COMPOSITIONS AND METHODS FOR SEALING NATURAL STONE TILES AND NATURAL STONE ARTICLES

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ABSTRACT

The present invention relates to a method of sealing natural stone tiles and stone articles by applying and curing by UV radiation a liquid, solventless sealant onto natural stone tiles and articles to provide permanent protection, abrasion resistance, chemical and stain resistance and resistance to mold and other biological growth stains. The UV-curable solventless sealing composition comprises an effective amount of carboxyl functional, UV-curable reagent to provide for adhesion of the cured coating to the stone article. Additionally, the method describes the application of an optional liquid primer sealant comprising a UV-curable aqueous dispersion of an acrylate-functional resin.
COMPOSITIONS AND METHODS FOR SEALING NATURAL STONE TILES AND NATURAL STONE ARTICLES

BACKGROUND OF THE INVENTION

[0001] The appearance and integrity of natural stone tiles and articles may become easily deteriorated by contact with water, dirt and grit as well as chemicals and cleaning substances. Natural stone is often quite porous and should be sealed to prohibit the penetration of water, dirt and chemical substances. Additionally, natural stone may be subject to efflorescence wherein water soluble salts may form exudates on the surface over time.

[0002] Currently available commercial sealers exist for the purpose of controlling the appearance and integrity of natural stone surfaces however these products are often only effective over a short term and must be re-applied periodically. These products may not fully protect the natural stone surface for even relatively short exposures to water, household cleaners and other reagents thereby allowing permanent dulling or deterioration of the natural stone surface. Further, commercial sealers may not offer abrasion or scratch resistance to the natural stone surface from abrasive materials such as may be expected from normal floor traffic or from abrasive cleaning products.

[0003] Some currently available commercial sealers may affect or enhance the color properties and other aspects of natural stone tiles and articles, however, these effects and enhancements can fade over time as the effectiveness of the sealers become worn, scratched or deteriorate. Additionally, most commercial sealers are generally used only after the natural stone tiles or natural stone articles are installed for use.

[0004] Furthermore, since currently available commercial sealers for natural stone may require multiple applications or reapplications, a more permanent solution for the protection of natural stone tile and natural stone articles would be preferable.

SUMMARY OF INVENTION

[0005] The present invention provides composition(s) (a sealant or sealants) and method(s) (one step or two step procedures) for sealing natural stone tiles and articles that solves the problems outlined above.

[0006] The detailed description of the methods for applying a permanent protective sealant to natural stone surfaces is disclosed below. In addition to the methods, the invention relates to liquid UV-curable solventless sealant compositions and, where required or desired, aqueous UV-curable primer sealant compositions. Additionally, the invention relates to equipment suitable for applying a liquid UV-curable solventless sealant to natural stone and also to the equipment suitable for applying, where required, an aqueous primer sealant just prior to the aforementioned liquid UV-curable solventless sealant, as well as to methods of use of said suitable equipment. In this regard, the invention relates to an economical process for applying a permanent sealant to natural stone tiles and related articles such as natural stone borders, trims, medallions, etc intended for installation as wall coverings, floorings, countertops and the like. Further, the invention relates to part to the use of a single liquid sealant system that self-primes the stone tile surface thereby sealing in one step. The sealing system contains one or more additives that enable the achievement of excellent adhesion to the stone surface. Further, the invention relates to the treatment of the unsealed stone tile surface by the use of radiant energy to dry the surface as well as to allow for improved wetting once the sealant is applied. The sealant is radiation curable immediately after application to the stone surface thereby enabling fast conversion times and brevity of the entire process.

[0007] Further, the invention relates to a process for applying a liquid water-based primer sealant to natural stone tiles and related articles followed immediately by the application of the same sealant described above. The water-based primer sealant is UV curable as is the subsequent sealant such that on exposure to UV radiation the sealing system is immediately and permanently cured. The presence of the water-based UV-curable primer sealant affects the ultimate appearance of the underlying stone substrate causing a more natural appearance not possible with the single sealant method described above. Further, modification of the water-based primer sealant with select water miscible UV-curable monomers and/or agents can allow for modulation of the ultimate appearance of the underlying stone substrate after application and curing of the subsequent UV-curable sealant.

[0008] The UV-curable sealant is designed without volatile solvents to enable an environmentally compliant process and minimize application equipment design features. The UV-curable sealant composition is also designed to provide for a durable, abrasion resistant and chemical stain resistant finish on the natural stone tile or natural stone article surface. The UV-curable sealant may also contain a biocidal agent for prohibiting mold, mildew and other fungal growth on the tile surfaces over the lifetime of the tile installation.

[0009] The UV-curable primer sealant (used where required or beneficial to tile appearance) is formulated from suitable water-based acrylate-functional dispersions in water wherein the glass transition of the disperse phase is low enough to allow for proper curing once applied to a tile surface conditioned at about 35 to 45° C. Further, the UV-curable primer sealant is formulated with a requisite amount of photoinitiator to allow for complete cure once exposed to UV irradiation. Even further, the UV-curable primer sealant can be formulated with additional components such as water miscible UV-curable agents or monomers. These monomeric materials are generally non-volatile and their levels of incorporation into the water-based primer sealant are chosen to provide intermediate effects on the level of darkening or enhancement or enrichment of the tile color, grain and/or marbling of the subject stone. Using a water-based UV-curable primer sealant in the absence of these agents will generally provide the least effect in tile color, grain and/or marbling enhancement or enrichment.

[0010] Equipment useful for these sealing methods and compositions takes into consideration the need for compactness, minimization of energy input and volatile emissions, and maximum transfer efficiency of the sealant (or sealants) during application. Further, the equipment may be self-contained and automated.

DESCRIPTION OF FIGURES

[0011] FIG. 1 shows a schematic diagram of a conveyer system suitable for applying the primer and finish sealant compositions of the present invention to natural stone tiles.
Fig. 2 shows a schematic diagram of a conveyer system suitable for applying the finish sealant composition of the present invention to natural stone tiles where a primer step is not needed or desired.

**DESCRIPTION OF INVENTION**

The detailed description of the methods for applying a permanent protective sealant to natural stone surfaces is disclosed below. In addition to the methods, the invention relates to liquid UV-curable solventless sealant compositions and, where required or desired, aqueous UV-curable primer sealant compositions. Additionally, the invention relates to equipment suitable for applying a liquid UV-curable solventless sealant to natural stone and also to the equipment suitable for applying, where required, an aqueous primer sealant just prior to the aforementioned liquid UV-curable solventless sealant, as well as to methods of use of said suitable equipment.

The method described below may have many embodiments as envisioned depending in part on the sealant application technique whether by spray, roller, curtain (i.e., a liquid spray curtain), mist, etc. Therefore the method should not be considered as limited based on the brief description given below. Further, the details of the sealant compositions below should not be considered as limited to those few examples given.

Normal preparation of the unsealed natural stone tiles or natural stone articles proceeds with cleaning of all milling dust from the surface through well understood means such as brushing, wiping, vacuuming or by air flow (e.g., blowing, air knife, etc.). Such techniques, however, do not necessarily remove excess water that may reside on or near the surface of unsealed natural stone tiles or articles. In accordance with this invention a radiation heating in the form of infrared (IR) heating, convection heating, or the like, is applied to the natural stone surfaces for a brief period to heat the surface to about 40⁰ to about 60⁰ C, just prior to the sealant application. This action is possible by passing the tiles or articles on a belt or conveyance under properly situated IR lamps or other heat lamps of heat generating source. As a further part of this invention the IR light intensity should be, but need not be, as high as possible to minimize the natural stone tile exposure time.

In accordance with this invention the UV-curable solventless sealant composition is comprised of a mixture of polymers, oligomers and reactive diluents having polymerizable functional groups as part of their chemical structure. Polymers and oligomers common to the art include, but are not limited to, acrylate and methacrylate type materials including urethane-acrylates, epoxy-acrylates, polyester-acrylates, melamine-acrylates, and the like. An example of a urethane-acrylate is BR-941 (Bomar Specialties Co., Torrington Conn.). An example of an epoxy-acrylate is Etcure 621-100 (Eternal Chemical Co Ltd., Kaohsiung, Taiwan). An example of a polyester-acrylate is SR355 (Sartomer Company, Exton, Pa.). An example of a melamine-acrylate is BMA-200 (Bomar Specialties Co.).

Reactive diluents, also called monomers, suitable for use in the solventless UV-curable sealant composition include, but are limited to, the following materials: hexanediol diacrylate, butanediol diacrylate, trimethylolpropane triacrylate, pentaerythritol tetraacrylate, tripropyleneglycol diacrylate, dipropyleneglycol diacrylate, isobornyl acrylate, N-vinyl pyrrolidone, and N-vinyl caprolactam.

The UV-curable solventless sealant by definition omits the use of conventional organic solvents to lower and regulate application viscosities. Instead, judicious amounts of reactive diluents as detailed above are utilized.

In addition, the UV-curable solventless sealant of this invention contains a requisite amount of photoinitiator or photoadditives to enable a response to the exposure of actinic radiation. These photoinitiators are comprised of select materials that generate free radical species through either direct α-cleavage or through hydrogen abstraction mechanisms. Typical photoinitiators include, but are not limited to, 1-hydroxy-cyclohexyphenyl ketone, 2-hydroxy-2-methyl-1-phenyl-1-propanone, phosphine oxide, phenyl bis(2,4,6-trimethylbenzoyl), benzophenone, and the like. Additionally, synergists may be used such as, for example, methyldiethanolamine.

More specifically the actinic radiation may be provided by light-emitting diodes or other similar solid state devices at wavelengths in the region of 395±20 nm. Consequently, the choices of proper photoinitiators are limited to those which absorb radiation at those same stated wavelengths. Such photoinitiators include but are not limited to the phosphine oxide types mentioned above.

Various other agents comprise the solventless UV-curable sealant including inorganic materials such as silicones and aluminas for gloss control and abrasion resistance. Examples of silicones include amorphous materials such as ACRYMAT™ 100 and AEROSIL® R 972 (Evonik DeGussa Corp., Waterford, N.Y.). Examples of aluminas include Tabular T60/T64 and A3000FL (Almatis, Bauxite, Ariz.).

Additionally, additives may be formulated into in the UV-curable sealant to provide for surface flow and leveling during and after application of the sealant. Examples of flow and leveling agents are BYK-333 and BYK UV-3500 (Byk-Chemie USA, Wallingford, Conn.). Further, special additives such as NANOBYK® 3601 (BYK-Chemie, Wallingford, Conn.) may be used to add nanoparticles of alumina for improved abrasion of the cured sealant and stone tile. Even further, incorporation of silane coupling agents may be used to improve adhesion to natural stone surfaces; select silane coupling agents may have UV-curable substrates as well.

Also in accordance with this invention is the use of specific amounts of carboxyl-functional UV-curable monomers. These carboxyl-functional monomers perform as coupling agents between the mildly basic surface of the natural stone tiles or natural stone articles and the UV-curable sealant. The carboxyl-functional monomers also have carbon-carbon double bond functional groups that polymerize into the UV-curable sealant matrix during exposure to UV radiation.

Examples of carboxyl-functional monomers include but are not limited to acrylic acid (AA), methacrylic acid (MAA), and beta-carboxethyl acrylate (B-CEA). Of these, B-CEA is preferred because of its relative non-volatility and lower odor. All of these carboxyl-functional monomers have fairly low molecular weight thereby improving their effectiveness as adhesion promoters to natural stone when used at low weight percentages in the UV-curable sealant composition.

For improving adhesion of the UV-curable sealant to natural stone surfaces the effective levels of these carboxyl-functional monomers is in the range of about 1% to about 4%.
by weight of the total sealant composition. At less than about 1% by weight of total sealant composition adhesion may be marginal. At greater than about 4% by weight no further improvement is noted. In the range of about 1% to 4% by weight the adhesion of the single solventless UV-curable sealant of the present invention is 100% as determined by standard methods including ASTM D 3359-Method B. [0026] The solventless UV-curable sealant compositions referred to previously, containing about 1% to about 4% of an effective carboxyl-functional monomer, various levels of acrylate-functional polymers and oligomers, various levels of alumina and/or silica agents and containing various levels of reactive diluents (monomers), as detailed herein, may have liquid viscosities that become excessive for the application method intended. Such application methods may include spraying (air or airless), roller, curtain, mist, etc. As part of this invention, the solventless UV-curable sealant can be heated just prior to the chosen application method to facilitate the transfer of the sealant to the intended natural stone surface. The recommended heating range for the sealant, using well known methods (such as by heat exchangers), is about 30°C to about 50°C. [0027] Preferred methods of sealant application are high transfer efficiency methods such as ultrasonic spray and low volume low pressure spray. For example, U.S. Pat. No. 6,102,298 to Bush, et al., which is incorporated herein by reference for ultrasonic spraying or, alternatively, U.S. Pat. No. 5,871,822 to Lepsche, et al., and U.S. Pat. No. 6,068,822 to Hynes, et al., both of which; are incorporated herein by reference, which describe devices and methods for spray application using low volume low pressure technology. [0028] As another aspect of this invention the composition of the water-based UV-curable primer sealant is based on formulations incorporating aqueous dispersions of acrylate-functional oligomers dispersed in water and also containing requisite amounts of photoinitiators selected to absorb at about 395±20 nm. Such water-based acrylate-functional dispersions can be based on urethane-acrylate polymers which are specifically useful for this invention. Further, the compositions of the water-based UV-curable primer sealants can be modified with water miscible agents that are also UV-curable. Such agents include, for example, vinyl pyrolidone, vinyl caprolactam, 2-(2-ethoxyethoxy) ethyl acrylate, etc. Modifications of the water-based UV-curable primer sealant with these materials allow for modulations, enrichment or enhancement of the appearance of the natural stone tile color and grain once sealed by the method described in this invention. 

Exemplification

[0029] In some of the following examples of this invention natural stone tiles consisting of various sizes such as four inch by four inch (or twelve inch by twelve inch, etc.) by 3/8 inch thick specimens of assorted tumbled marble, tumbled travertine and tumbled limestone were placed on a moving belt at 10 ft per minute and were subjected to an air knife (directed blower) to remove any loose particles, milling dust and other debris. The present invention is not limited to the size or shape of the natural stone object being sealed. On this belt the tiles were passed under a bank of infrared lamps set at approximately 600°F (~315°C) to provide radiant heating such that the tile surface temperature was raised ten to fifteen degrees above ambient to achieve approximately 35° to 40°C surface temperature as determined by a handheld IR temperature sensor. [0030] After this conditioning the tiles were sprayed with coatings described further below except where noted otherwise. It is noted that one of skill in the art will be able to, based on the teachings of the present invention, be able to modify the sealant compositions given below with compounds and skills known in the art at the time of the invention to adjust, for example, flowability, viscosity, sheen, final sealant thickness, sprayability, etc., and still be within the scope of the present invention. [0031] In one embodiment of this invention a single UV-curable sealant composition was tested with and without the presence of about 5% by weight beta-carboxyethyl acrylate monomer. Thus, [0032] Composition A: mixture of acrylate functional oligomer (approx. 15% by weight) with hexanediol diacylate (~50% by wt.) and isobornyl acrylate (~15% by wt.) and trimethylolpropane triacrylate (~5% by wt.) and dipropylene glycol diacylate (~5% by wt.) and alumina (~5% by wt.) and 1-hydroxycyclohexylphenyl ketone (~2.5% by wt.) and 2-hydroxy-2-methyl-1,4-phe ny1-1-propone (~2.5% by wt.). [0033] Composition B: same as Composition A plus 5% beta-carboxyethyl acrylate (B-CEA) by weight. [0034] On each of two twelve inch by twelve inch tumbled marble stone tiles were cast 6.0 mil wet films of Composition A and Composition B (above) using a Bird-type applicator, as is known in the art. The tiles were then exposed to UV radiation under an air atmosphere for a duration of 1 to 1.5 seconds [approximately 2.0 Watts/cm² UV-A intensity, type D bulb from Fusion UV Systems, Inc. (Gaithersburg, Md.)]. After this step both sealants (i.e., from compositions A and B) were hard and scratch resistant. However, on taped crosshatch adhesion [ASTM D 3359-Method B] the sealant of Composition A failed (rating 0B) whereas the sealant of Composition B passed completely (rating 5B). [0035] In similar fashion to the above, Composition A was modified with 1.7% by weight B-CEA to form Composition C or with 3.4% by weight B-CEA to form Composition D. Six mil wet films of these compositions were sprayed onto tumbled marble and followed by the same UV curing schedule passed taped crosshatch adhesion (4B and 5B ratings respectively). Further, the sealants of Composition C and Composition D enhance and deepen the appearance of the underlying natural stone tile surface. Surface hardness is gauged by the durability to 20 double raps of type 0000 steel wool pads. [0036] In another embodiment of this invention a quantity of a sprayable, solventless UV curable sealant was formulated as follows:

<table>
<thead>
<tr>
<th>Composition</th>
<th>2188 grams</th>
<th>B-CEA</th>
<th>87.5 grams [3.8% of total]</th>
</tr>
</thead>
<tbody>
<tr>
<td>UltraFresh® DM-25</td>
<td>4.4 grams</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

UltraFresh® DM-25 (Thomson Research Associates, Toronto, Canada) is a bacterical static and antifungal agent comprising 25% oethulione (2-n-Octyl-4-isothiazolin-3-one) as the active ingredient. UltraFresh® is effective in inhibiting the growth by microorganisms such as Aspergillus niger, Chaetomium globosum, Penicillium funiculosum, Aureobasidium pullulans, and others.
sidium pullulans, and Trichoderma virens. The above sealant (Composition E) had an approximate viscosity of 35 seconds (#2 Zahn cup) and was allowed to equilibrate to about 35°C prior to spraying. An assortment of tumbled marble, travertine and limestone tiles were cleaned and pre-conditioned under IR radiation to give an average surface temperature of about 35°C. The tiles were then sprayed with Composition E to deliver average film thicknesses of about 3.0 mil. The sealed tiles were immediately exposed to approximately 2.0 Watts/cm² of UV-A radiation for 1 to 1.5 seconds, and then tested for adhesion. Crosshatch adhesion was 100% pass (5B rating) on all tiles tested.

[0037] In another embodiment of this invention a lower amount of B-CEA (1.75%) was prepared (Composition F) in a similar manner to Composition E above, and was spray applied in a similar manner to the above example, at application weights of about 10 grams per ft² (equal to approximately 3.5-4.0 mils depending on the application). Taped crosshatch adhesion testing on all natural stone marble, travertine and limestone tiles was 100% pass (5B ratings). Further, hot water immersion of select sealed tiles showed no dislodgement of the sealant after 24 hours.

[0038] In still another sealing trial, Composition F was sprayed in a similar manner to those conditions described above, but at approximately 5.5 to 7.0 grams per ft² application weight (equal to approximately 2.0-3.0 mils depending on the application). For the natural stone tiles sealed and cured in this trial the crosshatch adhesion results were all 100% passes (5B ratings). Further, the tile surfaces were hard and abrasion resistant. By intention the components of Composition F and all of the UV-curable compositions of this invention are chosen to provide the natural stone tiles with an enhanced and deepened appearance of the underlying stone similar to the appearance of stone tiles treated with conventional sealants and enriching compounds, as well as to control the gloss or sheen of top surface.

[0039] Improvements of the present invention over conventional liquid sealants and enhancing materials for natural stone are described. On a rating scale of 1 to 10 where “1” represents the initial level of color and tone of an untreated natural stone tile and where “10” represents the fullest color and tonal enhancement achieved immediately after treatment with commercial penetrating & enhancing sealers such as the Enrich’N’Seal and Stone Enhancer products, the level of color & tonal enhancement achieved with Composition F over the range of tiles tested was from about 9 to 10.

[0040] An array of natural stone tiles consisting of tumbled marble, travertine and limestone specimens were treated as prescribed with two commercially available liquid products designed for-sealing and enhancing such surfaces: Enrich’N’S eal™ and Stone Enhancer™ (both from Aqua Mix Inc., Corona, Calif.). After taking several days to dry the tiles were compared visually to the same tile array prepared by the current invention as described above using Composition F (at 5.5 to 7.0 grams per ft²). The present invention showed equivalent levels of color and tonal enhancement as the conventional products. Of more value though, the method and sealant composition of the invention provide for improved protection to various household foods and cleaners for commercial value. Thus, one hour covered spot tests with lemon juice and apple cider vinegar showed distinct degradation and discoloration of a tumbled marble tile treated with either Enrich’N’Seal or Stone Enhancer, but no effect on the same tile sealed with Composition F by the method described in this invention.

[0041] One major problem with air spraying of the sealants as described above is the poor transfer efficiency from the gun nozzle to the tile or article surface due in large part to the high flux of air used to atomize the liquid sealant. Examples of high transfer efficiency sprays means with UV-curable sealants suitable for use in this invention are described below.

[0042] As an example, Composition G comprised of about 10.5% by weight urethane-acrylate oligomer, 10.5% dimethylolpropane tetra-acrylate, 39% hexanediol diacrylate, 24% tripropyleneeglycol diacrylate, 1.6% B-CEA, 4% alumina, 4% silica, and about 4% Esacure® KTO-46 (Lamberti, Gallarate, Italy) photoinitiator had a viscosity of about 60 cP at 1500 s⁻¹ at 25°C. Composition G was easily applied by ultrasonic spraying at 25 to 40°C. Further, a tile treated with Composition G via air spray or ultrasonic spray was permanently sealed upon exposure to UV radiation provided by an LED or other solid state devices emitting UV radiation at 395±20 nm (at or greater than 2 watts/cm² intensity). Tiles treated with Composition G exhibit considerably more darkening or enrichment of their natural color. This is especially exemplified for select marble tiles such as “Nero,” “Verdi Alpi” and “Rosa Antico” (supplied by Cottoveneto, Italy).

[0043] Optionally, a water-based UV-curable primer sealant can also be applied by ultrasonic spray just prior to the application of a UV-curable sealant (as in Composition G or any of Compositions A-F) to modulate the underlying color or provide color and grain enrichment to the surface of the tile or article. In this method, the optional water-based UV-curable primer sealant was flash dried (by applied or ambient heat, for example) to remove water prior to the application of the solventless UV-curable second coat. The solventless UV-curable second coat was applied directly after the application and flash drying of the primer sealant. After application of the solventless UV-curable coat, the UV-curable primer sealant and solventless UV-curable coat were cured as exemplified above.

[0044] Thus, the following water-based UV-curable primer sealants were prepared. All were based on LUX 480 (Alberdingk Boley, Inc., Greensboro, N.C.) which is a 40% by weight aqueous dispersion of a UV-curable urethane-acrylate resin.

[0045] Primer Sealant H: about 300 grams LUX 480 plus about 0.7 grams vinyl pyrrolidone plus about 0.7 grams KTO-46 photoinitiator

[0046] Primer Sealant J: about 300 grams LUX 480 plus about 40 grams vinyl pyrrolidone plus about 1.2 grams KTO-46 photoinitiator plus about 32 grams water.

[0047] Primer Sealant K: about 300 grams LUX 480 plus about 64 grams vinyl pyrrolidone plus about 1.3 grams KTO-46 photoinitiator plus about 32 grams water.

[0048] After application to “Nero” marble tiles the level of color (and grain) enrichment was strongly in order of the increasing vinyl pyrrolidone content with Composition K exhibiting a darker coloration and enhanced grain than Composition J and with both exhibiting much darker colorations and grain enhancement than Composition H. Since compositions H, J and K were UV-curable the color enrichment provided by their inclusion is permanent.

[0049] In another embodiment of this invention the application of a primer sealant (H) followed within approximately 15 to 60 seconds or within about 30 seconds by the spray...
application of a 100% solids (solventless) UV-curable sealant (Composition L, see below) over temperature conditioned (approximately 55°C) natural stone tiles (“Emperor Tumbled™,” from Anatolia Tile, Toronto) was conducted using low-volume low-pressure (LVLP) spray guns, which are known to those practiced in the art. A uniform deposition of both coatings was observed with a moderate to low degree of color enrichment (3 to 4 rating) of the underlying stone surface.

Composition L: approximately 11% by weight urethane-acrylate oligomer, about 11% by weight ditermethylolpropane tetra-acrylate, about 41% by weight hexanediol diacrylate, about 5% by weight tripropylene glycol diacrylate, about 1.7% by weight B-CEA, about 0.7% by weight alumina, about 3.1% by weight silica, and about 4.4% by weight Escure® KTO-46; viscosity of about 46 cP at 1500 s⁻¹ at 25°C.

After LVLP spraying of the primer sealant and solventless UV-curable sealant, the sealants are cured as described above.

The utility of such formulated primer sealants to affect and modulate the ultimate appearance of natural stone tiles coupled with the permanence of the primer sealant after treatment and UV curing of the second sealant (for example, Compositions A-G and L) is especially novel. A schematic depiction of equipment suitable to conduct an energy efficient sealing process for natural stone tiles is shown in FIG. 1.

FIG. 1 illustrates a schematic representation of a variable speed conveyor 8 for transporting natural stone tiles and articles 7 under six modules in the following order: a tile cleaning module 1, a surface temperature adjustment module 2, containing, for example, an infrared radiation element or elements, a spray head (e.g., a high transfer efficiency spray head) 3, for applying the water-based UV-curable primer sealant, a second spray head (e.g., a high transfer efficiency spray head) 4 for applying the liquid solventless UV-curable sealant, a fixture 5 for flooding the tile surface with inert gas just before exposure of the transported stone under the UV radiation emitting LED array 6. The use of a conveyor system for processing of the natural stone tiles and articles permits users regulation of the timing of the method such that the method may be performed in a controlled time sequence and such that said controlled time sequence may be modified as needed based on, for example, differences attributable to different types or grades of stone (e.g., heat absorption and/or heat retention, amount of residual water contained in the stone, etc.), minor differences in sealant formulation and/or temperature and/or ambient humidity, temperature, etc.

Alternatively, FIG. 2 illustrates a schematic representation of a device to conduct an efficient sealing process for the single sealant application (forgoing the application of a primer sealant). Thus, a variable speed conveyor 15 transports a natural stone tile or article 14 under five modules in the following order: a tile cleaning module 9, a surface temperature adjustment module 10 containing, for example, an infrared radiation element or elements, a spray head (e.g., a high transfer efficiency spray head) 11 for applying the liquid solventless UV-curable sealant, a fixture 12 for flooding the tile surface area with inert gas just before exposure of the transported tile under the UV radiation emitting LED array 13.

1. A method for applying a sealant to natural stone tile and articles comprising:
   a) cleaning the natural stone tile or article;
   b) conditioning the natural stone tile or article with a regulated amount of heat;
   c) conditioning a liquid UV-curable solventless sealant comprising a mixture of acrylate oligomers and monomers, photoinitiators, aluminum oxides, silicon oxides, carboxyl-functional reagents, flow and leveling agents and a biocide by heating;
   d) applying the liquid UV-curable solventless sealant to the natural stone tile or article, and;
   e) curing of the applied UV-curable solventless sealant by exposure to UV radiation.

2. The method of claim 1 wherein steps b), d) and e) are conducted in a controlled time sequence.

3. The method of claim 1 wherein the surface temperature of the stone tile or article is about 40°C to about 60°C at the time of application of the liquid UV-curable solventless sealant to the stone tile or article.

4. The method of claim 1 wherein the conditioned liquid UV-curable sealant is maintained at a temperature from about 30°C to about 50°C during application of the sealant to the natural stone tile or article.

5. The method of claim 1 wherein the liquid UV-curable sealant is applied to the sealant to the natural stone tile or article by spray, roller, spray curtain or mist.

6. The method of claim 1 wherein the liquid UV-curable sealant is applied to the stone tile or article by ultrasonic spray.

7. The method of claim 1 wherein the liquid UV-curable sealant is applied to the stone tile or article by low volume, low pressure spray.

8. The method of claim 1 wherein the liquid UV-curable sealant additionally comprises a carboxyl-functional reagent that is UV curable.

9. The method of claim 8 wherein the carboxyl-functional reagent is selected from a group consisting of one or more acrylate or methacrylate functional monomers.

10. The method of claim 9 wherein the carboxyl-functional acrylate functional monomer is beta-carboxyethyl acrylate (B-CEA).

11. The method of claim 1 wherein the carboxyl-functional reagent comprises from about 1% to about 4% by weight of the liquid UV-curable solventless sealant.

12. The method of claim 1 wherein the natural stone tiles and articles comprise one or more of marble, travertine and limestone.

13. The method of claim 12 wherein the liquid UV-curable solventless sealant imparts an enhanced and color controlled appearance of the surface and underlying substrate of the natural stone tile or article.

14. The method of claim 1 wherein the UV radiation is supplied by solid-state light-emitting diodes.

15. The method of claim 1 further comprising applying a UV-curable water-based primer/sealant to said natural stone tiles and articles before application of the liquid UV-curable solventless sealant.

16. The method of claim 15 wherein the surface temperature of the stone tile or article before application of the UV-curable water-based primer/sealant is at least 30°C.

17. The method of claim 15 wherein the UV-curable water-based primer/sealant is applied by spray, roller, spray curtain or mist.
18. The method of claim 15, wherein the UV-curable water-based primer/sealant is applied to the stone, tile or article by ultrasonic spray.

19. The method of claim 15, wherein the UV-curable water-based primer/sealant is applied to the stone, tile or article by low volume, low pressure spray.

20. The method of claim 15, wherein the liquid UV-curable solventless sealant is applied in a controlled time sequence onto the natural stone tile or article after application of the UV-curable water-based primer/sealant.

21. The method of claim 20, wherein the liquid UV-curable solventless sealant is applied by ultrasonic spraying.

22. The method of claim 20, wherein the liquid UV-curable solventless sealant is applied to the stone, tile or article by low volume, low pressure spray.

23. The method of claim 20, wherein the sealants are exposed to UV radiation after application.

24. The method of claim 23, wherein said UV radiation is supplied by light emitting diodes.

25. The method of claim 20, wherein the conditioning of the stone tiles or articles, the application of the UV-curable water-based primer/sealant and the liquid UV-curable solventless sealant and the curing of the sealants by UV radiation is performed on a continuous moving belt for transporting the tiles and articles at speeds of up to about 5 feet per minute and over a total length of about 20 feet or less.

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