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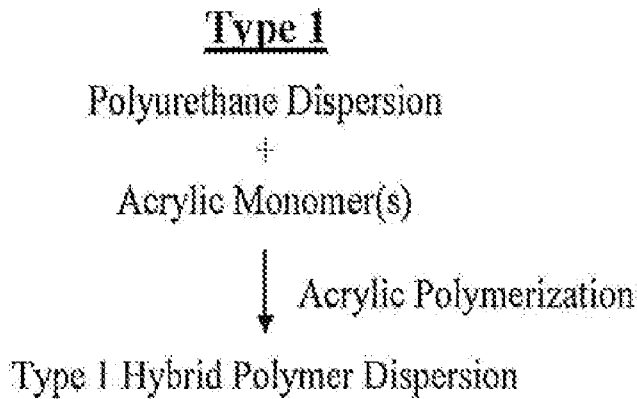
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(54) Title: PREMIXED HYBRID GROUT



(57) Abstract: Grouts, grout products and methods of applying such grouts that include a urethane- acrylic hybrid polymer dispersion (UA-HPD) and a filler material. The UA-HPD may be present in an amount of about 10-40% by weight of the composition, while the filler material may be present in an amount of about 60-90% by weight of the composition. Additional filler materials may also be provided within the UA-HPD grout composition to provide the resultant UA-HPD grout with desired characteristics and properties. The UA-HPD containing grouts are applied between spaced-apart tiles and/or masonry to fill voids and/or joints there-between.

Fig. 1A



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- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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- *with international search report (Art. 21(3))*
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PREMIXED HYBRID GROUT

Cross Reference to Related Applications

- 5 This invention disclosure claims priority from U.S. provisional patent application no. 61/829,143 filed May 30, 2013.

Technical Field

10 The present invention is directed to grout, and in particular, to premixed grouts containing a urethane/acrylic hybrid constituent as an active binding agent in the composition, and methods of using the premixed urethane/acrylic hybrid grouts of the invention.

Background Art

15 Various types of grouts exist in today's market for a wide variety of applications. A common usage of grouts is in the construction industry, and in particular, for use in joining tile, masonry and other types of building materials, as well as for filling joints and voids between such materials. Grouts exist in different forms including, for instance, cement-based grouts, polymer modified cement-based grouts, two-part polymer grouts
20 (e.g., epoxy grouts), and one-part polymer grouts. Each of these types of grouts has its advantages and disadvantages.

Cement-based grouts are relatively low cost, easy to apply, and eventually cure into a very hard surface. One of the more common and cost effective cement-based grout is
25 Portland cement. While cement-based grouts are advantageously low cost and readily available in the market place, one of the primary drawbacks of such grouts is in their mixing and slow-strength development. In mixing cement-based grouts, a cement-based material (e.g., a cementitious powder) is combined with water or a latex modifier (e.g., to form a polymer modified cement-based grout), which must then be well blended. A
30 mechanical mixer is often required to blending these cement-based mixtures, whereby such mixers may be costly and difficult to operate. Mixing via a mechanical mixer is also time-consuming process, messy, and often generates large amounts of dust. Other

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disadvantages of cement-based grouts are that they can often be non-uniform in color and even have poor stain resistance once cured.

Two-part polymer grouts exist as an alternative to cement-based grouts and/or polymer modified cement-based grouts. While two-part polymer grouts may have higher performance criteria, as compared to cement-based and/or polymer modified cement-based grouts, two-part grouts are often difficult to implement since such compositions must be used immediately after mixing. In these two-part polymer grout systems, the first and second parts must be combined in an appropriate ratio and mixed immediately prior to application. Once mixed, the two-part grout composition cures rather quickly, and as such, must be used in a relatively short period of time. Any unused portion of the two-part grout composition is generally wasted.

Epoxy-based grouts are an example of a two-part polymer grout systems, and may even be provided in the form of a three-part grout composition or system. While such epoxy grouts are often hard and resistant to chemicals and stains, drawbacks thereof are the multiple parts of such systems that require mixing as described above. Epoxy-based grouts can be extremely toxic, and often more expensive as compared to alternative grout materials.

As an alternative to grouts requiring mixing, currently available grouts also include premixed and/or one-part grout compositions. Since they come ready to use in a premixed state, these types of grouts are often easier to use than cementitious grouts and/or two- or three-part grout systems. One of the biggest advantages of such premixed grouts is that they do not need to be mixed with other constituent(s) prior to use thereof, which aids in their ease of use. Currently available premixed grouts are also relatively safe and do not generate dust.

A grout installer is provided with a longer time to work with premixed grouts since these types of grouts harden or cure primarily upon drying. In comparison, cementitious grouts often begin to cure or harden upon addition of the aqueous phase (e.g., water), while two-

part polymer grouts often begin to cure and harden upon the blending of such two parts. The longer dry time of premixed grouts provides the installer ample time to work with such grouts. Yet, this longer time dry or cure time can also be seen as a disadvantage since premixed grouts are slow to develop strength. The cure or hardening mechanism
5 for these materials is through loss of moisture (e.g., water), which can take several days to cure properly. As such, hardening in cool or humid environments is significantly slowed. Due to this moisture loss, several conventional premixed grouts are also susceptible to shrinkage and/or cracking, particularly, when used with water-absorbing materials (e.g., clay tiles). Another disadvantage is that the currently available premixed
10 grouts are often susceptible to staining.

Several premixed grout compositions exist in the market. For instance, currently available premixed grouts include those containing a water-based dispersion or latex polymer, along with fillers, thickeners and modifiers (e.g., defoamers, surfactants). The
15 water-based dispersion or latex polymer is typically a thermoplastic resin, and is used as a binder in the system. The composition is applied to grout joints and allowed to cure by drying to provide hardness and strength to the applied grout.

Premixed grouts having an acrylic binder (e.g., acrylic polymers and copolymers) were
20 among some of the first premixed grouts commercially available. These types of acrylic binder premixed grouts are designed for use in low demand applications, such as, for use in kitchen backsplashes and/or areas that are not subjected to water. U.S. Patent Nos. 3,859,233 and 4,472,540 (both to Barker) describe the use of acrylic binder dispersions in grout compositions.

25 Other premixed grouts on the market include those containing mere simple blends of polyurethane and acrylic. In these grouts, the polyurethane and acrylic components reside in the composition as separate constituents, and may be individually identified, isolated and separated from such composition. In these grouts, a polyurethane
30 component is added to the composition to improve performance of the acrylic-based material including, for instance, improving hardness, abrasion resistance and stain

resistance of the resultant grout. U.S. Patent No. 5,569,696 (to Abramson, et al.) discloses such a premixed grout containing a blend of a polyurethane part in combination with an acrylic part.

5 In further developments, polyurethane dispersion (i.e., a waterbourne polyurethane) grouts were introduced into the market. These types of premixed grouts contain the polyurethane dispersion as the active binder in the composition. U.S. Patent No. 7,183,338 (to Warren) describes grouts and grout products including waterbourne polyurethane binder systems. Polyurethane dispersion grout formulations generally
10 exhibit improved performance criteria over that of acrylic binder grout systems or such grouts blended with polyurethane. For instance, polyurethane (waterbourne polyurethane) binder grouts exhibit increased water resistance, hardness, durability and flexibility, as well as are enhanced stain resistance. However, these polyurethane dispersion (waterbourne polyurethane) grouts continue to have long cure or hardening
15 times, are expensive, and continue to need improved overall performance characteristics.

While many developments have been made in the grout industry, there continues to be a need for improved grout compositions having increased hardness, strength, durability, flexibility, water resistance, stain resistance, and even faster cure/hardening times as
20 compared to the above discussed prior art grouts.

Disclosure of Invention

Bearing in mind the problems and deficiencies of the prior art, it is therefore an object of the present invention to provide improved grout compositions that produce grout
25 products having increased hardness, strength, durability, flexibility, water resistance, stain resistance, and even faster cure/hardening times as compared to the above discussed prior art grouts.

It is another object of the present invention to provide grout compositions that include a
30 urethane-acrylic hybrid polymer dispersion (UA-HPD) as a binder in combination with filler materials. The filler material may be sand, silica sand, colored silica sand, fine

silica, glass, recycled glass, limestone, minerals, any other known filler, or any combinations thereof.

5 In various aspects of the invention, the UA-HPD grout formulations of the invention may include the UA-HPD binder in combination with a quartz filler material, as well as one or more additional constituent including, but not limited to, a freeze-thaw stabilizer co-solvent, plasticizer, short fibers, glass fibers, an adhesion promoter, a preservative, biocide, cellulose or starch ether, a thickening agent, silica fume, fumed silica, fumed silica/silica fume, a de-aerator, defoamer, and/or surfactant.

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It is another object of the present invention to provide UA-HPD grout compositions that include a urethane-acrylic hybrid polymer dispersion (UA-HPD) as a binder present in an amount of about 10-40% by weight of the composition, in combination with one or more filler materials present in an amount of about 60-90% by weight of the composition. The filler material may be sand, silica sand, colored silica sand, fine silica, glass, recycled glass, limestone, minerals, any other known filler, or any combinations thereof. These UA-HPD grout compositions may further include about 0-3 wt.% thickening agent, about 0-1 wt.% preservative, about 0-1 wt.% biocide, fungicide or mildewcide, about 0-3 wt.% defoamer, about 0-10 wt.% decorative fillers, about 0-15 wt.% film forming aids, about 15 0-5 wt.% crosslinking agents, about 0-5 wt.% stain resistant additives, about 0-5 wt.% adhesion promoters, about 0-5 wt.% coupling agents, about 0-5 wt.% anti-freeze agents, about 0-5 wt.% surfactants, about 0-10 wt.% water, about 0-5 wt.% water retention aid, about 0-5 wt.% UV stabilizers, about 0-5 wt.% acid or base component, about 0-5 wt.% strengthening fibers, as well as any combination of the foregoing materials.

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Another aspect of the invention is directed to UA-HPD grout compositions that include about 19-23 wt.% urethane-acrylic hybrid polymer dispersion as a binder, about 70-80 wt.% quartz filler present, with the remainder wt.% of the composition being one or more additional filler materials that add desired characteristics and properties to the UA-HPD 30 grout compositions. The quartz filler may be glass filler or silica sand. The additional filler materials may include one or more constituents comprising a freeze-thaw stabilizer

co-solvent, plasticizer, short fibers, glass fibers, an adhesion promoter, a preservative, biocide, cellulose or starch ether, a thickening agent, silica fume, fumed silica, fumed silica/silica fume, a de-aerator, defoamer, surfactant, and/or any combination of the foregoing.

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In still another aspect, the invention is directed methods of applying grout by providing spaced-apart building materials affixed to a substrate, whereby unfilled openings reside between the spaced-apart building materials. A grout comprising a one-part admixture of urethane-acrylic hybrid polymer dispersion (UA-HPD) as a binder and filler material is provided and applied between and into the unfilled openings, thereby filling such openings residing between spaced-apart building materials. The spaced-apart building materials may be tile or masonry that are affixed to a subfloor, wallboard or counter. The unfilled openings may be unfilled joints, cracks and lines residing between the spaced-apart building materials (e.g., joints, lines or cracks residing between adjacent tiles).

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The UA-HPD grout composition may include 10-40 wt.% of the UA-HPD, and 60-90 wt.% of the filler material. In various embodiments of the invention, the UA-HPD grout composition may include the UA-HPD, first filler material (e.g., a quartz filler material), and one or more additional filler materials that add desired characteristics and properties to the UA-HPD hybrid grout. In certain embodiments, the composition may comprise 19-23 wt.% UA-HPD, 70-80 wt.% quartz filler material, and a remainder wt.% of the one or more additional filler materials. The additional filler materials may include one or more of the following constituents: freeze-thaw stabilizer co-solvent, plasticizer, short fibers, glass fibers, an adhesion promoter, a preservative, biocide, cellulose or starch ether, a thickening agent, silica fume, fumed silica, fumed silica/silica fume, a de-aerator, defoamer, surfactant, decorative fillers, and any combination of the foregoing.

25

Brief Description of the Drawings

The features of the invention believed to be novel and the elements characteristic of the invention are set forth with particularity in the appended claims. The figures are for

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illustration purposes only and are not drawn to scale. The invention itself, however, both as to organization and method of operation, may best be understood by reference to the detailed description which follows taken in conjunction with the accompanying drawings in which:

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Figs. 1A and 1B show exemplary process flows of preparing a urethane-acrylic hybrid polymer dispersions (“UA-HPDs”) for use in the present grouts, grout products and methods of using the same in accordance with the various embodiments of the invention.

10 Fig. 2 shows dynamic mechanical analysis (DMA) data comparing a simple blend with UA-HPDs suitable for use in the various embodiments of the invention.

Fig. 3 shows tensile strengths of exemplary UA-HPDs suitable for use in the various embodiments of the invention.

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Fig. 4 is a table showing attributes of film coatings made using UA-HPDs suitable for use in the various embodiments of the invention.

20 Figs. 5A-B is a table showing various UA-HPD grout formulations in accordance with the numerous embodiments of the present invention.

Fig. 6 is a table showing one or more embodiments and/or examples of UA-HPD grout compositions in accordance with one or more embodiments of the invention.

25 Fig. 7 is a table showing one or more alternate embodiments and/or examples of UA-HPD grout compositions in accordance with various embodiments of the invention.

Fig. 8 is a table showing still further alternate embodiments and/or examples of UA-HPD grout compositions in accordance with various embodiments of the invention.

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Fig. 9 is a table showing comparative test results of the UA-HPD grout compositions of the invention as compared to results of a conventional one-part grout composition.

Description of the Preferred Embodiment(s)

5 In describing the preferred embodiment of the present invention, reference will be made herein to Figs. 1-9 of the drawings in which like numerals refer to like features of the invention.

The present invention is directed to a unique, ready to use grouting formulation suitable
10 for use in joining tile, masonry, mosaics and other types of building materials, as well as for filling joints and voids between such materials. There are many grouts currently available, with each grout having its own drawbacks, as discussed above. While polyurethane dispersion (i.e., waterborne polyurethane) grouts may have advantages over cement-based, two- or three-part grouts and even premixed acrylic binder grout
15 systems or blends thereof with polyurethane, such polyurethane dispersions (i.e., waterborne polyurethane) have disadvantages that in turn generate disadvantages in the grouts formed thereby.

Disadvantages of polyurethane dispersions are disclosed in the following references,
20 which are discussed herein below: "HYBRID VIGOUR: Waterborne Urethane-Acrylics combine High Performance with Low VOC Content;" *Lim, Galgoci, Walker and Yoxheimer*; ECJ (05), 24-30, (2005); and "Solvent-Free Urethane-Acrylic Hybrid Polymers for Coatings;" *Galgoci, Hegedus, Walker, Tempel, Pepe, Yoxheimer and Boyce*; *JCT CoatingsTech*, 2(13), 28-36 (February 2005).

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Waterborne polyurethane dispersions (referred to as "PUDs") have been used as binders for a variety of one-component coatings for wood (floors and furniture), plastic (business machine housings), leather, metal, and concrete. In general, PUDs are prepared by reacting an excess of diisocyanate with a polyol, dispersing the resulting prepolymer in
30 water, and completing the reaction by adding a water-soluble diamine to consume the

residual isocyanate and, thereby, chain-extend the prepolymer to a high molecular weight.

5 The dispersed PUD particles are usually anionically stabilized, which is commonly accomplished by incorporating a carboxylic acid-functional polyol into the backbone of the polyurethane and neutralizing the acid groups with a tertiary amine. Thus, in many cases, no external surfactants are present to contribute adversely to water sensitivity of PUD-based coatings. PUDs are available in both aromatic and aliphatic varieties.

10 One of the main disadvantages of PUDs is their relatively high cost. In order to reduce costs, formulators have blended PUDs with an acrylic polymer emulsion. However, the PUD and acrylic polymer remain as separate components (i.e., able to be separated and isolated from each other) within the blended formulation. Further, it has been found that the acrylics reduce the overall performance of the PUD binder within the composition.
15 On a molecular level, the acrylic polymers are not soluble in the polyurethane polymers, such that, the polymers remain phase-separated during use, which may diminish performance behavior.

To overcome the deficiencies of PUDs, and PUD and acrylic polymer blends, urethane-
20 acrylic hybrid polymer dispersions (referred to as "UA-HPD"), have been formulated. U.S. Patent No. 5,594,065 (to Tien, et al.), which is herein incorporated by reference in its entirety, describes urethane-acrylic hybrid polymer dispersions, which are commercially available from assignee Air Products and Chemicals, Inc. of Allentown, PA and sold under the trademark Hybridur®. These UA-HPD incorporate both urethane
25 and acrylic polymers into a single dispersion, whereby such constituents are chemically altered into a single, unique compound with such constituents being inseparable from each other (can not isolate one from the other).

30 UA-HPDs may be formed by different techniques and processes. Figs. 1A and 1B show exemplary alternate process flows for preparing a first UA-HPD (Type 1 hybrid) and a second UA-HPD (Type 2 hybrid). As shown in Fig. 1A, a Type 1 UA-HPD is

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formulated by first preparing a PUD followed by adding acrylic monomers to the PUD so that an acrylic polymer is formed in the presence of the PUD to generate the UA-HPD. Type 2 UA-HPDs may be formulated by forming a polyurethane prepolymer and adding acrylic monomers thereto, whereby the mixture is dispersed in water, and the urethane and acrylic polymerizations are completed concurrently.

The UA-HPD's are unique molecules and not a mere blend of one part with another part in the composition. It has been found that UA-HPD's generate a gel (via gel testing), have a single broad plateau for glass transition temperature (T_g) test, the polyurethane can not be extracted from the product, and the physical properties thereof are better than that of a simple waterborne polyurethane and acrylic polymer blend. All of the foregoing factors are evidence of cross-linking, which is indicative that an UA-HPD undergoes molecular change (i.e., it is a unique molecule and not a mere blend). In comparison, it has also been found that waterborne polyurethane and acrylic polymer blends do not generate a gel (via gel testing), produce two unique peaks in T_g testing, and the polyurethane or acrylic may be extracted from the blend, all of which are indicative that the two components remain separate in solution with no cross-linking.

Figure 2 shows dynamic mechanical analysis (DMA) data comparing a simple blend with different UA-HPD's. As shown, the simple blend has 2 distinct tan delta ($\tan \delta$) peaks, which correspond to the glass transition temperatures (T_g) for the phase-separated urethane and acrylic polymers. The Type 1 UA-HPD hybrid prepared from Fig. 1A shows 2 T_g peaks, but the peaks have become somewhat broader, which is indicative of molecular mixing.

Alternatively, the Type 2 UA-HPD hybrid prepared from Fig. 1B, in which the urethane prepolymer and acrylic monomers are homogeneously mixed prior to dispersion and subsequent polymerization, shows only a single, very broad $\tan \delta$ peak. The single peak, which spans the temperature range between the theoretical T_g s of the urethane and acrylic polymers, shows a significant amount of polymer-polymer, wherein it is believed these different polymer molecules are intertwined or cross-linked similar to that of an

interpenetrating network (IPN). This improved compatibility for the hybrids (especially Type 2) is at least partly the result of some molecular-level grafting (cross-linking) of the two polymers.

5 The Type 1 UA-HPD and Type 2 UA-HPD have been used to form film coatings, and the resultant coating have exhibited enhanced strength over that of PUDs or simple blends (e.g., a polyurethane blended with an acrylic polymer). Figure 3 shows tensile strengths of films prepared from blends and the Type 1 UA-HPD and Type 2 UA-HPD, which are compared to that predicted by a linear rule of mixtures. The blend and the UA-HPD
10 hybrids contained equal amounts of the same urethane and acrylic polymers. As shown, the tensile strength of the blend was found to be lower than that predicted by the simple averaging rule. On the other hand, the hybrid systems show higher tensile strengths than predicted. The Type 1 hybrid system showed slightly higher tensile strength than predicted. The Type 2 hybrid was found to have a tensile strength approximately equal to
15 that of the polyurethane. The Type 2 hybrid has the increased phase morphology of a unique urethane/acrylic polymer system, as compared to the Type 1 hybrid.

UA-HPDs may be prepared using an aprotic solvent such as N-methylpyrrolidone (NMP). The NMP is required in the polyurethane prepolymer step to dissolve the
20 dimethylolpropionic acid (DMPA), which is a crystalline carboxylic acid-polyol that is virtually insoluble in the polyoldiisocyanate mixture that reacts to form the urethane prepolymer. The NMP remains in the final dispersion product, with an amount that may range from 3% to 8% in the UA-HPD. NMP is beneficial in the final product as a coalescing solvent for film formation. However, since NMP and high levels of residual
25 acrylic monomers are undesired due to odor and regulatory issues, UA-HPDs are also available as NMP-free, low residual monomer UA-HPDs having acceptable workability and results criteria.

To date, the use of UA-HPDs has been limited to film or coating formations. Attributes
30 of test results from such films/coatings are shown in Fig. 4. The present invention extends the use and application of the various types of UA-HPDs by providing grouts,

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grout products and methods of using such grouts, whereby the grout contains at least a urethane-acrylic hybrid polymer dispersion (“UA-HPD”) as the active binding agent in combination with one or more filler materials.

5 While the Type 1 UA-HPDs and Type 2 UA-HPDs are described and discussed herein (as well as those in U.S. Patent No. 5,594,065), it should be appreciated and understood that the various grouts, grout products and methods of using such grouts of the invention are not limited to such UA-HPDs. Rather, any and all current and future UA-HPD formulations may be implemented in accordance with the various grouts, grout products
10 and methods of use thereof in accordance with the numerous embodiments of the invention.

While not meant to limit the invention, in one or more embodiments a preferred UA-HPD(s) for use in one or more embodiments may include those sold by Air Products and
15 Chemicals, Inc. of Allentown, PA, under the trademark Hybridur®. Again, it should be appreciated and understood that the present invention is not limited to the foregoing described urethane-acrylic hybrid polymer dispersions, and may include any known and/or to be developed urethane-acrylic hybrid polymer dispersion(s). Such UA-HPD(s) may contain a solvent (e.g., N-methylpyrrolidone (NMP) solvent), or be solvent-free
20 versions of UA-HPDs. The UA-HPD(s) suitable for use in one or more embodiments of the invention exhibit the hybrid nature of being a unique molecule formulated within the polymer dispersion (i.e., it is not a blend or mere mixture of two or more constituents).

Referring to the various grouts, grout products and methods of using such grouts in accordance with the invention, the table of Figs. 5A-B show various formulations of the
25 present UA-HPD containing grout compositions in accordance with different embodiments of the invention.

In one or more embodiments, the premixed grouts and grout products of the invention include a urethane-acrylic hybrid polymer dispersion (“UA-HPD”) as the active binding
30 agent in combination with one or more filler materials. The UA-HPD binding agent may be provided in an amount of about 10%-40% by weight of the total composition. In such

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embodiments, the filler materials may be provided in an amount of about 60%-90% by weight of the composition. Filler materials may be any material that fills voids between larger particles to improve shrinkage, hardness, reduce porosity, improve water resistance, etc. of the final grout. For instance, fillers suitable for use include, but are not
5 limited to, sand, silica sand, colored silica sand, fine silica, glass, recycled glass, recycled glass filler, limestone (calcium carbonate), minerals, any other known filler, or even combinations of the foregoing.

In one or more embodiments the premixed grouts and grout products of the invention
10 may include one or more of the additional constituents as listed in Figs. 5A-B. In particular, in addition to the UA-HPD and filler materials, the present grouts may further include a thickener for improving shelf stability of the grout. The thickening agent minimizes separation or settling of ingredients within the composition. It also improves rheology or workability of the final grout product. Suitable thickeners include, but are
15 not limited to, cellulose ether, starch ether, fibers, silica fume, fumed silica, associative and alkali swellable thickeners, an acrylic thickener, and the like. Thickening agents may be present in the compositions of the invention in amounts ranging from about 0-3% by weight of the composition.

Decorative fillers may also be provided within the present UA-HPD grouts. These
20 decorative fillers improve aesthetics of the grout product, and may even provide translucency or reflective effects in the final cured product. Decorative fillers may include, but are not limited to, reflective particles, glass or colored beads, dyes, pigments, and the like. The decorative fillers may be provided in the grout compositions in
25 amounts ranging from about 0-10% by weight of the composition.

In addition, the various UA-HPD grout compositions of the invention may include a variety of alternate binders in addition to the UA-HPD binders. These alternate binders may be provided in the present grout formulations, in addition to the UA-HPD binder, for
30 reducing costs of the resultant grout products and compositions. The alternate binders may be added in amounts of about 0%-25% by weight of the total composition, and may

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include blends with conventional binders such as acrylics. Fibers may also be added to the present grout compositions in amounts of about 0%-5% by weight. The fibers are added to improve cohesive strength of the instant wet formulations, improve their strength when cured, reduce shrinkage and even reduce cracking. Various types of fibers
5 may be added including, but not limited to, polymer or glass fibers of various lengths. The grout compositions may also include polyethylene fibers.

Preservatives or biocides may also be provided in the present grout compositions. The preservative/biocide component increases the shelf life of the present grout products by
10 inhibiting biological growth. Preservatives or biocides may be present in the compositions of the invention in amounts ranging from about 0-1% by weight of the composition. The compositions may also include one or more fungicides and/or mildewcides for improving performance of the grout by minimizing biological growth during use of the grouts, as well as the final cured product. Fungicides and/or
15 mildewcides may be present in the grouts of the invention in amounts ranging from about 0-1% by weight of the composition.

Another constituent that may be added to the UA-HPD grout compositions of the invention are defoamers. A defoamer reduces air entrainment during manufacturing and
20 application. It also improves strength and stain resistance of the final cured grouts of the invention. Defoamers may be present in the UA-HPD grouts of the invention in amounts ranging from about 0-3% by weight of the composition.

The UA-HPD grouts of the invention may further include film forming aids (co-solvents)
25 in an amount ranging from about 0-15% by weight of the composition. The film forming aids improve film formation at lower temperatures, and as such, provide higher strength and hardness. They may also improve stability to freezing and thawing of the present grouts. Crosslinkers or other reactive components may also be added to the present UA-HPD grout compositions in amounts ranging from about 0-5% by weight of the
30 composition. These constituents are added to improve hardness, water resistance, chemical resistance, stain resistance, and abrasion resistance.

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Adhesion promoters or coupling agents may further be added to the present UA-HPD grouts in amounts ranging from about 0-5% by weight of the composition. These adhesion promoters or coupling agents improve bonding or compatibility between binder
5 and fillers or substrates. The instant UA-HPD grout formulations of the invention may also include stain resistant additives including, but not limited to, wax emulsions, wax particles, fluoro-carbon based particles and emulsions, silicone-based particles and emulsions, hydrophobes such as oleates and stearates, and the like. These stain resistant additives may be added in amounts of 0-5% by weight to improve resistance to water-
10 based and/or oil-based stains, as well as improve water and oil resistance.

Surfactants may be added to the instant UA-HPD grout compositions in amounts of 0-5% by weight of the composition to improve wetting of fillers and substrates. These surfactants also help to reduce viscosity, eliminate entrained air, and even stabilize the
15 grout formulation. Water may be added in amounts of 0-10% by weight to reduce viscosity and act as a diluent. Still further, water retention aids (e.g., cellulose ethers, starches, co-solvents, etc.) may be added in amounts of 0-5% by weight to hold or retain moisture within the present UA-HPD grout compositions during use thereof. By holding or retaining water, the water retention improve application characteristics and assist
20 cleanup.

The various UA-HPD grouts of the even may also include about 0-5%, by weight, of UV stablizers, and about 0-5%, by weight, of acids or bases. The UV stabilizers improve resistance to UV light, as well as provide for improved color stability and reduce
25 yellowing or discoloration. The acids or bases allow for the adjustment of the composition pH to improve formulation stability. Still further, the instant UA-HPD grouts may be include anti-freeze components (e.g., glycols, various co-solvents, etc.) in amounts of 0-5%, by weight, to reduce the freezing point of the composition for preventing damage thereof during extreme temperatures. Hence, the anti-freeze
30 components also improve storage stability of the instant UA-HPD grouts.

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While the above embodiments disclose various formulations and constituents that may be added to the instant grout compositions that at least include an UA-HPD composition, it should be appreciated that the invention is not limited to such formulations. Referring to Fig. 6, one or more exemplary embodiments of the grout compositions of the invention are shown including, by weight percent of the composition: 19.5-23 wt.% UA-HPD (e.g., Hybridur® dispersion); 70-80 wt.% silica sand/recycled glass filler (100 mesh quartz particles) (preferably, 72-80 wt.% or 70-78 wt.%); 0.80-1.5 wt.% freeze-thaw stabilizer/co-solvent or plasticizer (preferably, 0.85-0.95 wt.% or 0.8-1.5 wt.%); 0-0.3 wt.% short fiber/rheological modifier -short fibers (polyethylene) or glass fibers; 0.14-0.2 wt.% adhesion promoter; 0.002-0.005 wt.% preservative; 0.01-0.02 wt.% biocide; 0-0.25 wt.% cellulose ether or starch ether; 0-0.20 wt.% acrylic thickener; 0-0.06 wt.% fumed silica/silica fume; 0.04-0.18 wt.% deaerator, defoamer or surfactant (preferably, 0.12-0.18 wt.% or 0.04-0.08 wt.%); and optionally 0-5 wt. % decorative dazzle fillers.

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Still other exemplary embodiments of the invention are shown in Figs. 7 and 8. Referring to Fig. 7, in one or more exemplary embodiments of the invention the present UA-HPD grouts of the invention may be formed as a translucent grout product. In these embodiments, the translucent UA-HPD grouts may include in combination : a first freeze thaw stabilizers/co-solvent (e.g., hydrophilic ethane-1, 2-diol) in an amount of 0.7-0.95 wt.%; a second freeze thaw stabilizers/co-solvent (e.g., hydrophobic glycol ether) in an amount of 0.7-0.95 wt.%; an in can preservative (e.g., a blend of benzisothiazolin and 2-hydroxyethyl-triazine) in an amount of 0.002-0.005 wt.%; a biocide (e.g., Microban™) in an amount of 0.01-0.02 wt.%; cellulose ether (e.g., hydroxyethylcellulose) in an amount of 0-0.25 wt.%; acrylic thickener (e.g, HEUR based rheological modifier) in an amount of 0-0.2 wt.%; anti-settling aid (e.g, modified urea or modified urea based anti-settling aid) in an amount of 0.05-0.1 wt.%; UA-HPD (i.e., hybrid polymer dispersion) in an amount of 15-20 wt.%; a de-aerator (e.g., a siloxane based defoamer) in an amount of 0.25-0.5 wt.%; and glass filler (e.g., recycled glass) in an amount of 70-90 wt.%. It should be appreciated that any combination of these constituents may be implemented in preparing the UA-HPD grouts and UA-HPD grouts products of the

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invention, or all of such constituents may be used in combination with each other in the above disclosed weight percent ranges.

As shown in Fig. 8, in one or more other exemplary embodiments of the invention, the
5 UA-HPD grouts of the invention may be formed as scaled-up sanded UA-HPD grout formulations. In one or more embodiments, these UA-HPD grouts may include at least one or more of the following constituents: a first freeze thaw stabilizers/co-solvent (e.g., hydrophilic ethane-1, 2-diol) in an amount of 0.7-0.95 wt.%; a second freeze thaw stabilizers/co-solvent (e.g., hydrophobic glycol ether) in an amount of 0.7-0.95 wt.%; an
10 in can preservative (e.g., a blend of benzisothiazolin and 2-hydroxyethyl-triazine) in an amount of 0.002-0.005 wt.%; a biocide (e.g., MicrobanTM) in an amount of 0.01-0.02 wt.%; cellulose ether (e.g., hydroxyethylcellulose) in an amount of 0-0.25 wt.%; acrylic thickener (e.g., HEUR based rheological modifier) in an amount of 0-0.2 wt.%; anti-settling aid (e.g., modified urea) in an amount of 0.05-0.1 wt.%; UA-HPD (i.e., hybrid
15 polymer dispersion) in an amount of 15-20 wt.%; a de-aerator (e.g., a siloxane based defoamer) in an amount of 0.25-0.5 wt.%; and sand filler (e.g., colored silica sand) in an amount of 70-90 wt.%.

The UA-HPD containing grout compositions of the invention have superior performance
20 as compared to mere PUD containing grout compositions. The various UA-HPD containing grout compositions of the invention have enhanced hardness, abrasion resistance and stain resistance, as well as harden or cure at an efficient and easy to use rate, as compared to currently available ready to use grouts (in particular, PUD containing grouts). The improved performance of the instant UA-HPD containing grouts
25 is in the unique interpenetrating network microstructure of the urethane-acrylic hybrid polymer dispersions, which is due to the interaction and grafting on a molecular level between the urethane and acrylic portions.

The various UA-HPD grouts of the invention preferably comprise premixed and/or one-
30 part grout composition mixtures that are easy and ready to use formulations, may be fabricated in a variety of colors, include different decorative features (e.g., sparkles,

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speckled patterns, etc.), resist to discoloration, fading and staining, and are resistant to abrasions and cracking due to applied stresses. The present UA-HPD grouts may be used in the installation of a variety of different tiles, masonry and other types of building materials, as well as for filling joints and voids between such materials. In use, the present UA-HPD grouts of the invention may be applied directly from a container,
5 without mixing, onto a substrate (e.g., floor, wall, counter, etc.) to fill openings, spaces, joints, cracks and/or lines residing there-between.

The premixed UA-HPD grouts of the invention have a workable consistency that enables such UA-HPD grouts to be applied into and fill thick and/or thin lines and cracks residing
10 between adjacent masonry, particularly, tiles (e.g., ceramic tiles) after such tiles have been affixed (e.g., with adhesive) to a substrate (e.g., subfloor, wall panel, counter, etc.). A trowel and/or other masonry tools may be used to work the UA-HPD grouts into and fill these lines and cracks. Once worked into the lines and cracks, excess UA-HPD grout material is removed from the surface of the tile, and the UA-HPD grouts of the invention
15 are allowed to cure over a period of approximately twenty-four hours.

Referring to Fig. 9, numerous different sanded formulation embodiments of the present UA-HPD grouts were prepared and comparison tested to a conventional one-part
20 premixed waterbourne polyurethane blend grout applied and cured under the same processing conditions. In the example comparative inventive UA-HPD grouts shown in Fig. 9, amounts of selected constituents were altered (i.e., +15%, -15%) in the grout formulations, and all allowed to cure under the same processing conditions. For instance, in the examples the following constituents were altered +15%, -15%: in examples 1 and
25 1A thickener wt.%, in examples 2 and 2A cellulose ether wt.%, in examples 3 and 3A anti-settling aid wt.%, in examples 4 and 4A defoamer wt.%, and in examples 5 and 5A sand filler wt.%. In examples 6 and 6A, the test UA-HPD grouts were altered by fabricating formulations in different aqueous phases with example 6 having +10% solvent and example 6A having -10% solvent.

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The comparative grouts were set up for a series of tests to measure the hardness and compressive strengths, including, testing for specific gravity (density), A shore hardness and compressive strength (psi, modified ANSI 118.3 method). The specific gravity (density) was measured by filling a standard cup of known volume and weight of material in the cup was recorded. For the hardness test, a standard cap was filled with the material and allowed to harden at ambient temperature for 24 hours. Shore A hardness was then recorded for each tested grout after 24 hours. For the compressive strength test, a standard one-inch cylindrical mold was filled with the material as per ANSI 118.3. The molds were heat cured for 3 days in a 50 deg. C oven. The samples were then de-molded and cured in a controlled temp chamber and tested after 25 days (28 day measurement from the day of filling the molds).

The results of Fig. 9 show that the specific gravity of each of the formulas was maintained within a certain range, which indicates that the workability was kept relatively constant. Also, all of the instant UA-HPD grout formulations had similar consistency for use as a grout. The table shows that the present UA-HPD grouts and grout products of the invention have both superior hardness after 24 hours and compressive strength as compared to the tested commercially available one-part water borne-polyurethane blend grout. The increased hardness measures of the UA-HPD grouts indicates quicker walk over time, or time to traffic. The compressive strength of one inch UA-HPD grout cylinders as tested per modified ANSI 118.3 were much higher than that of the commercially available one-part water borne-polyurethane blend grout. All of this performed testing and results shown in Fig. 9 evidences that the instant UA-HPD grouts and grout products of the invention are superior in performance as compared to the tested prior art water borne polyurethane based grout.

While the present invention has been particularly described, in conjunction with a specific preferred embodiment, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art in light of the foregoing description. It is therefore contemplated that the appended claims will embrace any such alternatives,

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modifications and variations as falling within the true scope and spirit of the present invention.

Thus, having described the invention, what is claimed is:

5

Claims

1. A grout composition comprising:
a urethane-acrylic hybrid polymer dispersion (UA-HPD) binder; and
filler material.
5
2. The grout composition of claim 1 wherein the UA-HPD is present in an amount of
about 10-40% by weight of the composition.
3. The grout composition of claim 2 wherein filler material is present in an amount
10 of about 60-90% by weight of the composition.
4. The grout composition of claim 1 wherein filler material is selected from the
group consisting of sand, silica sand, colored silica sand, fine silica, glass, recycled glass,
limestone, minerals, any other known filler, and combinations thereof.
15
5. The grout composition of claim 1 further including a thickening agent.
6. The grout composition of claim 5 wherein the thickening agent is selected from
the group consisting of cellulose ether, starch ether, fibers, silica fume, fumed silica,
20 associative and alkali swellable thickeners, an acrylic thickener, and combinations
thereof.
7. The grout composition of claim 1 further including a preservative.
- 25 8. The grout composition of claim 1 further including a biocide, fungicide or
mildewicide.
9. The grout composition of claim 1 further including a defoamer.
- 30 10. The grout composition of claim 1 further including decorative fillers.

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11. The grout composition of claim 10 wherein the decorative fillers are selected from the group consisting of reflective particles, glass or colored beads, dyes, pigments, and combinations thereof.
- 5 12. The grout composition of claim 1 further including film forming aids.
13. The grout composition of claim 1 further including crosslinking agents.
14. The grout composition of claim 1 further including stain resistant additives.
- 10 15. The grout composition of claim 15 wherein the stain resistant additives are selected from the group consisting of wax emulsions, wax particles, fluoro-carbon based particles and emulsions, silicone-based particles and emulsions, hydrophobes, oleates, stearates, and combinations thereof.
- 15 16. The grout composition of claim 1 further including adhesion promoters.
17. The grout composition of claim 1 further including coupling agents.
- 20 18. The grout composition of claim 1 further including anti-freeze agents.
19. The grout composition of claim 1 further including surfactants.
20. The grout composition of claim 1 further including a coloring or pigment agent.
- 25 21. The grout composition of claim 1 further including water or a water retention aid.
22. The grout composition of claim 1 further including UV stabilizers.
- 30 23. The grout composition of claim 1 further including an acid or base component.

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24. The grout composition of claim 1 further including strengthening fibers.
25. A grout composition comprising:
urethane-acrylic hybrid polymer dispersion (UA-HPD) in an amount of about 10-40%
5 by weight; and
one or more filler materials present in an amount of about 60-90% by weight.
26. The grout composition of claim 22 further including a thickening agent in an
amount of about 0-3 wt.%.
10
27. The grout composition of claim 26 wherein the thickening agent is selected from
the group consisting of cellulose ether, starch ether, fibers, silica fume, fumed silica,
associative and alkali swellable thickeners, an acrylic thickener, and combinations
thereof.
15
28. The grout composition of claim 22 further including a preservative in an amount
of about 0-1 wt.%.
20
29. The grout composition of claim 22 further including a biocide, fungicide or
mildewcide in an amount of about 0-1 wt.%.
25
30. The grout composition of claim 22 further including a defoamer in an amount of
about 0-3 wt.%.
30
31. The grout composition of claim 22 further including decorative fillers in an
amount of about 0-10 wt.%.
30
32. The grout composition of claim 31 wherein the decorative fillers are selected from
the group consisting of reflective particles, glass or colored beads, dyes, pigments, and
combinations thereof.

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33. The grout composition of claim 22 further including film forming aids in an amount of about 0-15 wt.%.
34. The grout composition of claim 22 further including crosslinking agents in an amount of about 0-5 wt.%.
35. The grout composition of claim 22 further including stain resistant additives in an amount of about 0-5 wt.%.
36. The grout composition of claim 35 wherein the stain resistant additives are selected from the group consisting of wax emulsions, wax particles, fluoro-carbon based particles and emulsions, silicone-based particles and emulsions, hydrophobes, oleates, stearates, and combinations thereof.
37. The grout composition of claim 22 further including adhesion promoters in an amount of about 0-5 wt.%.
38. The grout composition of claim 22 further including coupling agents in an amount of about 0-5 wt.%.
39. The grout composition of claim 22 further including anti-freeze agents in an amount of about 0-5 wt.%.
40. The grout composition of claim 22 further including surfactants in an amount of about 0-5 wt.%.
41. The grout composition of claim 22 further including water in an amount of about 0-10 wt.%.
42. The grout composition of claim 22 further including a water retention aid in an amount of about 0-5 wt.%.

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43. The grout composition of claim 22 further including UV stabilizers in an amount of about 0-5 wt.%.
- 5 44. The grout composition of claim 22 further including an acid or base component in an amount of about 0-5 wt.%.
45. The grout composition of claim 22 further including strengthening fibers in an amount of about 0-5 wt.%.
- 10 46. A grout composition comprising:
urethane-acrylic hybrid polymer dispersion (UA-HPD) as a binder present in an amount of about 19-23 wt.%;
a quartz filler present in an amount of about 70-80 wt.%; and
15 one or more additional filler materials that add desired characteristics and properties to said grout.
47. The grout composition of claim 46 wherein the quartz filler comprises glass filler.
- 20 48. The grout composition of claim 46 wherein the quartz filler comprises silica sand.
49. The grout composition of claim 46 wherein the additional filler materials include one or more constituent selected from the group consisting of freeze-thaw stabilizer co-solvent, plasticizer, short fibers, glass fibers, an adhesion promoter, a preservative,
25 biocide, cellulose or starch ether, a thickening agent, silica fume, fumed silica, fumed silica/silica fume, a de-aerator, defoamer, surfactant, and any combination of the foregoing.
50. The grout composition of claim 49 wherein the additional filler comprises said
30 freeze-thaw stabilizer co-solvent or plasticizer in an amount of about 0.80-1.5 wt.%.

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51. The grout composition of claim 50 wherein the additional filler comprises said adhesion promoter in an amount of about 0.14-0.2 wt.%.
5
52. The grout composition of claim 51 wherein the additional filler comprises said preservative in an amount of about 0.002-0.005 wt.%.
5
53. The grout composition of claim 52 wherein the additional filler comprises said deaerator, defoamer, surfactant are present each in amounts of about 0.04-0.18 wt.%.
10
54. The grout composition of claim 49 wherein the additional filler comprises said short fibers or glass fibers in an amount of about 0-0.3 wt.%.
10
55. The grout composition of claim 49 wherein the additional filler comprises said biocide in an amount of about 0-0.02 wt.%.
15
56. The grout composition of claim 49 wherein the additional filler comprises said cellulose or starch ether in an amount of about 0-0.25 wt.%.
15
57. The grout composition of claim 49 wherein the additional filler comprises said thickening agent is an acrylic thickener in an amount of about 0-0.20 wt.%.
20
58. The grout composition of claim 49 wherein the additional filler comprises said cabosil /silica Fume in an amount of about 0-0.06 wt.%.
20
59. The grout composition of claim 46 further including decorative fillers present in an amount of about 0-5 wt. %.
25
60. A method of applying grout between spaced-apart building materials comprising:
providing spaced-apart building materials affixed to a substrate whereby unfilled
30 openings reside between said spaced-apart building materials;

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providing a UA-HPD hybrid grout comprising a one-part admixture of urethane-acrylic hybrid polymer dispersion (UA-HPD) as a binder and filler material; and applying the UA-HPD hybrid grout to fill said unfilled openings residing between said spaced-apart building materials.

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61. The method of claim 60 wherein said spaced-apart building materials comprise spaced-apart tiles or masonry.

10

62. The method of claim 60 wherein said spaced apart building materials are affixed to a subfloor.

63. The method of claim 60 wherein said spaced apart building materials are affixed to a wallboard.

15

64. The method of claim 60 wherein said spaced apart building materials are affixed to a counter.

20

65. The method of claim 60 wherein said UA-HPD hybrid grout comprises 10-40 wt.% of said UA-HPD, and 60-90wt.% of said filler material.

66. The method of claim 60 wherein said UA-HPD hybrid grout comprises said UA-HPD, quartz filler material, and further includes one or more additional filler materials that add desired characteristics and properties to said UA-HPD hybrid grout.

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67. The method of claim 66 wherein said UA-HPD hybrid grout comprises 19-23 wt.% of said UA-HPD, 70-80 wt.% of quartz filler material, and a remainder wt.% of said one or more additional filler materials.

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68. The method of claim 67 wherein said quartz filler comprises glass filler.

69. The method of claim 67 wherein said quartz filler comprises silica sand.

70. The method of claim 67 wherein said additional filler materials include one or more constituent selected from the group consisting of freeze-thaw stabilizer co-solvent, plasticizer, short fibers, glass fibers, an adhesion promoter, a preservative, biocide,
5 cellulose or starch ether, a thickening agent, silica fume, fumed silica, fumed silica/silica fume, a de-aerator, defoamer, surfactant, decorative fillers, and any combination of the foregoing.

71. The method of claim 60 wherein said unfilled openings comprise unfilled joints,
10 cracks and lines between said spaced-apart building materials.

72. A method for applying grout between spaced-apart tiles comprising: providing a tile grout comprising a urethane-acrylic hybrid polymer dispersion (UA-HPD), and a filler material; and applying the tile grout between and within joints residing between the
15 spaced-apart tiles.

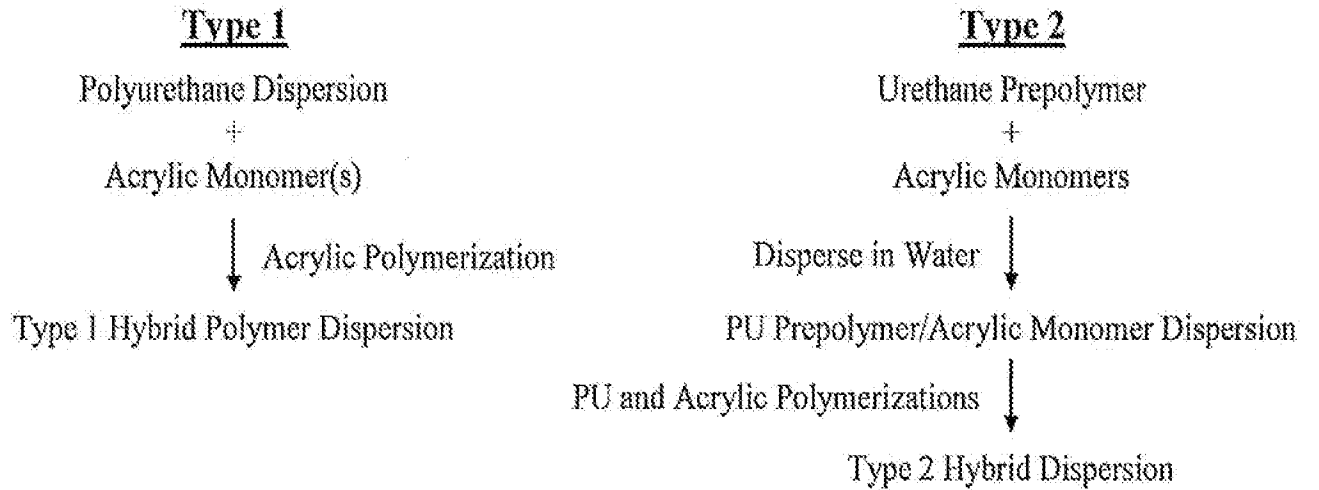


Fig. 1A

Fig. 1B

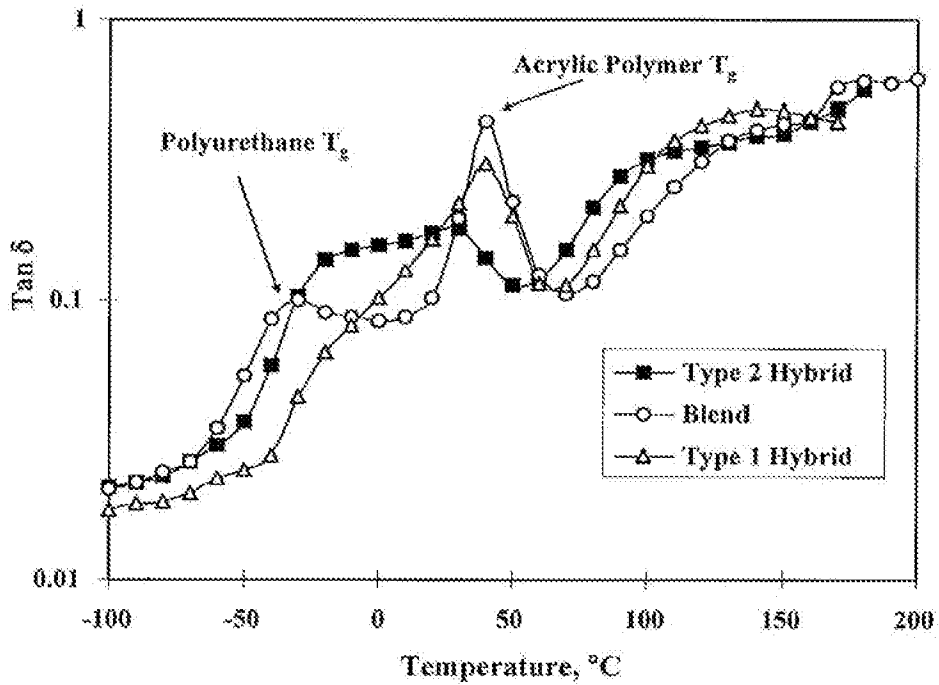


Fig. 2

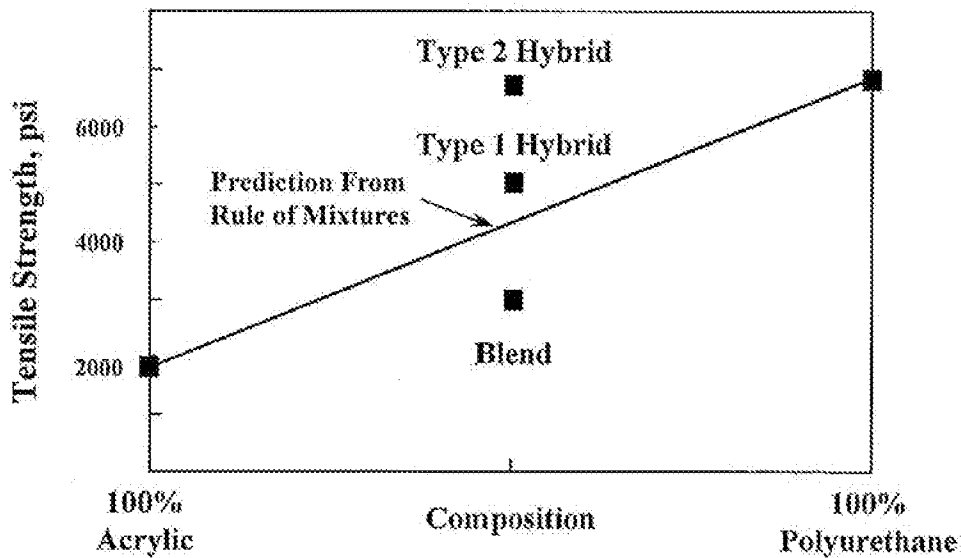


Fig. 3

Table 1. Typical Characteristics of the Type 2 Hybrid Polymer Dispersions Evaluated.

Property	Hybrid A ^a	Hybrid B ^b	Hybrid A _{SF} ^c	Hybrid B _{SF} ^d
Appearance	Opaque, Slight Milky	Opaque, Slight Milky	Opaque, Slight Milky	Opaque, Slight Milky
Viscosity, cP, 25 °C, Brookfield	50 - 150	50 - 150	50 - 150	50 - 150
Non-Volatiles, % by weight	39 - 41	39 - 41	39 - 41	39 - 41
Solvent Content, % by weight	6	6	<0.2	<0.1
Solvent	NMP	NMP	Acetone	Acetone
VOC, g/L (lbs/gal) ^e	160 (1.33)	164 (1.37)	30 (0.25)	24 (0.20)
Density, g/mL (lbs/gal)	1.03 (8.60)	1.04 (8.70)	1.05 (8.76)	1.07 (8.93)
pH	7.5 - 9.0	7.5 - 9.0	7.5 - 9.0	7.5 - 9.0
Acid Number, mg KOH/g ^f	14.5	14.5	16.0	14.5
T _g Range, °C ^g	-35 to 35	-35 to 100	-35 to 35	-35 to 100
Neutralizing Amine ^h	TEA	TEA	TEA	DMEA
Particle Diameter (Wt. Avg.), nm	75 - 85 ⁱ	75 - 85 ⁱ	75 - 85 ⁱ	75 - 85 ⁱ
Residual Acrylic Monomer, ppm	500 ⁱ	500 ⁱ	50 - 200 ⁱ	10 - 50 ⁱ
Particle Charge	Anionic	Anionic	Anionic	Anionic

^{a, b, c, d} Refer to Appendix C for material identification.
^e VOC includes contribution from the neutralizing amine (~1% by weight).
^f Calculated on a solids basis.
^g T_gs estimated from DMA measurements (breadth of tan δ peak) and polymer compositions.
^h TEA = triethylamine; DMEA = dimethylethanolamine. ⁱ Typical values.

Fig. 4

Minimum Constituents	Function	Examples	% Usage/ Range
UA-HPD (e.g., Hybridur)	Binder		10-40%
Sand, glass, limestone and other minerals	Filler		60-90%
One or More Additional Constituents	Function	Examples	% Usage/ Range
Thickener	Improved shelf stability (minimizing separation or settling of ingredients). Improved rheology (Workability)	Cellulose ether, starch ether, fibers, fumed silica, associative and alkali swellable thickeners.	0-3%
Preservative (Biocide)	Increase shelf life by inhibiting biological growth		0-1%
Fungicide and/or mildewcide	Improved performance by minimizing biological growth in use.		0-1%
Defoamer	Reduces air entrainment during manufacturing and application. Improve strength, improve stain resistance.		0-3%
Other fillers	Filling voids between larger particles to improve shrinkage, hardness, reduce porosity, improve water resistance.	Fine silica, limestone (calcium carbonate), other mineral fillers.	0-80%
Decorative fillers	Improved aesthetics. Achieve special effect.	Reflective particles, glass or colored beads, dyes and pigments.	0-10%
Film forming aids (co-solvents)	Improve film formation at lower temperatures, ultimately, higher strength and hardness. Can improve stability to freezing and thawing.		0-15%

Fig. 5A

One or More Additional Constituents Continued	Function	Examples	% Usage/ Range
Crosslinkers or other reactive components	Improve hardness, water resistance, chemical resistance, stain resistance, abrasion resistance	Polyacrylic acid compounds.	0-5%
Stain resistant additives	Improve resistance to water-based and/or oil-based stains. Improved water and oil resistance.	Wax emulsions, wax particles, fluoro-carbon based particles and emulsions, silicone-based particles and emulsions, hydrophobes such as oleates and stearates	0-5%
Adhesion promoters or coupling agents	Improve bonding or compatibility between binder and fillers or substrates.		0-5%
Anti-freeze	Reduce freezing point to prevent damage during extreme temperatures. Improved storage stability.	Glycols, Various co-solvents	0-5%
Surfactants	Improve wetting of fillers and of substrates. Reduce viscosity. Eliminate entrained air. Stabilize formulation.		0-5%
Water	Diluent. Reduce viscosity.		0-10%
Water retention aid	Hold moisture into system in use, so as to improve application characteristics and assist cleanup.	Cellulose ethers, starches, co-solvents.	0-5%
UV Stabilizers	Improve resistance to UV light. Improved color stability. Reduce yellowing or discoloration.		0-5%
Acid or base	Adjust pH. Improve stability of formulation.		0-5%
Alternate Binders	Provide reduced performance at a reduced cost	Blends with conventional binders such as acrylics.	0-25%
Fibers	Improve cohesive strength of wet formula, improve strength when cured, reduce shrinkage, reduce cracking.	Various types of polymer or glass fibers of various lengths can be used.	0-5%

Fig. 5B

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**UA-HPD Grout
Example 1****UA-HPD Grout
Example 2**

Component	Amount Range in Composition	Amount Range in Composition
Freeze-Thaw Stabilizer/Co-solvent	0.85-0.95%	0.8-1.5%
Short Filler/Rheological Modifier -Short Fibers (Polyethylene)	0-0.3%	0-0.3%
Adhesion Promoter	0.14-0.2%	0.14-0.2%
In Can Preservative	0.002-0.005%	0.002-0.005%
Biocide	0.01-0.02%	0.01-0.02%
Cellulose Ether	0-0.25%	0-0.25%
Acrylic Thickener	0-0.20%	0-0.20%
UA-HPD (e.g.,HYBRIDUR Dispersion	19.5-23%	19.5-23%
Fumed Silica/Silica Fume	0-0.06%	0-0.06%
Deaerator	0.12-0.18%	0.04-0.08%
Silica Sand/Recycled Glass Filler	72-80%	70-78%
Decorative Dazzle fillers		0-5%

Fig. 6

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UA-HPD Grout Example 3

Translucent Grout Scale up Formula		Range, %
Hydrophylic Ethane-1, 2-diol	Freeze Thaw Stabilizers/Co-Solvent	0.7-0.95
Hydrophobic Glycol Ether	Freeze Thaw Stabilizers/Co-Solvent	0.7-0.95
A blend of Benzisothiazolin and 2-Hydroxyethyl-triazine	In Can Preservative	0.002-0.005
Microban	Biocide	0.01-0.02
Hydroxyethylcellulose	Cellulose Ether	0-0.25
HEUR Based rheological modifier	Acrylic Thickener	0-0.2
Modified Urea based	Anti-Settling Aid	0.05-0.1
UA-HPD (Hybrid polymer dispersion)	Dispersion	15-20
Siloxane based Defoamer	Deaerator	0.25-0.5
Recycled Glass	Glass Filler	70-90

Fig. 7**UA-HPD Grout Example 4**

Sanded Grout Scale-up Formula		Range, %
Hydrophylic Ethane-1, 2-diol	Freeze Thaw Stabilizers/Co-Solvent	0.7-0.95
Hydrophobic Glycol Ether	Freeze Thaw Stabilizers/Co-Solvent	0.7-0.95
A blend of Benzisothiazolin and 2-Hydroxyethyl-triazine	In Can Preservative	0.002-0.005
Microban	Biocide	0.01-0.02
Hydroxyethylcellulose	Cellulose Ether	0-0.25
HEUR Based rheological modifier	Acrylic Thickener	0-0.2
Modified Urea based	Anti-Settling Aid	0.05-0.1
UA-HPD (Hybrid polymer dispersion)	Dispersion	15-20
Siloxane based Defoamer	Deaerator	0.25-0.5
Colored Silica Sand	Sand Filler	70-90

Fig. 8

Comparative Data Results of Prior Art Grout vs. UA-HPD Grouts of the Invention

	Prior Art Grout*	1	1A	2	2A	3	3A	4	4A	5	5A	6	6A
Hydrophilic Ethane-1, 2-diol		0.937	0.937	0.937	0.937	0.937	0.937	0.937	0.937	0.892	0.981	1.021	0.789
Hydrophobic Glycol Ether		0.937	0.937	0.937	0.937	0.937	0.937	0.937	0.937	0.892	0.981	1.021	0.789
A blend of Benzisothiazolin and 2-Hydroxyethyl-triazine		0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.005	0.004	0.004
Microban		0.019	0.019	0.019	0.019	0.019	0.019	0.019	0.019	0.018	0.019	0.018	0.018
HEUR Based rheological modifier		0.103	0.076	0.089	0.089	0.089	0.089	0.089	0.089	0.085	0.093	0.088	0.089
Hydroxyethylcellulose		0.019	0.019	0.022	0.016	0.019	0.019	0.019	0.019	0.018	0.02	0.019	0.019
Modified Urea based Anti settling aid		0.049	0.049	0.049	0.049	0.056	0.041	0.049	0.049	0.046	0.051	0.048	0.048
UA-HPD (Hybrid polymer dispersion)		18.91	18.915	18.912	18.913	18.911	18.913	18.911	18.913	17.999	19.799	18.688	18.775
Siloxane based Defoamer		0.049	0.049	0.049	0.049	0.049	0.049	0.056	0.041	0.046	0.051	0.048	0.048
Silica Sand		78.975	78.996	78.983	78.987	78.979	78.991	78.979	78.991	79.19	77.19	78.046	78.42
Data Measurement													
24 hour Shore A Hardness	45	79	68	65	78	65	75	70	65	76	55	65	78
Density, g/cm ³	1.75	1.77	1.76	1.74	1.78	1.73	1.78	1.78	1.71	1.76	1.75	1.75	1.79
Compressive Strength, psi***	636	875	892	867	964	969	1010	971	899	831	781	807	707

*Prior Art water-borne polyurethane grout
 **Measured as per modified ANSI 118.3

Fig. 9

A. CLASSIFICATION OF SUBJECT MATTER**C04B 26/16(2006.01)i, C04B 26/06(2006.01)i, C04B 14/06(2006.01)i, C04B 14/04(2006.01)i**

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 26/16; C08K 3/00; C08L 47/00; C08L 75/04; C08F 8/32; C08K 3/34; C04B 26/14; C09D 5/34; C08K 3/22; C04B 26/06; C04B 14/06; C04B 14/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords:grout, UA-HPD, urethane, acryl, binder, filler, quartz, glass, fill, tile

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0586782 A1 (LATICRETE INTERNATIONAL INC.) 16 March 1994 See abstract; page 3, lines 10, 53-54, 56-57; claims 1, 4, 7, 12.	1-72
Y	US 2009-0163630 A1 (JEFFERSON, GARY et al.) 25 June 2009 See abstract; paragraphs [0001], [0012], [0055], [0058], [0060]-[0063]; claims 1, 20, 21.	1-72
A	US 8263694 B1 (WARREN, CHRISTOPHER et al.) 11 September 2012 See abstract; column 1, lines 11-13; column 2, lines 49-51, 55-58; column 7, lines 1-3; column 8, lines 8-18; column 10, lines 9, 10; column 11, lines 1, 2; column 14, lines 40-42; column 15, lines 5-10; column 16, lines 62-66; column 17, lines 19, 24-26; claims 1, 11, 13, 18.	1-72
A	US 3940358 A (BERNETT, FRANK E. et al.) 24 February 1976 See abstract; column 3, lines 12-13, 25-27; claims 1-4, 6.	1-72
A	US 5594065 A (TIEN, CHAO-FONG et al.) 14 January 1997 See abstract; claims 1, 4.	1-72

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family


Date of the actual completion of the international search

23 September 2014 (23.09.2014)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/039956

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0586782 A1	16/03/1994	CA 2087111 A1	21/02/1994
US 2009-0163630 A1	25/06/2009	CN 101410464 A	15/04/2009
		EP 2004571 A2	24/12/2008
		GB 0606468 D0	10/05/2006
		GB 0625402 D0	31/01/2007
US 8263694 B1	11/09/2012	None	
US 3940358 A	24/02/1976	None	
US 5594065 A	14/01/1997	BR 9602158 A	30/12/1997
		DE 69613894 D1	23/08/2001
		DE 69613894 T2	31/10/2001
		EP 0742239 A1	13/11/1996
		EP 0742239 B1	18/07/2001
		JP 03319942 B2	03/09/2002
		JP 09-003400 A	07/01/1997
		KR 10-0203561 B1	15/06/1999
		MX PA96001698 A	19/04/2002