less than 4 PPHC; less than 3 PPHC; or less than 2 PPHC.

20

 In still another aspect of the invention there is provided an additive composition for mixing into a cementitious blend including an inorganic binder and an inorganic filler, the additive composition including a reactive polymeric composition comprising a nitrogen-containing polymer and a
25 reactive agent capable of crosslinking with the nitrogen of the polymer *in situ* within the cementitious blend; and wherein the reactive agent is also reactive with cellulose derivatives and vinyl alcohol polymers. The reactive agent suitably comprises a glutaraldehyde; a succinic dialdehyde; a blocked glyoxal; a cationic amine epichlorohydrin polymer; an
30 amide-epichlorohydrin polymer; a potassium zirconium carbonate; an

ammonium zirconium carbonate; a ketone formaldehyde; a styrene maleic anhydride copolymer; or a cyclic amide condensate.

In yet a further aspect of the invention, there is provided an additive
5 composition for mixing into a cementitious blend including an inorganic binder, an inorganic filler, the additive composition including a redispersible emulsion polymer composition as well as a nitrogen-containing additive polymer and a reactive agent capable of reacting with the nitrogen of the additive polymer *in situ* within the
10 cementitious blend; and wherein the reactive agent is also reactive with cellulose derivatives and vinyl alcohol polymers. The redispersible emulsion polymer composition generally includes an emulsion polymer formed from one or more unbranched alkylcarboxylic acid vinyl ester monomers, branched alkylcarboxylic acid vinyl ester monomers, alcohol
15 methacrylic acid ester monomers, vinyl aromatic monomers, olefin monomers, diene monomers, or vinyl halide monomers. A typical emulsion polymer comprises a copolymer of vinyl acetate and ethylene. Another suitable emulsion polymer comprises a copolymer of vinyl acetate and a vinyl ester of a versatic acid. Generally, the nitrogen-containing
20 additive polymer is present in the additive composition in an amount from 4% to 20% by dry weight and the redispersible powder is present in an amount of from 1% to 15% based on the dry weight of the cementitious blend and the additive composition mixed therewith. The redispersible powder may be present in an amount of less than 8% based on the dry
25 weight of the cementitious blend and the additive composition mixed therewith or the redispersible powder is present in an amount of less than 5% based on the dry weight of the cementitious blend and the additive composition mixed therewith. In some preferred cases, the redispersible powder is present in an amount of less than 2% based on the dry weight of
30 the cementitious blend and the additive composition mixed therewith.

While the invention has been described in detail, modifications within the spirit and scope of the invention will be readily apparent to those of skill in the art. In view of the foregoing discussion, relevant knowledge

5 in the art and references discussed above in connection with the Background and Detailed Description, the disclosures of which are all incorporated herein by reference, further description is deemed unnecessary. In addition, it should be understood that aspects of the various embodiments may be interchanged either in whole or in part.

10 Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention as further described in the appended claims.

WHAT IS CLAIMED:

1. In a cementitious composition of the class including an inorganic binder and a filler, the improvement comprising a reactive polymeric composition including a nitrogen-containing polymer and a reactive agent capable of crosslinking with the nitrogen of the polymer *in situ* within the cementitious composition.
5
2. The improvement according to Claim 1, wherein the nitrogen-containing polymer comprises an amine-functional polymer.
10
3. The improvement according to Claim 1, wherein the nitrogen-containing polymer comprises an amide-functional polymer.
4. The improvement according to Claim 1, wherein the nitrogen-containing polymer is a vinyl alcohol and vinyl amine copolymer.
15
5. The improvement according to Claim 1, wherein the nitrogen-containing polymer contains from 2 mole percent to 30 mole percent vinyl amine.
20
6. The improvement according to Claim 1, wherein the nitrogen-containing polymer contains from 2 mole percent to 12 mole percent vinyl amine.
25
7. The improvement according to Claim 1, wherein the nitrogen-containing polymer is a vinyl amine homopolymer.
8. The improvement according to Claim 1, wherein the nitrogen-containing polymer is a vinylformamide-vinylamine copolymer.
30

9. The improvement according to Claim 1, wherein the nitrogen-containing polymer is an ethyleneimine polymer.
- 5 10. The improvement according to Claim 1, wherein the nitrogen-containing polymer is present in the cementitious composition in an amount of from 0.01% to 5% based on the dry weight of the cementitious composition.
- 10 11. The improvement according to Claim 1, wherein the nitrogen-containing polymer is present in the cementitious composition in an amount of from 0.1% to 2% based on the dry weight of the cementitious composition.
- 15 12. The improvement according to Claim 1, wherein the reactive agent comprises a polyaldehyde.
13. The improvement according to Claim 1, wherein the reactive agent comprises a dialdehyde.
- 20 14. The improvement according to Claim 1, wherein the reactive agent comprises glyoxal.
15. The improvement according to Claim 1, wherein the reactive agent comprises a dicarboxylic anhydride.
- 25 16. The improvement according to Claim 1, wherein the reactive agent comprises a maleic anhydride copolymer.

17. The improvement according to Claim 1, wherein the reactive agent comprises a styrene maleic anhydride copolymer.
18. The improvement according to Claim 1, wherein the reactive agent
5 comprises an epichlorohydrin resin.
19. The improvement according to Claim 1, wherein the reactive agent comprises a zirconium salt.
- 10 20. The improvement according to Claim 1, wherein the reactive agent comprises a gluteraldehyde; a succinic dialdehyde; a blocked glyoxal; a cationic amine epichlorohydrin polymer; an amide-epichlorohydrin polymer; a potassium zirconium carbonate; an ammonium zirconium carbonate; a ketone formaldehyde; a styrene
15 maleic anhydride copolymer; a cyclic amide condensate; a polyacid; a polyacrylic acid selected from polyacrylic acid and polymethacrylic acid; a polyacid ester; a polyacid ester selected from polymethacrylate and polymethylmethacrylate; a polyvinyl alcohol ester; or a polyvinyl alcohol- acetoacetic acid ester.
- 20 21. The improvement according to Claim 1, wherein the dry weight ratio of reactive agent to nitrogen-containing polymer in the reactive polymeric composition is from 0.01 to 0.3.
- 25 22. The improvement according to Claim 1, wherein the dry weight ratio of reactive agent to nitrogen-containing polymer in the reactive polymeric composition is from 0.025 to 0.1.
- 30 23. The improvement according to Claim 1, wherein the molar equivalent ratio of the reactive moieties of the reactive agent to nitrogen in the nitrogen-containing polymer is from 1:1 to 1:500.

24. The improvement according to Claim 1, wherein the molar equivalent ratio of the reactive moieties of the reactive agent to nitrogen in the nitrogen-containing polymer is from 1:10 to 1:200.
- 5
25. The improvement according to Claim 1, wherein the molar equivalent ratio of the reactive moieties of the reactive agent to nitrogen in the nitrogen-containing polymer is from 1:25 to 1:75.
- 10
26. The improvement according to Claim 1, wherein the reactive agent is reversibly reacted with a carrier prior to being provided to the reactive polymeric composition.
- 15
27. The improvement according to Claim 26, wherein the carrier is a cellulose derivative, polyvinyl alcohol, or an inorganic carrier selected from clays, calcium carbonate and calcium oxide.
- 20
28. The improvement according to Claim 27, wherein the carrier is a cellulose derivative.
29. The improvement according to Claim 26, wherein the dry weight ratio of reactive agent:carrier is from 0.001:1 to 0.5:1.
- 25
30. The improvement according to Claim 26, wherein the dry weight ratio of reactive agent:carrier is from 0.01:1 to 0.1:1.
31. The improvement according to Claim 28, wherein the cellulose derivative is hydroxypropyl methyl cellulose.
- 30
32. The improvement according to Claim 28, wherein the cellulose derivative is hydroxyethyl methyl cellulose.

33. The improvement according to Claim 1, wherein the reactive polymeric composition comprises a cellulose derivative.

5 34. The improvement according to Claim 33, wherein the cellulose derivative comprises methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, ethyl hydroxyethyl cellulose, ethyl cellulose or mixtures thereof.

10

35. The improvement according to Claim 33, wherein the dry weight ratio of the nitrogen-containing polymer to the cellulose derivative is from 1:5 to 5:1.

15 36. The improvement according to Claim 33, wherein the dry weight ratio of the nitrogen-containing polymer to the cellulose derivative is from 1:4 to 4:1.

20 37. The improvement according to Claim 33, wherein the dry weight ratio of the nitrogen-containing polymer to the cellulose derivative is from 1:2 to 2:1.

25 38. The improvement according to Claim 33, wherein the reactive polymeric composition further comprises a polyvinyl alcohol polymer or copolymer thereof.

39. The improvement according to Claim 38, wherein the dry weight ratio of the cellulose derivative to the vinyl alcohol polymer or copolymer thereof is from 5:1 to 1:5.

30

40. The improvement according to Claim 38, wherein the dry weight ratio of the cellulose derivative to the vinyl alcohol polymer or copolymer thereof is from 1:4 to 4:1.
- 5 41. The improvement according to Claim 38, wherein the dry weight ratio of the cellulose derivative to the vinyl alcohol polymer or copolymer thereof is from 1:1 to 3:1.
42. The improvement according to Claim 38, wherein the vinyl alcohol
10 polymer or copolymer thereof is present in an amount of from 0.05% to 1% based on the dry weight of the cementitious composition.
43. The improvement according to Claim 1, wherein the reactive
15 polymeric composition is present in the cementitious composition in an amount of from 0.1% to 15% based on the dry weight of the cementitious composition.
44. The improvement according to Claim 1, wherein the reactive
20 polymeric composition is present in the cementitious composition in an amount of from 0.25% to 5% based on the dry weight of the cementitious composition.
45. The improvement according to Claim 1, wherein the reactive
25 polymeric composition is present in the cementitious composition in an amount of from 0.5% to 2% based on the dry weight of the cementitious composition.
46. The improvement according to Claim 1, wherein the cementitious composition is a joint filler composition.

47. The improvement according to Claim 1, wherein the cementitious composition is an exterior insulation finishing composition.
48. The improvement according to Claim 1, wherein the cementitious
5 composition is a tile adhesive composition.
49. The improvement according to Claim 1, wherein the cementitious composition is selected from troweling compositions; thin bed mortar compositions; sealing slurry compositions; powder paint compositions;
10 rendering plaster compositions; patch and repair mortar compositions; mineral plaster compositions; gypsum compositions; grout compositions; façade coating compositions; concrete repair compositions; coatings; or self-leveling compositions.
- 15 50. The improvement according to Claim 1, wherein the reactive polymeric composition is admixed dry with the other components of the cementitious composition which are likewise dry.
51. The improvement according to Claim 1, wherein the reactive
20 polymeric composition is admixed wet or dry with a wet cementitious composition.
52. The improvement according to Claim 1, wherein the reactive
25 polymeric composition is admixed wet with the other components of the cementitious composition, where the other components are wet or dry.

53. A cementitious composition comprising:
- (a) an inorganic binder;
 - 5 (b) an inorganic filler;
 - (c) a polymeric composition including a nitrogen-containing polymer and a reactive agent capable of crosslinking with the nitrogen of the polymer *in situ* within the
10 cementitious composition; and
 - (d) a cellulose derivative or a vinyl alcohol polymer which is also reactive with the reactive agent.
- 15 54. The cementitious composition according to Claim 53, which includes a cellulose derivative.
55. The improvement according to Claim 54, wherein the cellulose derivative is hydroxyethyl methyl cellulose.
20
56. The improvement according to Claim 54, wherein the cellulose derivative is hydroxypropyl methyl cellulose.
- 25 57. The cementitious composition according to Claim 54, wherein the cellulose derivative comprises methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, ethyl hydroxyethyl cellulose, ethyl cellulose or mixtures thereof.

58. The composition according to Claim 54, wherein the dry weight ratio of the nitrogen-containing polymer to the cellulose derivative is from 1:5 to 5:1.
- 5 59. The improvement according to Claim 54, wherein the dry weight ratio of the nitrogen-containing polymer to the cellulose derivative is from 1:4 to 4:1.
60. The improvement according to Claim 54, wherein the dry weight ratio
10 of the nitrogen-containing polymer to the cellulose derivative is from 1:2 to 2:1.
61. The composition according to Claim 53, which includes a polymer of polyvinyl alcohol or copolymer thereof.
- 15 62. The cementitious composition according to Claim 53, wherein the inorganic binder comprises cement, gypsum, an aluminate or mixtures thereof.
- 20 63. The cementitious composition according to Claim 53, wherein the filler comprises calcium carbonate, quartz, or mixtures thereof.
64. The cementitious composition according to Claim 53, further comprising an additive, the additive comprising a lubricant,
25 hydrophobic agent fibers, pigments or mixtures thereof.
65. The cementitious composition otherwise as defined in Claim 53, wherein the binder is present in an amount from 20 parts to 50 parts per hundred dry weight cement (PPHC), the filler is present in an
30 amount from 10 parts to 90 PPHC and the nitrogen-containing polymer is present in an amount from 0.01 to 2 PPHC .

66. The cementitious composition according to Claim 65, which further comprises a cellulose derivative in an amount of from 0.01 to 3 PPHC.
- 5 67. The cementitious composition according to Claim 65, which further comprises a polyvinyl alcohol polymer or copolymer thereof in an amount of from 0.01 to 2 PPHC.
- 10 68. The cementitious composition according to Claim 65, containing a redispersible polymer powder, the redispersible polymer powder being present in an amount from 0.1 to 15 PPHC.
- 15 69. The cementitious composition according to Claim 68, containing a redispersible polymer powder, the redispersible polymer powder being present in an amount from 0.2 to 8 PPHC.
- 20 70. The cementitious composition according to Claim 68, containing a redispersible polymer powder, the redispersible polymer powder being present in an amount from 0.25 to 5 PPHC.
71. The cementitious composition according to Claim 68, wherein the redispersible polymer powder is present in the composition in an amount greater than 0.2 and less than 2 PPHC.
- 25 72. The cementitious composition according to Claim 53, further comprising a redispersible powder.
73. The cementitious composition according to Claim 72, wherein the redispersible powder is present in an amount of up to 15 PPHC.
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74. The cementitious composition according to Claim 72, wherein the redispersible powder is present in an amount of up to 8 PPHC.
- 5 75. The cementitious composition according to Claim 72, wherein the redispersible powder is present in an amount of from 0.1 to 8 PPHC.
76. The cementitious composition according to Claim 75, wherein the redispersible powder is present in an amount of less than 4 PPHC.
- 10 77. The cementitious composition according to Claim 75, wherein the redispersible powder is present in an amount of less than 3 PPHC.
78. The cementitious composition according to Claim 75, wherein the redispersible powder is present in an amount of less than 2 PPHC.
- 15 79. An additive composition for mixing into a cementitious blend including an inorganic binder and an inorganic filler, the additive composition including a reactive polymeric composition comprising a nitrogen-containing polymer and a reactive agent capable of crosslinking with the nitrogen of the polymer *in situ* within the cementitious blend; and wherein the reactive agent is also the reactive with cellulose derivatives and vinyl alcohol polymers.
- 20 80. The additive composition according to Claim 79, wherein the nitrogen-containing polymer composition comprises an amine-functional polymer.
- 25 81. The additive composition according to Claim 79, wherein the nitrogen-containing polymer composition comprises an amide-functional polymer.
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82. The additive composition according to Claim 79, wherein the nitrogen-containing polymer is a vinyl alcohol and vinyl amine copolymer.
- 5 83. The additive composition according to Claim 79, wherein the nitrogen-containing polymer contains from 2 mole percent to 30 mole percent vinyl amine.
84. The additive composition according to Claim 79, wherein the
10 nitrogen-containing polymer contains from 2 mole percent to 12 mole percent vinyl amine.
85. The additive composition according to Claim 79, wherein the
15 nitrogen-containing polymer is a vinyl amine homopolymer.
86. The additive composition according to Claim 79, wherein the nitrogen-containing polymer is a vinylformamide-vinylamine copolymer.
- 20 87. The additive composition according to Claim 79, wherein the nitrogen-containing polymer is an ethyleneimine polymer.
88. The additive composition according to Claim 79, wherein the
25 nitrogen-containing polymer is present in the composition in an amount from 4% to 20% by dry weight.
89. The additive composition according to Claim 79, wherein the reactive agent comprises a polyaldehyde.
- 30 90. The additive composition according to Claim 79, wherein the reactive agent comprises a dialdehyde.

91. The additive composition according to Claim 79, wherein the reactive agent comprises glyoxal.
- 5 92. The additive composition according to Claim 79, wherein the reactive agent comprises a dicarboxylic anhydride.
93. The additive composition according to Claim 79, wherein the reactive agent comprises a maleic anhydride copolymer.
- 10 94. The additive composition according to Claim 79, wherein the reactive agent comprises a styrene maleic anhydride copolymer.
95. The improvement according to Claim 79, wherein the reactive agent
15 comprises a zirconium salt.
96. The additive composition according to Claim 79, wherein the reactive agent comprises a gluteraldehyde; a succinic dialdehyde; a blocked glyoxal; a cationic amine epichlorohydrin polymer; an
20 amide-epichlorohydrin polymer; a potassium zirconium carbonate; an ammonium zirconium carbonate; a ketone formaldehyde; a styrene maleic anhydride copolymer; a cyclic amide condensate; a polyacid; a polyacrylic acid selected from polyacrylic acid and polymethacrylic acid; a polyacid ester; a polyacid ester selected from polymeth-
25 acrylate and polymethylmethacrylate; a polyvinyl alcohol ester; or a polyvinyl alcohol- acetoacetic acid ester.
97. The additive composition according to Claim 79, wherein the dry weight ratio of reactive agent:nitrogen-containing polymer in the
30 reactive polymeric composition is from 0.01 to 0.3.

98. The additive composition according to Claim 79, wherein the dry weight ratio of reactive agent:nitrogen-containing polymer in the reactive polymeric composition is from 0.025 to 0.1.
- 5 99. The improvement according to Claim 79, wherein the molar equivalent ratio of the reactive moieties of the reactive agent to nitrogen in the nitrogen-containing polymer is from 1:1 to 1:500.
- 10 100. The improvement according to Claim 79, wherein the molar equivalent ratio of the reactive moieties of the reactive agent to nitrogen in the nitrogen-containing polymer is from 1:10 to 1:200.
- 15 101. The improvement according to Claim 79, wherein the molar equivalent ratio of the reactive moieties of the reactive agent to nitrogen in the nitrogen-containing polymer is from 1:25 to 1:75.
- 20 102. The additive composition according to Claim 74, wherein the reactive agent is reversibly reacted with a carrier prior to being provided to the additive composition.
103. The additive composition according to Claim 102, wherein the carrier is a cellulose derivative, polyvinyl alcohol, or an inorganic carrier selected from clays, calcium carbonate and calcium oxide.
- 25 104. The additive composition according to Claim 102, wherein the carrier is a cellulose derivative.
105. The additive composition according to Claim 102, wherein the dry weight ratio of reactive agent:carrier is from 0.001:1 to 0.5:1.
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106. The additive composition according to Claim 102, wherein the dry weight ratio of reactive agent:carrier is from 0.01:1 to 0.1:1.
107. An additive composition for mixing into a cementitious blend
5 including an inorganic binder, an inorganic filler, the additive composition including a redispersible emulsion polymer composition as well as a nitrogen-containing additive polymer and a reactive agent capable of reacting with the nitrogen of the additive polymer *in situ* with the cementitious blend; and wherein the reactive agent is
10 also reactive with cellulose derivatives and vinyl alcohol polymers.
108. The additive composition according to Claim 107, wherein the redispersible emulsion polymer composition includes an emulsion polymer formed from one or more unbranched alkylcarboxylic acid
15 vinyl ester monomers, branched alkylcarboxylic acid vinyl ester monomers, alcohol methacrylic acid ester monomers, vinyl aromatic monomers, olefin monomers, diene monomers, or vinyl halide monomers.
- 20 109. The additive composition according to Claim 108, wherein the emulsion polymer comprises a copolymer of vinyl acetate and an olefin.
110. The additive composition according to Claim 108, wherein the olefin
25 comprises ethylene.
111. The additive composition according to Claim 108, wherein the emulsion polymer comprises a copolymer of vinyl acetate and a vinyl ester of a carboxylic acid.

112. The additive composition according to Claim 111, wherein the carboxylic acid comprises versatic acid.
113. The additive composition according to Claim 107, wherein the
5 nitrogen-containing additive polymer is present in the additive composition in an amount from 4% to 20% by dry weight.
114. The additive composition according to Claim 107, wherein the
10 redispersible powder is present in an amount of from 1% to 15% based on the dry weight of the cementitious blend and the additive composition mixed therewith.
115. The additive composition according to Claim 114, wherein the
15 redispersible powder is present in an amount of less than 8% based on the dry weight of the cementitious blend and the additive composition mixed therewith.
116. The additive composition according to Claim 114, wherein the
20 redispersible powder is present in an amount of less than 5% based on the dry weight of the cementitious blend and the additive composition mixed therewith.
117. The additive composition according to Claim 114, wherein the
25 redispersible powder is present in an amount of less than 2% based on the dry weight of the cementitious blend and the additive composition mixed therewith.
118. An additive composition for mixing into a cementitious blend
30 including an inorganic binder, an inorganic filler, the additive composition including a redispersible emulsion polymer composition comprising an emulsion polymer stabilized with a nitrogen-containing

stabilizing polymer and a reactive agent capable of crosslinking with the nitrogen of the stabilizing polymer *in situ* within the cementitious blend; and wherein the reactive agent is also reactive with cellulose derivatives and vinyl alcohol polymers.

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119. The additive composition according to Claim 118, wherein the redispersible emulsion polymer composition includes an emulsion polymer formed from one or more unbranched alkylcarboxylic acid vinyl ester monomers, branched alkylcarboxylic acid vinyl ester
10 monomers, alcohol methacrylic acid ester monomers, vinyl aromatic monomers, olefin monomers, diene monomers, or vinyl halide monomers.

120. The additive composition according to Claim 119, wherein the
15 emulsion polymer comprises a copolymer of vinyl acetate and an olefin.

121. The additive composition according to Claim 120, wherein the olefin
20 comprises ethylene.

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122. The additive composition according to Claim 118, wherein the emulsion polymer comprises a copolymer of vinyl acetate and a vinyl ester of a carboxylic acid.

25 123. The additive composition according to Claim 122, wherein the carboxylic acid comprises versatic acid.

124. The additive composition according to Claim 118, wherein the additive composition is present in an amount of from 1% to 15%
30 based on the dry weight of the cementitious blend and an additive composition mixed therewith.

- 5 125. The additive composition according to Claim 124, wherein the additive composition is present in an amount of less than 8% based on the dry weight of the cementitious blend and the additive composition mixed therewith.
- 10 126. The additive composition according to Claim 124, wherein the additive composition is present in an amount of less than 5% based on the dry weight of the cementitious blend and the additive composition mixed therewith.
- 15 127. The additive composition according to Claim 124, wherein the additive composition is present in an amount of less than 2% based on the dry weight of the cementitious blend and the additive composition mixed therewith.
- 20 128. The improvement according to Claim 118, wherein the nitrogen-containing polymer composition comprises an amine-functional polymer.
129. The improvement according to Claim 118, wherein the nitrogen-containing stabilizing polymer comprises an amide-functional polymer.
- 25 130. The additive composition according to Claim 118, wherein the nitrogen-containing stabilizing polymer is a vinyl alcohol and vinyl amine copolymer.
- 30 131. The additive composition according to Claim 118, wherein the nitrogen-containing stabilizing polymer contains from 2 mole percent to 30 mole percent vinyl amine.

132. The additive composition according to Claim 118, wherein the nitrogen-containing stabilizing polymer contains from 2 mole percent to 12 mole percent vinyl amine.
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133. The additive composition according to Claim 118, wherein the nitrogen-containing stabilizing polymer is a vinyl amine homopolymer.
134. The additive composition according to Claim 118, wherein the
10 nitrogen-containing stabilizing polymer is a vinylformamide-vinylamine copolymer.
135. The additive composition according to Claim 118, wherein the
15 nitrogen-containing stabilizing polymer is an ethyleneimine polymer.
136. The improvement according to Claim 118, wherein the molar equivalent ratio of the reactive moieties of the reactive agent to nitrogen in the nitrogen-containing polymer is from 1:1 to 1:500.
- 20 137. The improvement according to Claim 118, wherein the molar equivalent ratio of the reactive moieties of the reactive agent to nitrogen in the nitrogen-containing polymer is from 1:10 to 1:200.
- 25 138. The improvement according to Claim 118, wherein the molar equivalent ratio of the reactive moieties of the reactive agent to nitrogen in the nitrogen-containing polymer is from 1:25 to 1:75.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2008/013177

A. CLASSIFICATION OF SUBJECT MATTER

INV. C04B28/02 C04B28/06 C04B28/14 C04B40/00 C04B20/10

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)

C04B

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 practical, search terms used)

EPO-Internal

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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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.

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INTERNATIONAL SEARCH REPORT

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