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(54) Title: METHOD FOR PREPARING AN IMPROVED FINISHED CONCRETE PRODUCT

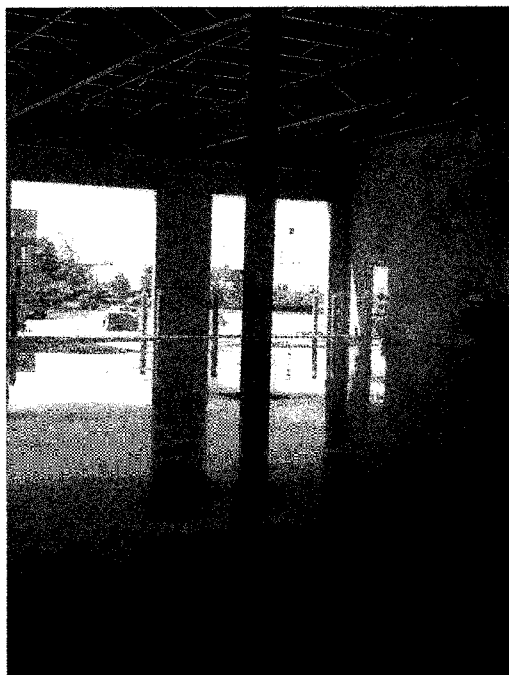


Fig. 1

(57) Abstract: A method for preparing and finishing concrete is disclosed, comprising preparing a cement surface by a process comprising the admixture addition, to an industrial concrete mixer/pourer, of a formulation comprising nanosilica, after some or all water is combined and mixed with cement mix, sand and aggregate; followed by pouring and floating; followed by the addition, before or during combination, to the concrete surface, of a formulation comprising water, an alpha-hydroxy acid, a glycol alkyl ether and a polyethylene glycol.



METHOD FOR PREPARING AN IMPROVED FINISHED CONCRETE PRODUCT**Priority claim**

This application claims priority to Provisional Application 62/761,393. Filed on March 22, 2018, and Provisional Application 62/765,597, filed on September 1, 2018, both of which are incorporated herein by reference for all that they teach without exclusion of any portion thereof. Provisional Application 62/761,064, filed on March 9, 2018 is also incorporated herein by reference for all that it teaches without exclusion of any portion thereof.

The finishing of concrete is an important step in the production of concrete forms such as concrete slabs. Typically, the finishing process occurs after the concrete has hardened, but before the concrete has fully cured. One purpose of finishing processes known in the art is to reduce the roughness of raw concrete surfaces by mechanical smoothing. Often, in the case of concrete poured with existing methods, evaporation from the hardening concrete surface gives a surface which is too dry to finish easily, risking damage to the concrete surface if undertaken without the use of additional water. Such added water introduces prolonged water emission issues, as discussed *infra*. However, with the addition of water, the surface can be more easily smoothed with a minimum of damage.

A second purpose of finishing is to coat the surface of the concrete. Concrete slabs which have been poured by existing methods tend to exhibit evaporation, which, as discussed above, can dry the cement surface. Often the result is capillaries (discussed in more detail *infra*) in the surface caused by water, largely displaced by settling, which has flowed up through the surface. Such capillaries can compromise the compressive strength of the concrete product, as well as serve as a conduit for water into the concrete during its lifetime, facilitating water-mediated damage. As with the surface, the capillaries allow water which could otherwise participate in the curing reaction to be lost. Existing finishing agents act to coat the upper surfaces of the concrete, as well as the inner surfaces of the capillaries in order to reduce water loss during curing, as well as prevent water entry later in the life of the concrete.

Thus, in summary, existing finishing methods couple a mechanical smoothing with a finishing agent which deposits a protective layer. The result is a smoothed surface having a coating in the surface which densifies the surface, and cuts evaporation losses during curing, theoretically enhancing curing efficiency, while reducing water regress and ingress during in-use.

Surprisingly, it has been found that the use of water-diluted formulations of Korkay Concrete Dissolver, (available from Tate's Soaps and Surfactants), available as E5 Finish from Specifications Products produces a durable, water protective finish when used as a finishing agent would be used, but as a finishing agent replacement; and on concrete surfaces prepared with amorphous silica, as

disclosed and described *infra*. The resultant concrete surface is generally characterized by a smooth, wear-resistant finish; an improved resistance to surface water penetration (without desiring to be bound by theory, it is though this may be due to filled capillaries); and a maintained compressive strength over a longer life (again, possibly due to filling of any capillaries, which prevents life-reducing water damage). The high-quality surface obtained is surprising in that Korkay is well-known among those in the art in its capacity as a cutting or cleaning agent: it is used throughout the industry to dissolve concrete deposits, such are left on concrete mixing and pouring equipment after a large-scale pour. Its effectiveness extends to concretes which contain commonly used silica materials, such as fumed silica, silica fume, etc. Rather than leave a finish, the formulation would be expected to efficiently dissolve a concrete surface.

The concrete prepared according to the present invention, i.e., with tailwater addition of silica as described *infra*, generally has greatly reduced absorption of finishing water, and thus, without desiring to be bound by theory, it is thought that the concrete prepared as described *infra*, and containing amorphous silica having the characteristics as described *infra*, retains water as described, and has reduced presence of capillaries with respect to concrete prepared by existing methods. Thus, little or no additional water is needed in order to smooth the surface, and water which is applied during finishing, including that which is contained with the diluted formulations of Korkay applied as indicated herein, is not readily taken into the concrete. Thus, the use of Korkay with the tailwater addition of silica is particularly beneficial. Furthermore, experimental pours have confirmed that concrete in which the mix is prepared by methods other than those disclosed herein (for example, in which the silica is combined with the cement mix simultaneously with, or prior to, the addition of the water) have much higher rates of delamination upon use of the finishing compositions and methods of the present invention. Thus, it is preferred to use the finishing formulations and methods of the present invention with the improved formulations and methods of concrete mix preparation described herein, in which nanosilica, preferably colloidal amorphous nanosilica, is combined with other components of the concrete mix, only after some or all of the water has been combined with the cement mix and optionally, the aggregate/sand components and mixed for a time. The full description of the “improved formulations and methods of concrete mix preparation” are disclosed below

However, some benefits of the invention may be obtained when the finishing methods and compositions described herein are used with silica-containing concrete mixes which are prepared according to methods which do not include the tailwater addition of amorphous silica. For example, concrete which has been prepared with the addition of silica at points prior to the mixing of some or all the water with cement mix and aggregate/sand. Such concretes generally exude significantly more bleed water than the concretes described in detail herein. Such concretes may also absorb more of the finishing water than the concretes specifically disclosed herein. Other silica-containing concretes, such as those with somewhat larger particles, such as, for example silica fume (average particle size of

about 145 nm) or fumed silica, *may* show some benefits of the invention, but the surfaces of concrete prepared with such larger particles are more likely to be damaged or destroyed.

It is thought that the diluted Korkay interacts with the amorphous nanosilica in the concrete, and through this interaction with at least the superficial amorphous silica, a hard finish is formed on and/or in the superficial regions of the concrete. Such a result is indicated by experiments in which E5 Internal Cure is mixed directly with E5 Finish, in a container, without the presence of a concrete C-S-H matrix, giving a tough translucent or clear substance, such as is thought likely to be the substance of the observed concrete finish. It is known that reducing the pH of a formulation of nanosilica, such as, for example, a colloidal silica formulation to a pH below pH 7, can cause the nanosilica formulation to form a gel. The disclosed formulation contains an acid (preferably glycolic acid). However, the formulation is used to break down the C-S-H matrix of commonly-used types of concrete. Included are concretes which contain other types of larger (non-nano-sized), commonly-used silicas. Nevertheless, when such a formulation (a water-diluted Korkay formulation, or its formulation variations, as described herein) is used, on concrete prepared by the late addition of amorphous nanosilica, as disclosed in detail herein, the concrete is not damaged or destroyed. Instead, the concrete can be finished to a surface which, surprisingly, is more durable, harder, and of a higher gloss than other finishing methods.

The surface-forming process of the present invention is preferably used with concrete comprising amorphous silica prepared and poured as described in the section below entitled "Novel Compositions for Improved Concrete Performance".

Description of the Drawings

Fig. 1) depicts a high gloss finish which is achieved after floating, combination and final finishing steps.

Fig. 2) depicts a dull finish on a surface which has not been finished to the degree of Drawing 1).

Fig. 3) depicts the surface which is prepared in Example 3, which is suitable for outdoor use, having no water penetration.

Fig. 4) depicts the surface prepared in Example 1, as it appeared after the finishing step. Undiluted Korkay was applied after floating. The surface is brittle and easily damaged by the finishing step.

Fig. 5) depicts a surface as it appeared after the finishing step. A 12:1 water dilution of Korkay was applied after floating. The surface is thin, with inferior flatness and gloss.

Fig. 6) depicts a surface as it appeared after the finishing step. A 7:1 water dilution of Korkay was applied after floating. The surface is smooth and has an excellent gloss.

List of Tables

Table 1-Data referred to in Example 6.

Detailed Description

While the invention disclosed in this provisional application refers to Korkay Concrete Dissolver ("Korkay") of the formulation available for sale on March 20, 2017, one of skill in the art will recognize that Korkay, and water dilutions thereof, are chemical formulations, and such chemical formulations can be prepared by various different sources and/or methods and be suitable for use in the present invention, in order to obtain the benefits of the present invention. In one embodiment, the formulation composition comprises or consists essentially of a water dilution of Korkay.

It should be recognized that formulations comprising the same chemical components of Korkay or water dilutions thereof, but in which the concentrations of one or more components, not including water, deviate from the concentration with respect to Korkay or a water dilution thereof, respectively, by less than 50, 40, 30, 20, 10 or 5 % by weight, with respect to the weight of Korkay or its water dilutions, respectively, can be useful in the present invention. Such chemical compositions can be used in the recommended amounts and rates disclosed herein.

In further embodiments, the formulation comprises or consists essentially of water; an alpha-hydroxy acid, a glycol alkyl ether, and a polyethylene glycol with an average molecular weight in the range of from about 500 to about 1500 mw. It is preferred that the water be essentially free of ionic contamination. The presence of certain ions, such as, for example, carbonates, may affect the clarity of the finish obtained. If the water to be used has ionic or organic contamination, it is preferred to use water that has been subjected to a removal step, such as, for example, reverse osmosis. It is preferred to use water that has a pH of about 7, but benefits of the invention can still be obtained if the water pH is above or below 7, particularly if the pH of the formulation is 7 or below. In further embodiments, the alpha-hydroxy acid contains in the range of from about 5 to about 1 carbons, with glycolic acid preferred. Glycolic acid is available from Chemsolv. The glycol alkyl ether is preferably a polypropylene methyl ether, with dipropylene glycol methyl ether preferred. Dipropylene glycol methyl ether is available from many sources, for example, Dow Chemical, Lyondell Bassell, and Shell. The polyethylene glycol having an average molecular weight in the range of from about 500 to

about 1500 molecular weight is preferably polyethylene glycol having an average molecular weight in the range of from about 750 to about 1250 molecular weight, and even more preferably in the range of from about 950 to about 1050 molecular weight. One example of a suitable polyethylene glycol is PEG(1000).

In additional embodiments, the alpha-hydroxy acid is preferably present in the formulation in the range of from about 5 to about 20 weight percent, with a weight percent in the range of from about 10 to about 15 weight percent more preferred. The weight percent of glycol alkyl ether is preferably in the range of from about 5 to about 20 weight percent, with a range of about 10 to about 15 weight percent more preferred. The weight percent of polyethylene glycol is preferably in the range of from about 1 to about 15 weight percent, with a range in the range of from about 1 to about 9 weight percent more preferred. Water is present in the range of from about 70 to about 80 weight percent, with a range of about 71 to about 77 weight percent more preferred.

In further embodiments, the formulation comprises, consists, or consists essentially of a water dilution of the following four-part mixture:

- 1) about 74% water;
- 2) about 13% glycolic acid;
- 3) about 8% dipropylene glycol methyl ether (DPM glycol ether);
- 4) about 5% polyethylene glycol (PEG 1000 type);

wherein the dilution is preferably comprises, consists, or consists essentially of one part mixture to between about 4 and about 20 parts of water, with a more preferred dilution of between about 5 and about 12 parts water, with an even more preferred dilution being from about 6 to about 8 parts of water, with a range of from about 6.5 to about 7.5, or even from about 6.8 to about 7.2 being particularly suitable. The component equivalent of such a dilution; where by "component equivalent," it is meant that the formulation comprises, consists, or consists essentially of the same components and relative proportions as the foregoing, but the formulation was not prepared by the prescribed dilution, but by other means, such as, for example, directly mixing the components. (The E5 Finish formulation can be formed by creating a mixture which comprises about 7 parts water to about 1 part Korkay). In an embodiment, the formulation comprises the E5 Finish formulation. In other embodiments, the formulation comprises a water-diluted or water-removed concentration of the E5 finish or a chemically identical preparation of the foregoing. In other embodiments, the formulation comprises or consists essentially of the *E5 Finish*.

Preferred modes of application comprise the application of the following or the chemical equivalent of the following at the following rates of application.

A formulation comprising or consisting essentially of one part Korkay to between about 4 and about 20 parts of water, with a more preferred dilution of between about 5 and about 12 parts water, with an even more preferred dilution being from about 6 to about 8 parts of water.

The formulation is applied to the concrete surface preferably at a rate of between about 200 and about 2000 sq ft per gallon, with about 500 to about 1500 sq ft per gallon more preferred, and about 800 to 1200 sq ft per gallon even more preferred. In a preferred embodiment, the formulation is a Korkay dilution in the range of from about 6 to about 8 parts water per part Korkay and the application rate is between about 800 and 1200 sq ft per gallon. While Korkay is specifically referred to, the chemical equivalents, as indicated above, can be used, or used in the above dilutions.

In further embodiments, the formulation comprises or consists essentially of water; an alpha-hydroxy acid, a glycol alkyl ether, and a polyethylene glycol with an average molecular weight in the range of from about 500 to about 1500 mw. In further embodiments, the alpha-hydroxy acid contains in the range of from about 5 to about 1 carbons, with glycolic acid preferred. Glycolic acid is available from Chemsolv. The glycol alkyl ether is preferably a polypropylene methyl ether, with dipropylene glycol methyl ether preferred. Dipropylene glycol methyl ether is available from many sources, for example, Dow Chemical, Lyondell Bassell, and Shell. The polyethylene glycol having an average molecular weight in the range of from about 500 to about 1500 molecular weight is preferably polyethylene glycol having an average molecular weight in the range of from about 750 to about 1250 molecular weight, and even more preferably in the range of from about 950 to about 1050 molecular weight. One example of a suitable polyethylene glycol is PEG(1000).

In additional embodiments, the alpha-hydroxy acid is preferably present in the formulation in the range of from about 5 to about 20 weight percent, with a weight percent in the range of from about 10 to about 15 weight percent more preferred. The weight percent of glycol alkyl ether is preferably in the range of from about 5 to about 20 weight percent, with a range of about 10 to about 15 weight percent more preferred. The weight percent of polyethylene glycol is preferably in the range of from about 1 to about 15 weight percent, with a range in the range of from about 1 to about 9 weight percent more preferred. Water is present in the range of from about 70 to about 80 weight percent, with a range of about 71 to about 77 weight percent more preferred.

The pH of the formulation to be applied to the concrete surface is preferably in the range of from about 3.0 to about 7.2. More preferred is a pH in the range of about 4.0 to about 7.0, with a pH in the range of from about 4.5 to about 6.8 more preferred. Korkay undiluted has a list pH of about 4.3.

It is preferred to apply the formulation to the concrete after the floating process has been performed. It is more preferred to apply the formulation to the concrete *after the floating process has*

been performed, but before or as the combination process is performed. While the formulation can be applied after the combination process, including during the finishing process, the benefits of the invention are found to be reduced. It is generally found that for optimal benefits of the invention, the formulation should be applied after floating has been performed, but before the combination process has been performed.

The present invention can be used in the surface preparation of both indoor-use and outdoor-use concretes. The finishing of concrete for inside use generally involves three successive steps after a poured slab begins to cure: floating, combination, and a final finishing step. Each is undertaken at specific curing stages, and the ascertainment of when to commence each step is within the skilled judgement of the practitioner. Because many or most slabs are often the first element of new construction, the outside elements, such as temperature, relative humidity and wind speed play a role in the determination. As discussed in the section entitled “Methods and Compositions for Improved Concrete Performance,” the use of a specific type of amorphous silica, in the context of a specific process for preparing the concrete, minimizes many of the outside element effects on curing. Thus, the standard three-step finishing process is much easier, with each step often requiring less energy, and less risk of concrete damage during finishing. For example, all three are generally required to get the standard finish on the concrete of construction slabs, which are the basis for most home and commercial construction. In the context of the present invention, floating is generally easier than with standard concrete due to the excellent water retention properties of the concrete described *infra*. Floating can be done by methods known in the art, such as, for example, hand trowel, walk behind, power ride-on trowel, or with use of 48 or 60-inch pans. Generally, the effort needed to float is reduced with respect to that needed to float traditional concrete, and thus the machine speeds can be significantly lower, again, minimizing the potential for damage to the concrete surface.

It is preferred to apply the E5 Finish solution to the surface, in the prescribed dilutions and at the prescribed rates, after floating, but before or during combination. In some situations, it can be convenient to apply the solution after some floating has taken place, and float it into the surface with floating tools, such as, for example, those used for the prior floating. The formation of a plastic-like finish on the surface of the concrete is often apparent after floating if it has been floated into the surface. It is generally formed evenly over the entire concrete surface. It can generally be easily visually ascertained by simple observation by one of skill, but also in many cases, by one of no special skill. The description of “plastic-like” describes a coating which looks like a plastic film has been deposited on the concrete surface. Before extensive additional finishing, the surface is generally dull, cloudy and smooth. Without desiring to be bound by theory, it is surmised that the E5 Finish interacts with the amorphous silica in the concrete, and the interaction is promoted by structural interruptions such as floating. It is generally, but not necessarily somewhat cloudy.

The combination step is then generally performed as known in the art, such as by, for example, a ride on power trowel with combination blades. It is during this step that the plastic-like nature of the surface generally becomes more apparent and pronounced. It may or may not take on the glassy texture and appearance as with later finishing steps. The use of higher combination speeds than used with traditional concrete may give an improved finish at this point in finishing, but not necessarily. It should be noted that there may be situations in which the combination is not performed, or is otherwise deemed unnecessary.

The surface is generally distinctly different from the surface developed during combination by concretes which do not contain both the following; 1) the inventive amorphous silica amounts, particle sizes and surface areas as disclosed herein, and 2) the topical formulations as disclosed herein. The effect has been described by the inventors as “plastic-like.” The surface develops a smoother appearance, which generally increases, to a degree, with combination time, the surface having a reduced incidence of large pores, as well as improved flatness, when compared to widely-used concrete formulations at like stages of finishing that lack the inventive formula and process details as disclosed herein. By “plastic-like,” it is meant that the surface at least has the appearance of, a coating, said coating generally not of high clarity during combination, being occluded to a degree which can be decreased, to a degree, with the progress of combination and/or increasing combination blade speed. At later times during combination, it may or may not take on the glassy texture and even greater clarity as with later finishing steps. The use of higher combination speeds (*above about 190 rpm*) than used with traditional concrete may give an improved finish with respect to clarity and glossiness, but not necessarily. (It should be noted that there may be situations in which the combination is not performed or is otherwise deemed unnecessary.) Again, the higher amount of water retained by the concrete at its surface generally results in less friction between the surface and the combination blades, and thus less energy is required by the machine to maintain a given speed. The risk of machine damage to the surface is generally greatly reduced.

The finishing step can then be performed. The methods known in the art can be used, such as, for example, a ride on power trowel or walk behind trowel with finishing blades. Those who have worked with the inventive finishing methods and formulations indicate that with the finishing step, the surface increasingly takes on glassy characteristics, such as a clarity which is increased over concrete finishes known in the art and prepared in the same fashion, although not as clear as can generally be obtained with a burnishing step. Without desiring to be bound by theory, it is thought that the increased clarity is a consequence of the retention of moisture in the concrete surface, attributable to the inventive inclusion of silica as disclosed herein. The clarity, gloss and flatness achievable after the finishing step is generally enough to qualify as a “Grade 1” finish. With traditional concretes (i.e., wherein the disclosed topical use of the prescribed formulations and the disclosed amorphous silica

are not used), the finishing step does not necessarily give this glassiness, i.e., heightened clarity and/or glossiness, with traditional top finishing speeds of about 190 rpm.

Most available finishing machines are limited to a top speed of about 190 rpm, but some older machines can attain top speeds of about 220 rpm. One characteristic often seen with the use of the topical inventive formulations is that the use of higher finishing blade speeds (such as, for example, 200-220 rpm) than traditionally used (such as, for example, 180-200 rpm) can improve the finish over that achievable at traditional speeds, such that the surface takes on yet greater glossiness and clarity than that achievable at lower speeds. The surface thereby achieved is often still a "Grade 1" finish, but with an increased clarity and gloss with respect to surfaces of the invention which have not been finished at such increased speeds. As far as is known by the inventors, such clarity enhancement at higher speeds is specific to concrete and finishing formulations of the present invention.

The time of finishing is until the surface has the desired appearance. For example, two passes may be necessary in order to observe a finish having superior clarity, glossiness and flatness. It should be noted that the finish can take on a more matte appearance during the combination step, which, if desired can be retained by not performing the final finishing step. In order to obtain a finish having a more glass-like appearance and texture, it is generally necessary to proceed to the final finishing stage.

Alternatively, concrete for outside use, such as, for example, sidewalks, curbs, and parking lots, generally does not require extensive finishing, although some degree of floating is generally performed. The small imperfections in the surface are allowed to remain, and eventually the surface weathers and renders the issue of imperfections moot. However, with outside concrete, water damage during the life of the concrete is an issue. Often, measures are taken to reduce the likelihood of water damage. One measure is the application of a cure and seal agent. The protection given by these agents are generally short-lived. Another measure is the use of air-entrained concrete such that the damage done by absorbed water during freezing is minimized. In practice, neither is a long-term, structural solution. However, it has been found that the application of the solutions and dilutions of the present invention to a surface which has been floated, followed by what is essentially additional floating, done with floating equipment known in the art, such as, for example, hand floating equipment, can prevent the absorption of water into outdoor cement. No further finishing is necessary.

The normal absorption of water of outdoor cement according to the Rilum test is about 1.5 to 3 ml in 20 minutes. The surfaces treated according to the processes and compositions of the present invention absorbed no water. Without desiring to be bound by theory, it is surmised that once applied to the surface, the solution or dilutions went into surface imperfections and capillaries, such as those which can form during curing, and interacted directly or indirectly with the amorphous silica to form

solid plugs in the capillaries, preventing the uptake of water. The floating process is thought to promote the uptake of the solution into the capillaries and other surface imperfections.

Finishing can be done to various grades, based upon the desired glossiness and clarity of the concrete surface. Finishing with a finishing machine, as described above and as performed in the industry, at top speeds of 190 rpm, generally results in a "Grade 1" finish, as is well-known in the art. Further elevations in the quality of the surface, i.e., heightened gloss and clarity, can generally be achieved with the use of a burnishing machine, also well-known in the art, in order to develop a "Grade 2" or "Grade 3" finish. One of skill in the art can generally ascertain the grade of a finish by visual inspection of the finished surface. (Approximate RA (roughness average) reading corresponding to the various grades: Grade 1 generally corresponds to RA of 50-20; Grade 2 generally corresponds to an RA of 19-11; Grade 3 generally corresponds to a RA of 5-0.) It should be noted that the quality of finish upon burnishing depends on the quality of the finish given by the finishing step, which generally gives a Grade 1 surface. The higher-grade finishes achieved by burnishing generally have a polished look to them. Note that unlike with traditional concretes, the gloss of a burnished surface of the present invention is achieved without the use of a protectant or sealant.

Because floor burnishing machines operate at much higher speeds (rpm) than finishing machines, it has heretofore been necessary to wait for some time after completion of finishing, such as at least about three or four days, and as long as 28 days or even longer, before using a burnishing machine on a finished surface. It is known in the art that earlier use generally risks significant damage, such as scratching (which can go quite deep: 2-4 mm) and exposed aggregate, to the finished surface. Remarkably, concrete which has been prepared with amorphous silica, as disclosed and described herein, as well as the topical finishing use of the formulations disclosed and described herein, can be burnished immediately after finishing, if desired, without damage to the concrete surface.

More specifically, concrete which has been prepared with the amorphous silica as described in the Methods and Compositions For Improved Concrete Performance section below and additionally having been prepared with the topical, finishing use of said formulations as described herein can be burnished immediately after the finishing step without damaging the surface of the concrete. For example, Fig. 1 depicts a concrete slab containing 4 oz per hundred weight E5 Internal Cure, with E5 Finish used topically as a finish at rates of 1000 square feet per gallon. The burnishing process was initiated directly after the conclusion of the finishing step. Fig. 1 shows the undamaged surface, despite the fact that the 27 inch burnisher is being run at 2500 rpm. Fig. 2 shows the conversion of the surface from approximately Grade 1 to approximately Grade 2.

Burnishing machines generally come in three sizes (17, 20 and 27-inch diameter) with the larger diameter machines reaching speeds as high as 2500 rpm. Generally, the higher speeds give better clarity and gloss. One remarkable feature of the present invention is that concretes prepared by traditional methods generally require the application of a guard or sealer prior to burnishing in order to attain the Grade 2 or Grade 3 quality of glossiness, with a wait as long as 28 days often required before burnishing can be commenced. Concretes of the present invention can be burnished immediately following finishing without the application of guards or sealers, without damaging the concrete surface. Without desiring to be bound by theory, it is thought that the finishing and burnishing steps cause the amorphous silica to react with the topical formulation to create a glassy substance or phase, with a more complete reaction associated with higher finishing machine and burnishing machine rpms. It has also been observed that, as with the finishing step, less friction is present between the machine and the floor, giving lower RA (Roughness Average) numbers and increased burnishing pad lifetimes.

The number of burnishing passes utilized is generally simply what is required to achieve the clarity and glossiness. The number of passes required to transform a Grade 1 finish to a Grade 2 finish could be as low as 3-4 or as high as 4-20. For every 1000 sq ft of surface, approximately 20 minutes of high speed burnishing may be required to transform a Grade 1 to a Grade 2. It has been noticed that if the floor does not develop a gloss during finishing, it is unlikely to burnish. Experience suggests that waiting some time after finishing, such as, for example, from 1-24 hours, or more, to commence burnishing, may, in some circumstances, give better clarity upon burnishing.

Disclosed below are improved formulations and methods of concrete mix preparation which are preferably used with the inventive finishing (or surface treatment) formulations and methods disclosed above. The final three Examples pertain to the concrete formulations and methods disclosure.

Methods and Compositions for Improved Concrete Performance

Concrete has been the basic element of construction since ancient times. Depending upon the type, concrete can have enough compressive strength to withstand the rigors of the elements and continuous public use with little structural degradation over time. Essential to its usefulness is the pourable rheology of water-containing mixtures of uncured concrete. Pourability of concrete enables structural shaping, such as for example, with a mold or other constraint, prior to curing into a hard form. Water functions in both the shaping and curing of concrete. However, heretofore, it has been necessary to carefully manage the water which gives rise to the pourability of concrete; too much or

too little water in the concrete at any time during curing can negatively affect the concrete curing process, leading to a structurally compromised concrete product.

Water in curing concrete generally has three important functions. First, water is required for the hydration of the dry cement. The hydration reaction (curing) is the concrete-forming reaction (C-S-H forming reaction): water participates in a reaction by which the bonds are formed which give concrete its compressive strength. Theoretically, the concrete with the greatest compressive strength is formed when the hydration reaction goes to completion. In reality, the hydration reaction generally proceeds to a significant degree during the first stages of curing, but is limited at later times by evaporation of water from the surfaces of the curing concrete. Concrete hydration can be greatly affected by ambient conditions such as wind speed, relative humidity and temperature. Thus, concrete can “dry” even though it is only partially cured. If the concrete surface dries out prematurely, hydration can be incomplete, giving a surface that is both porous and weak. In order for concrete to reach its full-strength potential, it is generally required that water be in place continuously for extended periods of time, often for days. In practice, concrete is seldom cured to its full-strength potential.

A second function of water is to aid in pourability of concrete. Upon the addition of water to the cement, but before hydration takes place on a large-scale, much of the water that will ultimately participate in hydration is already associated with the additives and calcium hydroxide in the concrete. Water in excess of this associated water generally benefits flowability of concrete, with more “extra” water generally correlating with a greater flowability of the concrete.

In general, it is thought in the industry that even relatively small amount of such extra water is detrimental to the concrete product. Environmental conditions (wind, relative humidity and temperature) can cause the surface of the slab to dry faster than the interior. Internal water is often trapped interiorly. A degree of hydration begins with the addition of water to the cement, and shortly after pouring, hydration can be well underway. The trapped water can escape to the surface through capillaries formed by the relatively dried, partially cured surface. The trapped water may instead form reservoirs inside the curing concrete, resulting in voids in the cured concrete product. Both capillaries and reservoirs can compromise the compression strength of the resultant cured concrete. They also enable environmental water to enter the concrete during its lifetime of service, allowing the concrete to be degraded by freeze damage and other water-mediated damage processes.

Furthermore, it is thought that water that does not participate in hydration (i.e., water that does not combine chemically with the concrete) essentially adds volume to the poured concrete, and the loss of this water during drying generally results in some degree of shrinkage of the concrete during curing. Nevertheless, the concrete must be workable. Thus, the inclusion of the optimum amount of water such that hydration (curing) and workability are maximized, while shrinkage and structural damage to the concrete during hydration/drying is minimized remains a delicate balancing act, made all the more difficult by environmental factors.

A third function of water is to enable finishing of partially cured surfaces which may also be desiccated due to evaporation. Surfaces which dry prematurely are generally difficult to finish. It is a normal practice to add water to such surfaces to facilitate strike-off, closing and finishing. Added water can penetrate the surface, particularly when capillaries are present. Such water generally leaves the concrete slowly over an extended period, often even when the concrete appears dry. Often further steps, such as sealing or steps which require securing components such as floor tiles or carpeting to the floor are affected by the slow release of finishing water. For example, it is not unusual for adhesives to fail within a short time of floor installation due to the slow emission of water. This water is often primarily finishing water. Even when water is added, the finishing machines often must be operated at higher settings in order to effectively finish a surface which has partially dried.

The use of additional cementitious materials in concrete to improve concrete properties, such as, for example, water impermeability, compressive strength and abrasion resistance, is well-known. Various types of particulate silica, such as, for example silica fume, have been used in concrete as additional cementitious materials to improve water-impermeability and compressive strength. A general problem with silica is that it can raise the water demand of a concrete formulation such that the likelihood of capillaries and void formation during curing is increased due to the higher likelihood of significant bleedwater. In order to reduce bleed water, it is common in the art to use relatively large amounts of silica fume (5 to 10 percent by weight of cementitious materials), with water minimized or carefully rationed to relatively low amounts, such as, for example, below a ratio of about 0.5 by weight of water to cementitious materials. (*Design and Control of Concrete Mixtures*, Sixteenth Edition, Second Printing (revised); Kosmatka, Steven H.; pg. 156). Such low amounts of water are generally below what is recommended by the cement manufacturer, and can significantly impair the rheology of the concrete, causing it to be difficult to pour or work.

Surprisingly it has been found that the use, in poured concrete installations, of nanosilica (i.e., amorphous silica having particles with an average particle size of less than about 55 nm, and in some embodiments, less than about 7.8 nm, or, in other embodiments, between about 5 and about 55 nm, or between about 5 and about 7.9 nm; and having a surface area in the range of from about 300 to about 900 m²/g, or in other embodiments, from about 450 to about 900 m²/g, in amounts such that it is present in the concrete in a weight ratio in the range of from about 0.1 to about 4 ounces amorphous silica per 100 lbs of cement (i.e., not including water, aggregate, sand or other additives) can result in a significantly lower rate of water loss during curing than concrete which is hydrated in the absence of such amorphous silica. Thus, the surfaces of newly-poured, partially-cured concrete of the inventive method remain easily workable for longer periods than those of concrete prepared by other methods, and are less sensitive to environmental conditions which ordinarily speed evaporation. Bleedwater, curling, cracking and shrinkage are generally greatly reduced. Compressive strength of the resultant cured concrete is generally significantly increased. Remarkably, important to the realization of the

benefits of the invention is the introduction of the silica to the concrete mix after the water and other dry components have been mixed such that the dry components are thoroughly wetted. The introduction of the silica at an earlier stage, such as prior to the wetting, generally does not give a significant reduction in bleedwater, cracking and shrinkage, and may in fact be worse in such aspects than non-silica controls. The foregoing holds true even if there is an improvement in compressive strength with respect to non-silica controls.

A concrete is disclosed which comprises small-particle-size, high-surface-area amorphous silica, used in much smaller proportions to the cement than generally used in the industry for structural purposes: only about 0.1 to about 4 ounces per hundred weight of cement mix ("cwt"). In an additional aspect, the improved concretes are prepared by a process-specific addition of the silica. These improved concretes can be prepared using the standard amount of water recommended by the cement manufacturer, or even water in excess of the recommended amount, without significantly compromising compressive strength. Such a result is truly surprising. Despite the use of such water amounts, little or no bleedwater is observed during curing. The formation of capillaries and voids is minimal or even essentially completely suppressed, and more water is retained in the concrete during curing, allowing more water to participate in curing over an extended period of time, and compressive strength, both early (3 day) and, particularly late (28 day) is greatly improved.

Despite their allowance for relatively high amounts of water, the low-silica concretes have improved compressive strength and abrasion resistance, among other improved characteristics. An improvement in compressive strength, is surprising, considering the small amounts of silica employed, while known methods use much larger amounts to achieve gains which are, in some cases, significantly less. Furthermore, large improvements in concrete abrasion resistance have generally not been observed with the use of silicas such as, for example, silica fume, even in the larger amounts usually used. (*id.*, pg. 159). The low-silica concretes, described herein, give profound improvement in abrasion resistance as measured by test ASTM C944. (Note that with regard to the foregoing standard, the version employing a 22 pd, 98 kg load was used in all references to the standard herein.) Standard concretes (i.e., not comprising the high-surface-area amorphous silica taught *infra*) can have a value of in the range of from about 2.5 to about 4.0 grams of loss. The low-silica concretes taught herein can have an ASTM C944 value is as low as 1.1 grams of loss or less.

Even more remarkably, the specific steps of the process for mixing the components to form the cement mix are important for the realization of the increased water retention, compressive strength and workability of the newly-poured, partially-cured concrete surfaces. Essentially all of the amorphous silica is added after the combination of some or essentially all water and the dry ingredients (for example, cement mix, aggregate, sand), within a mixing machine, such as, for example, a Ready-mix to be used in the mixing stage (i.e., prior to the actual pour). By "essentially all of the water," it is meant that water which is part of the amorphous silica formulation, such as, for

example, water involved in creating a colloidal suspension of the amorphous silica, generally being much less than the water added to the concrete mix, is not included within the meaning of “essentially all.” It is particularly convenient to add the small particle-size silica after (or in some embodiments, with) a final portion of water (i.e., “tailwater”) prior to final mixing and pouring. The breaking of water addition into two portions is particularly convenient with the use of a Ready-mix, in that the second portion can be used to rinse remnant dry components from near the mouth of the drum down into the bulk.

That small particle silica is more effective after tailwater addition is unexpected. The general thinking in the art is that the addition of silica to concrete has heretofore been thought generally effective even if it is added to the mix of cementitious materials prior to the addition of water. However, it has been found on the scale required for construction of building slabs, footings and other large scale concrete pours, such that mixing and pouring equipment such as Ready-mixes are used, the addition of the small amount of small-particle-size silica, as described herein, has been demonstrated, as indicated herein, to be much more effective when added after the quantity of water, or, in preferred embodiments, with or after a second portion of water (“tailwater”) to concrete which has been wetted and, optionally, mixed for a period of time, as disclosed herein, than when it is added before the water, or with the portion of water used to wet the cementitious materials.

The amorphous silica is added after the water, cement mix and solids (aggregate and sand) are mixed, such as for example, with a Ready-mix or other mixer. The formation of capillaries and reservoirs can be reduced or eliminated. The benefits of the invention can generally be obtained even when the concrete mix contains significant amounts of water in excess of that required by the concrete in order to fully hydrate it (cement mixes generally have a recommended amount of water to give the concrete which can be fully hydrated according to the manufacturer specification). Concrete having water equal to, or even in excess of the amount required for full hydration, or recommended by the cement mix manufacturer, are preferred.

While silica of larger sizes has been shown to improve compressive strength of concrete, it is well-known that silica has a water requirement and as size is decreased and surface area is increased, the amount of water required by the concrete increases. Thus, the perception in the art is that there is a tension between 1) decreasing silica particle size and 2) keeping water content low enough such that the formation of capillaries and voids are minimized. Thus, it is thought that at small particle sizes, a risk exists that the water requirement would override the structural benefits provided by silica. Illustrating this fact, the applicants have found that if the prescribed amorphous silica is added to the cement or concrete mix at other points in the preparation of the pourable concrete mixture, such as, for example, at any time prior to relatively complete mixing of water and cement mix (before or with the water which wets the cement mix, the resulting poured concrete can exhibit significantly more capillaries, voids and/or resulting surface bleed water than if the amorphous silica is added after complete mixing of the water and cement mix. Thus, it is truly surprising that if the silica is added,

(preferably as amorphous colloidal silica or precipitated silica) at a point after the cement and water have been completely mixed, the formation of capillaries and voids is reduced or eliminated, water evaporation is slowed, and newly-poured, partially-cured surfaces are generally easily worked, often without the addition of finishing water. In general, it would be expected that some degree of benefit can be observed when the silica is added after the water even if complete mixing of the water and cement mix has not taken place.

The success of delayed addition of nanosilica is particularly surprising in light of what has been discovered about how factors such as nanosilica particle size and surface area affect concrete properties, most notably compressive strength, when introduced as colloidal silica into concrete-forming mixtures. A summary of some findings in the art, the most recent findings of which the inventors only become aware after their own experimentation, is as follows. The use of colloidal nanosilica (silica having average particle sizes of less than about 100 nm, and particularly silica having average particle sizes of less than about 10-15 nm) in concrete-forming mixtures has been fraught with issues pertaining to compressive strength, among other properties, of the resulting concrete. For example, past studies have shown that larger particle-size silica, such as, for example, silica fume (about 145 nm) generally has a positive effect upon compressive strength in a wide range of particle sizes and loadings. However, smaller silica particles have a much more complicated correlation with compressive strength. Recent studies have shown that nanosilica particles tend to agglomerate in colloidal solutions. (Non-nano-sized silica particles, such as, for example, silica fume, have larger surface potentials, and are much less inclined to agglomerate.) The studies further show that such agglomerates, when introduced into concrete-forming mixtures and not subsequently sufficiently dispersed, such as, for example, by agitation, can become spaces in the final concrete product which are devoid of concrete matrix structure, negatively affecting compressive strength and other properties. However, the studies also show that the extensive surface area afforded by nanosilica for pozzolanic reaction, being much greater (by more than one order of magnitude, often several) than that of non-nano-sized silica, causes the C-S-H matrix-forming reaction to experience competition from reactions at the silica surface. As a result, the availability of a large amount of surface area can result in a weaker C-S-H matrix, resulting in lower compressive strength. Thus, in the search for nanosilica loading parameters which increase compressive strength, there can be a tension between 1) the persistence of aggregates in the concrete-forming mixture, and 2) agitation of the concrete-forming mixture or the application of other modes of dispersion, such that the aggregates are reduced or eliminated, but resulting in a surge in the amount of exposed silica surface area.

Setbacks were encountered in the inventor's attempts to use nanosilica in the field. It was found that silica loadings which clearly produce compressive strength gains in the lab when prepared by standard procedures such as ASTM 305-06 often failed to give compressive strength gains when used in standard fashion in a larger-scale process subject to the preparation constraints of an industrial pour, e.g. a Readymix process. Furthermore the concrete was often rheologically compromised,

having poor pourability, as well as often exhibiting greater bleedwater, cracking, curing and shrinkage than a silica-free control.

Such a procedural dependence for the same loading levels of nanosilica could be considered unexpected because the apparent differences are in scale, as well as increased time to complete component mixing associated with the Readymix. One of skill in the art may not expect the processes which affect compressive strength to occur on the relatively brief timescale involved in the initial mixing of the concrete components, such that the differences in mixing times would affect compressive strength. This is especially true given that test cylinders are taken at pour time; i.e., differences in measured compressive strength could be argued to be not even partially attributable to larger bulk size of slab vs. size of sample.

Furthermore, upon extensive experimentation, the addition of the silica late in the mixing process as described *infra* was found to restore the compressive strength-boosting effect of nanosilica. This was an unexpected result because much, if not almost all of the mixing agitation has taken place by the time the nanosilica is finally added. Thus, any aggregates are less likely to be completely dissipated into the concrete mix, and would theoretically weaken the concrete as described above. In general, it has been found that on a construction scale, adding the colloidal nanosilica after the addition of water gives a concrete mixture which is more pourable and a concrete product which of increased compressive strength, pourability, and wear resistance; as well as decreased cracking, curling and shrinking with respect to standard addition samples and silica-free control samples.

A concrete mix is created from components comprising quantities of a) a dry cement mix; b) water; c) amorphous silica; and d) aggregate and or sand.

Dry cement mixes generally have a recommended water content which gives a water/cement ratio providing a concrete mix which has a combination of desirable pouring and curing characteristics. In some cases, the recommended water content encompasses a range of water contents. As indicated *infra*, the initial water content of concrete mix prior to pouring can give rise to issues during curing and finishing which reduce the quality of the resulting concrete installation (slab, footing, etc.). It is common for water-reducing measures, such as the use of “water-reducers” and superplasticizers to be employed in the interests of reducing water-mediated structural flaws in the cured concrete. It should be noted that while the benefits of the present invention should be evident in circumstances in which the water content is being reduced below that recommended by the manufacturer, the present invention can be used to give the inventive concrete in situations in which the water included in the concrete mix is equal to or greater than the amount specified by the manufacturer of the dry cement mix. Water-reducers in the concrete mix are generally unnecessary.

Thus, in a broad aspect, the cement mix and the water are present in the concrete mix are present in the mix in the following proportions:

A quantity of water; and a quantity of dry cement mix, said cement mix characterized by:

i) a manufacturer suggested water/cement ratio value; wherein said suggested ratio falls in the range of from about 0.35 to about 0.65 ; and whereupon combination with the quantity of water, the water/cement ratio is greater than the value corresponding to about 10% less than the suggested value but less than the value corresponding to about 30% more than the suggested value;

or

ii) a manufacturer suggested water/cement ratio range, having an upper value and a lower value, and whereupon combination with the quantity of water, the water/cement ratio is greater than the value corresponding to about 10% less than the lower value and not greater than the value corresponding to about 30% more than the upper value;

or

iii) an amount such that, whereupon combination with the quantity of water, the water/cement ratio is in the range of from about 0.35 to 0.65;

The benefits of the invention are generally expected to be manifest with the use of commercially useful types of Portland cement. The cement mix is one or more of the types commonly used in construction, such as, for example, Portland cements of Types I, II, III, IV and V.

The quantity of water above is added to the cement mix. This quantity is inclusive of all water which is combined with the concrete mix comprising at least the cement mix, except water introduced with the silica in the case of water-containing formulations such as colloids, dispersions, emulsions, and the like. As further detailed below, the water can be combined with the concrete mix comprising at least the cement mix in multiple portions, such as, for example, the addition of a second portion of water (for example, "tailwater") after a first portion of water has been combined with the concrete mix and agitated for a time. Note that water is sometimes applied to the surface of concrete after it has partially cured, to prevent the premature drying of the surface, which could result in shrinkage, as well as later difficulties in working and finishing. This "finishing" water is not included within the quantity of water. In other embodiments, the water/cement ratio is in the range of from about 0.38 to 0.55, or, in more specific embodiments, in the range of from about 0.48 to about 0.52, or in the range of from about 0.38 to about 0.42.

In a more preferred embodiment, in reference to i), ii), and iii), above, the water and cement mix are present in the concrete mix in the proportions wherein upon combination of the quantity of dry cement mix with the quantity of water, the water/cement ratio is: equal to or greater than the suggested value, but not greater than the value corresponding to 30% more than the suggested value; or

equal to or greater than the upper value of the suggested range, but not greater than the value corresponding to about 30% more than the upper value; or at least 0.35, but not greater than 0.65.

Particle size of amorphous silica is particularly important. Larger particle sizes, such as will be found in micronized silica, generally do not reduce the formation of capillaries and voids to the degree seen when amorphous silica sized as prescribed herein is used in the prescribed amounts. The inventive concrete mix comprises a quantity of amorphous nanosilica, which is preferably present in an amount in the range of from about 0.1 to about 7.0 ounces per hundredweight of cement (cwt) in a), and having particle sizes such that the average silica particle size is in the range of from about 1 to about 55 nanometers, and/or wherein the surface area of the silica particles is in the range of from about 300 to about 900 m²/g, or in other embodiments, from about 450 to about 900 m²/g.

Amorphous silica from various sources is generally suitable as long as it is characterizable by the particle size and surface area parameters above. Nonlimiting examples of suitable amorphous silica include colloidal silica, precipitated silica, silica gel and fumed silica. However, colloidal amorphous silica and silica gel are preferred, and colloidal amorphous silica is most preferred.

In further embodiments, the silica particle size is in the range of from about 5 to about 55 nm. Preferred are particles with average particle size of less than about 25 nm, with average particle size of less than about 10 nm more preferred, and average particle size of less than about 7.9 nm even more preferred. A preferred weight proportion in the concrete is from about 0.1 to about 3 ounces of amorphous silica per 100 lbs of cement (not including water, aggregate, sand or other additives). A more preferred weight proportion in the concrete is from about 0.1 to about 1 ounces of amorphous silica per 100 lbs of cement (again, not including water, aggregate, sand or other additives). Even more preferred is about 0.45 to about 0.75 ounces of amorphous silica per 100 lbs of cement (again, not including water, aggregate, sand or other additives). Surprisingly, above about 3 to about 4 ounces of the amorphous nanosilica per 100 lbs cement mix, the concrete mix can become difficult to pour or work, and compressive strength can suffer greatly, even with respect to non-silica controls. Otherwise, amounts above about 1 ounce per 100 lbs cement generally give decreasing compressive strength gains with respect to the preferred range of about 0.45 to about 0.75 ounces of amorphous silica per 100 lbs cement. The preferred range given is the most economically feasible range, i.e., above that, the compressive strength gains are less per additional unit of silica, and cost of silica per unit increase of compressive strength may cause the cost of the concrete to become prohibitive.

Amorphous silicas having surface areas in the range of from about 50 to about 900 m²/gram are preferred, with about 150 to about 900 m²/gram more preferred, and about 400 to about 900 m²/gram even more preferred, and 450 - 700 m²/gram or 500 - 600 m²/gram even more preferred. Amorphous silica with an alkaline pH (about pH 7 and above) is preferred, with a pH in the range of from 8 to 11 being more preferred.

In yet another embodiment, the amorphous silica is provided by the use of E5 INTERNAL CURE, an additive available commercially from Specification Products LLC, which contains about 15 wt% amorphous silica in about 85 wt% water. The silica particle characteristics are an average particle size of less than about 10 nm (measured by BET method), and a surface area of about 550 m²/g. In one embodiment, the weight proportion of E5 INTERNAL CURE to cement is in the range of from about 1 to about 20 ounce of E5 INTERNAL CURE to 100 lb cement (not including water, sand, aggregate or other additives). More preferably the weight proportion of E5 INTERNAL CURE to cement is in the range of from about 1 to about 10 ounces of E5 INTERNAL CURE to about 100 lb cement (not including water, sand, aggregate or other additives). A more preferred weight proportion of E5 INTERNAL CURE to cement is in the range of from about 1 to about 5 ounces of E5 INTERNAL CURE to about 100 lb cement, with about 3 to about 5 ounces of E5 INTERNAL CURE to about 100 lb cement (not including water, sand, aggregate, or other additives) even more preferred. Surprisingly, the use of more than about 20 ounces of E5 to about 100 lb cement (again, not including water sand, aggregate or other additives) can cease to be of benefit in that additional beneficial water or compressive strength benefits may not be observed or may be minimally observed. The resulting concrete mix may be difficult to pour, and any resulting concrete may be of poor quality. Note that the quality of the concrete diminishes with the distance from the preferred range of about 3 to about 5 ounces per 100 lb cement, but the compressive strength may still be improved over that in the absence of the E5 INTERNAL CURE colloidal amorphous silica. In preferred embodiments the colloidal silica added to the concrete mix is in the range of from about 40 to about 98 wt% silica, with 60 to 95 wt% preferred and 70 to 92 wt% more preferred, and 75 to 90 wt% even more preferred.

Aggregate and sand can generally be used in the inventive concrete in amounts as known in the art for construction purposes. In one embodiment, a quantity of aggregate and/or a quantity of sand is used such that they total an amount in the range of from about 400 to about 700 wt% bwoc. In general, a concrete mix is prepared with components comprising cement mix, water, and, preferably, a quantity of aggregate and sand (sometimes referred to in the art as "large aggregate" and "small aggregate," respectively). It is permissible for the concrete mix to comprise only one of the two, such as only sand or only aggregate, but it is preferred the mix comprise at least a quantity of each. Sand and aggregate can contribute to the silica content of the cement mixture, and thus they can affect (i.e., raise somewhat) the water requirement of the concrete mix. Generally, most types of aggregate which are appropriate for the use to which the concrete is to be put can be used. Included are larger aggregates such as coarse, crushed limestone gravel, larger grades of crushed clean stone, and the like, as well as smaller aggregates such as the smaller grades of crushed clean stone, fine limestone gravel, and the like. Likewise, many types of sand, such as pit (coarse) sand, river sand and the like can be used. Generally, in concrete applications, "coarse sand" is preferred to "soft sand," which is known to be more appropriate for use in mortars. However, soft sand may generally be expected to have a different water requirement than coarse sand when used in concrete preparation. As is known in the

art, weight-bearing applications may require larger aggregate, such as coarse, crushed limestone. Such larger aggregate is preferred for poured concrete applications, particularly for use in poured building slabs are the larger aggregates, such as, for example, coarse crushed limestone gravel and larger grades of crushed clean stone, and pit sand.

The proportion of aggregate and sand, taken together, based on weight of cement (bwoc) is preferably in the range of from about 2000 to about 4000 lbs per yard of dry cement mix (in the range of from about 520 to about 610 lbs per yard, or more preferably from about 560 to about 570 lbs per yard, even more preferably, about 564 lbs per yard). More preferred is a combined proportion of aggregate and sand in the range of from about 2700 to about 3300 lbs per yard of dry cement mix. More preferred is a range of from about 2900 to about 3100 lbs per yard of dry cement mix. In another embodiment, the weight of aggregate and sand is between 50 and 90 wt % based upon the weight of the concrete, with a range of from about 70 to about 85 wt % preferred. The relative amounts of aggregate and sand are not critical, but are preferably in the range of from about 20 wt % to about 70 wt % sand based upon the combined weight of the sand and aggregate, with about 40 wt% to about 50 wt % sand preferred.

It has been discovered, especially in commercial scale pours, that even the small amounts of amorphous nanosilica required to effect the disclosed benefits, when added to the cement mix prior to the water, can be detrimental to the pourability of the concrete mix, as well as the quality of the resultant concrete, even rendering the concrete unsuitable. The process of the present invention generally includes the situation in which at least a portion of the quantity of water is added prior to the addition of the quantity of amorphous nanosilica, with at least a time period of agitation between the additions to distribute the water prior to the addition of the amorphous silica. In practice, some water may be added later in the preparation process, if desired. For example, it is known to add water in two (or more) portions, such as the practice of adding a portion as "tailwater" after the addition and agitation of a first portion. In one embodiment, the amorphous silica is added as a colloidal silica with a second portion of water. In a preferred embodiment, the colloidal silica is added after the addition of water which has been added in two portions, with agitation after the addition of each portion.

Thus, more generally, the quantity of water can be added in its entirety or added in portions comprising an initial portion, comprising in the range of from about 20 wt% to about 95 wt% of the quantity of water, and a tailwater portion, comprising the remainder; wherein the initial portion of water is combined with the quantity of cement mix and the aggregate/sand components to form a first mix; and wherein the amorphous silica is added to a mix comprising the quantity of cement mix, the aggregate/sand components and the initial portion of water to form a second mix. Even more preferred is an initial portion comprising in the range 35 to about 60 wt% of the quantity of water.

(The below three situations (i.e., “situation 1”, “situation 2” and “situation 3”) correspond, respectively to i) the addition of the silica after the addition of the tailwater; ii) the addition of the silica before the addition of the tailwater; and iii) the co-addition of the silica with the tailwater.)

In embodiments with split water addition, wherein the tailwater is 1) added to the first mix; or 2) added to the second mix; or 3) co-added with the amorphous silica to the first mix, wherein the amorphous silica and the tailwater are, optionally, intercombined; and wherein 1) the first mix is agitated for a time t_{11} prior to the addition of the tailwater, for a time t_{12} after the addition of the tailwater but before the addition of the amorphous silica, and for a time t_{13} after the addition of the amorphous silica; or 2) the second mix is agitated for a time t_{21} prior to the addition of the amorphous silica, for a time t_{22} after the addition of the amorphous silica but before the addition of the tailwater, and for a time t_{23} after the addition of the tailwater; or 3) the second mix is agitated for a time t_{31} prior to co-addition of the amorphous silica and the tailwater, and whereupon the concrete mix is then agitated for a time t_{32} .

In situation 1), in which the second portion of water (tailwater) is added to a concrete mix comprising a first portion of water, the quantity of cement mix and the sand/aggregate components, t_{11} is preferably in the range of from about 2 to about 8 minutes, with about 3 to about 6 minutes more preferred, and at a mixing speed (such as for example, in a Ready-mix) preferably in the range of from about 2 to about 5 rpm. Time t_{12} is preferably in the range of from about 0.5 to about 4 minutes, with a more preferred range of from about 1 to 2 minutes, at a mixing speed in the range of from about 2 to about 5 rpm. Time t_{13} is preferably in the range of from about 2 to about 10 minutes, with a range of from about 5 to about 10 minutes more preferred, with a relatively high mixing speed at a rate in the range of from about 12 to about 15 rpm. After the high rate mixing, the rate can be lowered to a rate in the range of from about 2 to about 5 rpm for a time, such as, for example, a transit time to a pour site. Transit time standards are set by the American Concrete Institute. For example, the concrete must be poured within 60 minutes of the end of high-rate mixing if the temperature is 90 F or greater, and within 90 minutes if the temperature is less than 90 F.

In situation 2), in which the second portion of water (tailwater) is added to a concrete mix comprising a first portion of water, the quantity of cement mix and the sand/aggregate components, and the amorphous silica, t_{21} is preferably in the range of from about 2 to about 8 minutes, with about 3 to about 6 minutes more preferred, and at a mixing speed (such as for example, in a Ready-mix) preferably in the range of from about 2 to about 5 rpm. Time t_{22} is preferably in the range of from about 0.5 to about 2 minutes, with a more preferred range of from about 0.5 to 1 minutes, at a mixing speed in the range of from about 2 to about 5 rpm. Time t_{23} is preferably in the range of from about 2 to about 10 minutes, with a range of from about 5 to about 10 minutes more preferred, with a relatively high mixing speed at a rate in the range of from about 12 to about 15 rpm. After the high rate mixing, the rate can be lowered to a rate in the range of from about 2 to about 5 rpm for a time,

such as, for example, a transit time to a pour site. As noted above, transit time standards are set by the American Concrete Institute.

In situation 3), in which the tail water is co-added with the amorphous silica to the first mix, wherein the amorphous silica and the tailwater are, optionally, intercombined, t_{31} is preferably in the range of from about 2 to about 8 minutes, with about 3 to about 6 minutes more preferred, and at a mixing speed (such as for example, in a Ready-mix) preferably in the range of from about 2 to about 5 rpm. Time t_{32} is preferably in the range of from about 2 to about 10 minutes, with a range of from about 5 to about 10 minutes more preferred, with a relatively high mixing speed at a rate in the range of from about 12 to about 15 rpm. After the high rate mixing, the rate can be lowered to a rate in the range of from about 2 to about 5 rpm for a time, such as, for example, a transit time to a pour site. As noted above, transit time standards are set by the American Concrete Institute.

In another embodiment, the entire quantity of water is added to the quantity of cement mix and the aggregate/sand components to form a mix, whereupon said mix is agitated for a time t_a prior to the addition of the amorphous silica, whereupon the concrete mix is then agitated for a time t_b prior to pouring. The addition of the entire quantity of water at once is useful in the case of wet batch processes. Time t_a is preferably in the range of from about 2 to about 8 minutes, with about 3 to about 6 minutes more preferred, and at a mixing speed (such as for example, in a Ready-mix) preferably in the range of from about 2 to about 5 rpm. Time t_b is preferably in the range of from about 2 to about 10 minutes, with a range of from about 5 to about 10 minutes more preferred, with a relatively high mixing speed at a rate in the range of from about 12 to about 15 rpm. After the high rate mixing, the rate can be lowered to a rate in the range of from about 2 to about 5 rpm for a time, such as, for example, a transit time to a pour site. As noted above, transit time standards are set by the American Concrete Institute. While benefits of the invention would generally be observed in the case of a single addition of water, in practice, the two-portion division of water is generally adhered to. After the agitation of a concrete mix comprising a first portion, the use of a second portion has the advantage of washing down into the Ready-mix remnants of insufficiently mixed cement mix from near the mouth of the barrel.

The concrete mixture can be prepared in a wet ("central mix") or dry ("transit mix") batch situation. In wet batch mode, the dry components are mixed with the quantity of water followed by the amorphous silica to give a concrete mix, in one of the ways indicated above. The mix is agitated as above or introduced into a Ready-mix and agitated therein as indicated above. Essentially, the wet and dry batch situations are similar except that part of the procedure for a wet batch is performed outside of the Ready-mix (for example, at the plant). Dry batching ("transit mix") is somewhat preferred. For example, 40 plus or minus 20%, or, in further embodiments, plus or minus 10% of the total quantity of water to be utilized in the preparation of the concrete mix, sand and coarse aggregate used in the batch is loaded into a Ready-mix. The cement mix, coarse aggregate and sand are mixed

together and loaded into the Ready-mix. The remaining water is then loaded into the Ready-mix. Once the dry components and the water are completely mixed, the amorphous silica is added, and the mixture is mixed for 5 to 10 minutes. The mixing preferably takes place at relatively high drum rotation speeds, such as, for example, a speed in the range of from about 12 to about 15 rpm. Once the higher-speed mixing has occurred, the batch can then be poured. However, it is permissible to have a period of time between the higher-speed mixing and pouring, such as transport time to the pouring site. In general, as long as the concrete is mixed at lower speeds, such as, for example, about 3 to about 5 rpm, a time between the high-speed mixing and the pouring of in the range of from about 1 to about 60 minutes is permissible.

In one embodiment, it is particularly convenient to add the silica to a Ready-mix, which contains the water, cement and other dry components, once the Ready-mix has arrived at the pour site. It has further been found that after the amorphous silica has been added, the concrete/silica mixture should be mixed, prior to pouring, for a time, most preferably at least from about 5 to about 10 minutes. However, other periods of time may be permissible with respect to at least partially obtaining the benefits of the invention.

The benefits of the invention can be expected in commercially used variants of the foregoing process, as long as the amorphous silica is added at the end, after the mixing together of the dry components and the first and second portion of water (or with the second portion of water), and the silica-added mixture is mixed for a time as specified herein prior to pouring.

The concrete mix is then poured to form a concrete installation. In a preferred embodiment, the concrete mix is formed and agitated in the context of an industrial scale pour, such as the preparation of footings or slabs. In an additional embodiment, the concrete mix is created with and within equipment which holds the mix as it is being created, and which also has the capacity to agitate the mix, such as, for example, a Ready-mix.

One advantage of the present inventive process is that water in concrete formation, such as for example, a slab, formulated according to the present invention, appears to be immobilized in the formation rather than lost to evaporation. The likely fate of much of this water is to participate in hydration at extended periods of time rather than form capillaries and voids. Thus, it is expected that, regardless of thickness, concrete slabs, walls and other formations will display a reduction or lack of voids and capillaries, and a correlative gain in compressive strength. Concrete formation having improved structure and compressive strength with thicknesses up to about 20 feet can be formed with the concrete of the present invention.

An advantage of the present inventive process is that poured concrete are less damaged by drying caused by environmental conditions, such as temperature, relative humidity and air motion such as wind. For example, concrete of good quality can be produced at wind speeds as high as 50

mph, temperatures as high as 120°F and as low as 10°F, and relative humidities as low as 5% and as high as 85% or even higher.

The compressive strength of the concrete formed by the method of the present invention is generally increased with respect to concrete formed by methods which are similar or, preferably, the same save for the addition of silica after the mixing of the water, cement mix and filler materials (aggregate, sand and the like). “Similar” or “the same” applies to environmental conditions such as wind speed, relative humidity and temperature profile, as well as other environmental factors, such as shading or heat radiating surroundings with respect to the assessment of increase in compressive strength. Factors within the pourer’s control, such as mixing times and parameters, pouring parameters (i.e., slab dimensions) are more easily accounted for. An increase in compressive strength is preferably assessed from pours which are identical except for the addition of the amorphous silica. In a preferred embodiment, the assessment is made from pours which are prepared from identical amounts of identical ingredients, simultaneously but in separate Ready-mixes, poured side-by-side, at the same time, but using separate Ready-mixes. Such pours are “substantially identical.”

The increase in compressive strength can be in the range of from about 5 to about 40% or even more, based upon the compressive strength of the non-silica-containing pour of a pair of substantially identical pours. In more commonly observed embodiments, the compressive strength increase as assessed through substantially identical pours is in the range of from about 10 to about 30%.

The concrete of the present invention can generally be used in applications which require poured concrete, such as, for example, slabs, footings, and the like. An advantage of the present invention is that the concrete prepared therefrom is generally of increased resistance to water penetration, and can thus be used in poured applications which are particularly prone to moisture exposure and the associated damage, such as footings.

As indicated *infra*, the present invention involves the discovery that nanosilica, when added to a concrete mix, preferably as a colloidal silica, after the addition of at least a portion of water, gives a cement having an improved compressive strength among other improved properties, such as abrasion resistance and water permeability.

The additive concrete components such as sand and aggregates of sizes which are used in the art can generally be used in the concrete of the present invention without destroying the benefits provided by the present invention.

Thus, it is possible to utilize a concrete, comprising of ample water for hydration, pouring and working, in the preparation of concrete which generally lacks the deficiencies otherwise associated with concrete from concrete having high amounts of water of transport. The inventive compositions result in concrete which retains water such that exposed surfaces are less likely to dry prematurely than concrete which have not had amorphous silica added. The relative water retention effect is observed even in ambient conditions under which the surface would ordinarily be predisposed to

desiccate. Concrete can thus be poured under a broader range of environmental conditions than standard concrete. Surfaces can thus be finished with reduced amounts of surface water, or even, in some cases, without adding surface water.

Remarkably, shrinkage is reduced with respect to concrete containing comparable amounts of water. More remarkably, the compressive strength is increased. This result is generally obtained even though the concrete contains amounts of water of transport that would risk capillary and void formation in absence of amorphous silica.

Without desiring to be bound by theory, it is surmised that the amorphous silica may immobilize the water during curing such that the water is prevented from migrating, retarding evaporation as well as capillary and void formation. Surprisingly, the immobilization does not prevent the water from participating in long term, extended hydration, which gives the unexpected increase in compressive strength.

An overarching benefit of the present invention is the ability not to use excess water in the curing reaction (hydration) due to generally losing the water to evaporation. Such a benefit can be obtained even in the case of concrete which are poured having water levels which are less than theoretically required for full hydration of the concrete, as well as at water levels which are in excess of that theoretically required for hydration.

A problem with existing concrete preparation and pour processes is the risk taken when a pour is done in less than optimum conditions. As indicated *infra*, relative humidity, wind speed and temperature, among other environmental factors, routinely compromise standard pours because of their effect on the water levels at various locations on and within the concrete. This can occur even when the amount of water included complies with the recommended amount of water specified by the cement mix manufacturer, whether it is a recommended range of values or a single specified optimum value. The present invention enables the operation at the cement manufacturer's suggested water contents with a reduced risk of water-related issues. These suggested values generally correspond to the amount of water which would be required to enable the hydration reaction to proceed to an acceptable degree, or in some cases, to completion. In the practice of this invention, use of water in the amounts specified by the cement manufacturer is preferred. However, the present invention also reduces the risk of water issues with respect to other processes even when the water content deviates from that specified by the manufacturer. Thus, in some embodiments, the water content is within the range of from about -30% of the lowest value specified by the manufacturer specifications and +30% of the greatest value specified by the manufacturer specifications, based upon the weight of the water added to the cement before the addition of the colloidal amorphous or other silica described herein.

Yet another benefit of the present invention follows from the ability of formulations thereof to retain water for the benefit of extended hydration without the formation of capillaries and void reservoirs. It

is known in the art that the addition of aggregate, sand and other commonly included bulking and strengthening materials to cement to form concrete generally require additional water to accommodate them in the concrete and can actually promote the formation of capillaries and, especially, void reservoirs. Such reservoirs are associated with and located in relation to the surfaces of the included materials. In general, the most preferred aggregates and materials are of a quality such that they associate closely with the concrete over their surface areas such that during hydration, reservoir formation is minimized, as is the associated loss of compressive strength. However, such high quality included materials are generally uneconomical. Surprisingly, even in the presence of aggregates, the inclusion of amorphous silica particles can reduce or prevent the formation of void reservoirs and capillaries. Without desiring to be bound by theory, the reduction of such imperfections, particularly void reservoirs, and the associated increase in compressive strength, tends to indicate that the high surface area amorphous silica particles are participating in a direct association with the included material, regardless of material suboptimal quality. This association may exclude water and strengthen the attachment of the concrete to the included material.

Yet another benefit of the present invention is that concrete formulations prepared thereof can be pourable and/or workable without the use of so-called “superplasticizers”. Non-limiting examples of such superplasticizers include ligninsulfonate, sulfonated naphthalene formaldehyde polycondensates, sulfonated melamine formaldehyde polycondensates, polycarboxylate ethers and other superplasticizer components whether they are emulsions, dispersions, powders or other chemical forms. In one embodiment, the concrete formulations of the present invention are pourable without the inclusion of superplasticizers and are superplasticizer-free or essentially superplasticizer-free. By “essentially superplasticizer-free”, it is meant that the superplasticizer content is in trace amounts of less than about 0.1% based upon the weight of the cement.

Below is a non-limiting list of admixtures which can be used with the present invention. Alternatively, the concrete mixture of the present invention can be free of any or all of the below additives, or of other additives. The list below is ordered as per ASTM C 494 categories. Included are admixtures that are certified and not certified by ASTM C-494.

Admixtures can be added as a powder or liquid.

- Normal water reducers and retarders (Type A, B, D)
- Nominal dosage range: 0.5 - 6 OZ / C
- Super-Plasticizers: Normal setting and retarding (Type F, G)
- Nominal dosage range: 2 - 40 OZ / C
- Accelerating Admixtures: water-reducing or non-water-reducing (Type C, E)

- Nominal dosage range: 2 - 45 OZ / C
- Type S admixtures as defined in ASTM C 494:
 - Mid-Range water-reducers and retarders
 - Nominal dosage range: 2 - 45 OZ / C
 - Corrosion inhibitors
- Nominal dosage range: 0.25 – 5 GAL / YD
- MVRA (Moisture vapor-reducing admixtures)
- Nominal dosage range: 5 - 24 OZ / C
- SRA (Shrinkage -reducing admixtures)
- Nominal dosage range: 0.25 - 5 GAL / YD
- Hydration stabilizers
- Nominal dosage range: 0.5 - 24 OZ / C
- Viscosity modifiers
- Nominal dosage range: 0.25 - 8 OZ / C
- Air-entraining admixtures;
- Nominal dosage range: OZ as needed to entrain air: 0.1 - 36 OZ / C
- Color agents; Liquid and solid
- Nominal dosage range: 0.1 - 20 LB/ YD

Example 1-concentrated formulation (undiluted Korkay)

Interior Slab having a pour size of 15,000 Sq ft was poured. Weather conditions were as follows: temperature of 52-78 F; relative humidity of 60 %; and sunny. The pour started at approximately 6am and finished at 4pm. Concrete was placed utilizing normal practice.

1- A traditional class A concrete design of 6 bags (564 lbs) cement to 31 gallons of water (SSD – Saturated Surface Dry) per cubic yard (9 yards total) was used to place a 4-inch thick interior concrete slab with a non-air-entrained concrete. Roughly 12 gallons of water per cubic yard was added to the Ready-mix, followed by the dry cement mix (564 lbs per yard) as well as the aggregate and sand (1250 lbs of sand, and 1750 lbs of Stone per yard). The water and dry components were mixed for 1-2 minutes, and roughly 19 gallons of additional water per yard was then added to the Ready-mix. The mixture was mixed (in a concrete drum that has a high speed of 12 – 15 RPM's for mixing of the concrete) for an additional time of 5 – 10 Minutes. When the driver was ready to transport the concrete to the job location he then slowed the concrete barrel to 3 -5 RPM's.

2- 203.04 total ounces of E5 INTERNAL CURE (4 ounce / 100 lbs cement) were then added after the 9 yards loaded and batched. Again, there were 564 lbs cement and 31 gallons of water per cubic yard.

3- The team allowed the ready-mix driver to mix the batch for 5 minutes.

4- After the slab was placed there was a 3 hour wait time until floating process was started.

5- A concrete ride on trowel machine was used to perform the floating (panning) process. The pan speed of the floating process was 132-146 revolutions per minute. The floating process was performed for an hour and a half, at which time it was determined that the slab was ready for the next power ride on trowel (i.e., the combination process). Such determinations are standard in the industry and are based largely upon the surface texture of the slab.

6- In an attempt to help create a more workable surface with less friction, after the panning process, Korkay Concrete Dissolver, available from Tate's Soaps and Surfactants, was sprayed on full concentrate (i.e., undiluted) at a rate of 500 sq ft per gallon.

7- The ride on power trowel was then fitted with combination blades and combination process was performed. During the combination process after about 2 passes at the beginning of the slab it was discovered that the surface had developed the appearance of a plastic-like finish. At that time the blade speed was around 160-175 revolutions per minute. Such an effect was unexpected and abnormal. The operator interrupted the combination process and, with a hammer, poked through the surface. It was extremely brittle and cracked easily, something very undesirable in a concrete surface.

This plastic-like surface formed a film over the entire slab. The surface was dull, cloudy and smooth. The surface was nearly impossible to finish in that the friction between the surface and the combination blades was so great that it stopped the rotation of the blades, largely thwarting effective further finishing. This friction tears and micro-cracks the surface, leading to additional degeneration.

Example 2-optimum formulation-about 7:1 dilution (water:Korkay)

- 1- On the following day, experiment 1 was repeated with the same component weight ratios as above. However, in order to economize, the pour size square footage was cut in half.
- 2- After the pan floating process, but before the combination process, Korkay Concrete Dissolver, available from Tate's Soaps and Surfactants, E5 Finish (diluted at 7 parts water to one part Korkay), was sprayed onto the surface at a spray rate of 1000 sq ft per gallon.
- 3- The same finishing technique as above was followed, but a 3rd power trowel machine with finish blades was added. The machine was run at its maximum speed (200-210 rpm, the standard speed is 180-200 rpm) revolutions per minute. The concrete developed a plastic-like sheen, however, unlike Example 1, the surface did not develop a high friction, but instead appeared to be lower friction than that encountered even with the standard finishing of traditional concrete. This result was unexpected. Furthermore, it was discovered that with further finishing at such high speeds, the surface appeared more and more like glass. Without desiring to be bound by theory, it is thought that, despite the lower apparent friction, the higher rotation speeds were resulting in heat that was giving the glass-like effect with extended finishing times.
- 4- After finishing, the concrete was examined, and test results show that the surface was 35% to 40% more abrasive (harder to score or scratch according to a Mohs hardness test 7-8 after 3-7 days) than traditional concrete (around 4-5 in 28 days). The surface was left intact- unlike experiment 1.

Example 3-Rilum Test

This Example was performed to determine if the surface could be used in external applications such as the creation of the plastic- or glass-like surface on exterior surface such as sidewalks, curbs, concrete paving, etc. The pour size dimensions were 50 ft long by 5ft wide by 4 inches thick. The temperature was 60°F. The pour was started at 9 AM and finished at 12 PM.

- 1-The concrete cement, aggregate, sand and E5 content and preparation details are as with Examples 1 and 2.
- 2- The slab was placed and waited an hour.
- 3- After one hour, the process of hand floating the surface was started. Hand joints were cut in.
- 4- Thirty minutes after floating was finished, E5 Finish (available from Specification Products) which

is equivalent to a 7 parts water / 1 part Korkay dilution was applied to the surface at 1000 sq ft per gallon. It was floated into the surface with the hand floats.

5- The joints were reopened and the sides were edged.

6- Upon the elapse of 15 minutes, the surface was evaluated and the plastic-like surface was observed.

7- The surface was then scored with a concrete broom.

8- The following day, a Rilum tube test was performed. The Rilum test is an assessment of the surface porosity to determine if the surface will absorb water. The test takes approximately 30 minutes. Unlike traditional concrete which will take in at least about 1.5 to 3 ml in 20 minutes, the new surface absorbed no water. This lead to the realization that the procedure could be used for both inside and outside surfaces.

Example 4

Location: Shelbyville, Indiana at the Shelby Materials ready-mix plant.

Environmental Conditions: The start time of the pour was 07:30 AM with a starting temperature of approximately 60°F. The ambient temperature peaked in the high 80's during the day. The relative humidity ranged from 18% to 67%. The wind speed range was from 3 to 13 mph.

Steps and results:

1- A traditional class A concrete design of 6 bags (564 lbs) cement to 31 gallons of water (SSD – Saturated Surface Dry) per cubic yard (9 yards total) was used to place a 4-inch thick interior concrete slab with a non-air-entrained concrete. Roughly 12 gallons of water per cubic yard was added to the Ready-mix, followed by the dry cement mix (564 lbs per yard) as well as the aggregate and sand (1250 lbs of sand, and 1750 lbs of Stone per yard). The water and dry components were mixed for 1 - 2 minutes, and roughly 19 gallons of additional water per yard was then added to the Ready-mix. The mixture was mixed (in a concrete drum that has a high speed of 12 – 15 rpm for mixing of the concrete) for an additional time of 5 – 10 Minutes. When the driver was ready to transport the concrete to the job location he then slowed the concrete barrel to 3 - 5 rpm.

2- 380.7 total ounces of E5 INTERNAL CURE (7.5 ounce /100 lbs cement) were then added after the 9 yards loaded and batched. Again, there were 564 lbs cement and 31 gallons of water per cubic yard.

- 3- The team allowed the ready-mix driver to mix the batch for 5 minutes at 12 - 15 rpm.
- 4- The ready-mix was then slowed to 2 - 5 rpm and driven 15 minutes to the job site. The concrete was then poured into the slab forms. The slab located against a metal building.
- 5- The traditional finishing process took place. After the pour, the slab was leveled. A bull float was then used to close the surface. Once the surface is hard enough to begin the mechanical finishing process appropriate methods used widely in the art were used to complete the finishing.
- 6- During the bull floating process, it was noted that the concrete was much easier to close than that of a traditional ready-mix process.
- 7- During the finish process where bleed water is generally present, this process presented no bleed water. However, the surface remained moist. The team speculated that unlike concrete prepared from traditional ready-mix products, the water, surprisingly, was retained within the concrete surface under conditions which would, with ready-mixes in the absence of E5 INTERNAL CURE, likely give a much drier surface.
- 8- The team then spent 4 hours completing the concrete finishing process. Unlike concrete prepared from traditional ready-mixes, the finishing process could be performed with the machines running at half throttle because of the moisture still present at the concrete surface. This lead to a much easier finishing process. Traditional concrete requires machines to be run at a throttle of 100% and is a more labor-intensive process involving an increased risk of surface damage during finishing.
- 9- The team also noted that the internal thermal temperature swing was in excess of 50°F. In fact, because the pour was located against a metal building, the internal concrete temperature swing as measured by internal sensors was from a daytime high of 145°F to a night time low 70°F. In the experience of the team, these temperature swings would be expected to result in significant cracking of the concrete during curing (see 10, below). In the vast experience of the team, thermal temperatures are generally one of the greatest accelerators to the evaporation of moisture at the surface of concrete. The day of this pour the team noticed that the moisture remained at the surface and seemed relatively unaffected by the thermal temperature swings. The team knew such behavior was entirely different than that of traditional poured concrete and could be extremely useful in the industry.
- 10- In the experience of the team, traditional concrete would normally require saw cutting within 24 hours of the pour. However, the team did not saw cut because of the increased amount of water clearly

retained in the upper surface of the concrete and the likelihood that as a result, the shrinkage timing (time over which shrinking would normally occur) would be decreased and likely reduce cracking. Therefore, the concrete slab was allowed to remain undisturbed so that the team could determine how long it would take for the slab to internally release. To the surprise of the team, the slab did not internally release itself for 10 days. It should be noted that there were significant environmental changes such as temperature and rain. Without desiring to be bound by theory, the team surmised that the addition of E5 INTERNAL CURE was causing much of the water to be retained, likely through chemical association with the amorphous silica in E5 INTERNAL CURE, rather than lost through evaporation. It is further surmised that much of the retained water ultimately participated in hydration to give internal curing. The retention of water through chemical association with amorphous silica in E5 INTERNAL CURE (added to concrete prior to pouring, such as, for example to the ready-mix truck), to be later incorporated through hydration (internal curing), has not been observed before, as can best be determined by the team.

Example 5

This was done to ensure consistency in the performance of the product and to understand the process for maximum effect of internal cure.

Location: Beach Grove, Indiana at the Shelby Materials ready-mix plant

Timeframe: poured between 08:30 am and 09:35 am.

Environmental Conditions: 79°F, relative humidity ranged from 61% to 93%, cloudy and wind speed ranged from 6.9 to 12.7 mph.

Steps and results:

1- The concrete for two samples was 5.5 bags (517 lbs) of cement, 0.5 water to cement ratio (31 gallons of water (SSD – Saturated Surface Dry) non-air entrained, 5.5 inch slump (517 lbs. of cement, 1225 lbs. of Sand, and 1800 lbs. of Stone per yard). The finishing process was the same as that of Example 1.

2- Sample 1 was poured as a reference. Sample 1 was done and placed as a 4" thick slab. The concrete slab was also cured by applying plastic sheeting on top of the slab for 7 days as recommended by the American Concrete Institute (ACI). The compressive strength was measured 7 days after pouring to be 5760 psi.

3- Sample 2 was poured as with Sample 1, but with the addition, after mixing of cement, aggregate and sand, (517 lbs. of cement, 1225 lbs. of Sand, and 1800 lbs. of Stone per yard) of E5 INTERNAL CURE (3.5 oz per 100 lbs. of cement). It was cured as Sample 1. 7 days after pouring, the compressive strength was measured to be 6580 psi. The difference between sample 1 and 2 (with E5 INTERNAL CURE) was a 14% increase in strength.

4- The team of professionals then did a 28-day strength test as recommended by ACI (American Concrete Institute) to further support the idea that E5 INTERNAL CURE promoted internal curing, thus chemically binding the water to the concrete. The 28-day test results were as follows: Reference compressive strength: 6910 psi. Compressive strength when E5 INTERNAL CURE is included in the poured concrete: 8040 psi. The E5 INTERNAL CURE increases the compressive strength psi by 16%.

Example 6

Sixteen industrial-scale batches of concrete were prepared. Cylinders from each sample were taken and tested for compression strength in accordance with ASTM C-39, at 3, 7 and 28 days. All samples included 1350 lbs sand. For all samples, the Ready-mix was driven an average of 20 minutes to the job site, and concrete test cylinders were then poured in accordance with ASTM C-39. The results are given in **Table 1**.

The first group of four (samples 1-4), the "Concrete Control" group, are prepared without the addition of colloidal silica. Water/Cement ratio of 0.51. They were prepared by adding roughly 40% of the indicated water to a Ready-mix which was rotating at 2-5 rpm, followed by the addition of the total indicated quantities of cement mix, aggregate and sand. The aggregate in all samples in the study was (3/4" #8 ASTM C-33 #8 INDOT approved) gravel. The water and dry components were mixed for 1-2 minutes, which includes the time it took to add the components to the Ready-mix drum. The remaining water (approximately 60 % of the water indicated) was then added to the Ready-mix. The mixture was mixed in a concrete drum that has a high speed of 12 - 15 RPM's for mixing of the concrete) for an additional time of 5 – 10 Minutes. When the driver was ready to transport the concrete to the job location he then slowed the concrete barrel to 3 -5 RPM's. The Ready-mix was driven to the job site, and concrete test cylinders were then poured in accordance with ASTM C-39.

The second group of four (Samples 5-8) are prepared with the addition of 4 oz of a colloidal silica solution (E5 Internal Cure: approximately 15 wt% silica, average particle size of less than 10 nm, with a BET surface area of approximately 550 m²/g, and 85 wt% water) per hundredweight cement (cwt).

The procedure for samples 7 and 8 (4oz/cwt **after** tail water) is the same as for samples 1-4, but, additionally, 4oz/cwt E5 Internal Cure were then added after the barrel was slowed to 3 - 5 rpm.

The Ready-mix mixed the batch for about 5 minutes at 12 - 20 rpm. The Ready-mix was slowed to 3 - 5 rpm and driven to the job site, and concrete test cylinders were then poured in accordance with ASTM C-39.

The procedure for samples 5 and 6 (4oz/cwt **before** tail water) was as for samples 1 - 4, except that E5 Internal Cure was included in the initial concrete mix, and the order of addition was cement mix, aggregate/sand, 4oz/cwt E5 Internal Cure, 40 % of water.

The procedure for Samples 9 - 12 (2, 4, 6 and 8 oz/E5 Internal Cure/cwt **before** tail water; W/C=0.41) is the same as that for Samples 6 and 7. Note that the amount of E5 Internal Cure increases for each sample, and the water/cement ratio is not 0.51, as with samples 1 - 8, but 0.41.

The procedure for Samples 13 - 16 (2, 4, 6 and 8 oz/E5 Internal Cure/cwt **after** tail water; W/C=0.41) is the same as that for Samples 7 and 8. Note that the amount of E5 Internal Cure increases for each sample, and the water/cement ratio is not 0.51, as with samples 1 - 8, but 0.41.

For each sample, the compressive strength was measured from cylinders aged to 3, 7 and 28 days.

Note that the compressive strength measured for groups of similar samples (1 - 4; 5 and 6; 7 and 8; 9 - 12; 13 - 16) reflect a natural spread which is the result of variations in many factors which prevent the samples from being perfectly identical. The samples are ordered in order of ascending compressive strength only for convenience.

In every case in which the silica was added after the tailwater, the concrete showed little, if any bleedwater, curling, cracking or shrinkage. The same amount of silica added prior to the water gave a cement which had a bleedwater amount which was similar to the control, or in some cases, worse than the control. The foregoing held true for both water/cement ratios (0.51 and 0.41). The compressive strength generally showed an increase with the use of the silica, with more silica giving a higher increase in compressive strength. However, the post-tail water addition gave a significantly larger increase than the pre-water addition of the silica. This advantage is in addition to the earlier-noted advantage of greatly reduced bleedwater and curling cracking and shrinkage. Without desiring to be bound by theory, it is thought that the silica, when added after the water has been mixed with the other dry components, can reduce the water evaporation from the upper layers more efficiently than if it is added to the dry components prior to the water, or possibly even to insufficiently mixed concrete mix which contains water. Thus, the examples above illustrate that adding the silica to a well-mixed and wetted concrete mix, particularly after the addition of the tailwater, unexpectedly gives an unexpectedly large improvement in compressive strength, as well as less or no bleedwater, and fewer or no defects associated with high evaporation from the exposed upper surface of the curing concrete.

	Cement Mix (lbs)	Coarse Agg (lbs)	Agg Vol (% vol)	Water (lbs)	Water/ Cement	Slump	Air (% vol)	3 day (psi)	7 day (psi)	28 day (psi)	
		Gravel									
1	500	1,750	11.	255	0.51	7.75	2.	3,250.	3,920.	4,520.	Concrete Control
2	500.	1,750.	11.	255.	.51	7.5	2.	3,810.	4,590.	5,050.	Concrete Control
3	500	1,750.	11.	255	0.51	7.75	2.	4,020.	4,770.	5,420.	Concrete Control
4	500	1,750.	11.	255	0.51	7.5	1.9	4,220.	4,990.	5,910.	Concrete Control
5	500	1,750.	11.	255	0.51	7.75	2.	3,340.	4,010.	5,150.	4oz/cwt before tail water; W/C=.51
6	500.	1,750.	11.	255.	.51	7.5	2.1	3,750.	4,450.	5,420.	4oz/cwt before tail water; W/C=.51
7	500	1,750.	11.	255	0.51	7.5	2.1	3,910.	4,620.	5,980.	4oz/cwt after tail water; W/C=.51
8	500	1,750.	11.	255	0.51	7.5	1.8	4,290.	5,200.	6,420.	4oz/cwt after tail water; W/C=.51
9	600.	1,750.	11.	245.	.41	7.	2.1	3,500	4,250	4,800	2 oz/cwt before tail water; W/C=.41
10	600.	1,750.	11.	245.	.41	7.75	2.1	3,650	4,375	5,020	4 oz/cwt before tail water; W/C=.41
11	600.	1,750.	11.	245.	.41	7.25	2.	3,980	4,980	5,675	6 oz/cwt before tail water; W/C=.41
12	600.	1,750.	11.	243.	.41	7.75	1.9	4,025	5,100	5,875	8 oz/cwt before tail water; W/C=.41
13	600.	1,750.	11.	245.	.41	7.	2.1	4,050.	5,200.	5,880.	2 oz/cwt after tail water; W/C=.41
14	600.	1,750.	11.	245.	.41	7.75	2.1	4,110.	5,010.	6,320.	4 oz/cwt after tail water; W/C=.41
15	600.	1,750.	11.	245.	.41	7.25	2.	4,080.	5,190.	6,450.	6 oz/cwt after tail water; W/C=.41
16	600.	1,750.	11.	243.	.41	7.75	1.9	4,200.	5,020.	6,650.	8 oz/cwt after tail water; W/C=.41

Table 1

We claim:

A method for preparing concrete installation having improved wear-resistance, said method comprising:

1) A process for the preparation of a concrete installation, said process comprising the steps of:

A) creating a concrete mix from components, said components comprising each of the following:

a) a quantity of dry cement mix, said cement mix characterized by:

i) a manufacturer suggested water/cement ratio value; wherein said suggested ratio falls in the range of from about 3.5 to about 6.5 ; and whereupon combination with b), the water/cement ratio is greater than the value corresponding to about 10% less than the suggested value and not greater than the value corresponding to about 30% greater than the suggested value;

or

ii) manufacturer suggested water/cement ratio range, having an upper value and a lower value, and whereupon combination with b) below, the water/cement ratio is greater than the value corresponding to about 10% less than of the lower value and less than the value corresponding to about 30% greater than the upper value;

or

iii) an amount such that, whereupon combination with b) below, the water/cement ratio is in the range of from about 0.35 to 0.65;

b) a quantity of water,

c) a quantity of amorphous silica in the range of from about 0.1 to about 7.0 ounces per hundredweight of cement in a); wherein the average silica particle size is in the range of from 1 to 55 nanometers and/or wherein the surface area of the silica particles is in the range of from about 300 to about 900 m²/g;

d) a quantity of aggregate and/or a quantity of sand in the range of from about 400 to about 700 wt% bwoc; and

B) wherein the water of b) is added in its entirety or in portions comprising an initial portion, comprising at least about 20 wt% of the quantity of water, and a tailwater portion; wherein the initial portion of water is combined with a) and the components of d) to form a first mix; and wherein the amorphous silica is added to a mix comprising a), d) and the initial portion of b) to form a second mix;

AND

wherein the tailwater is 1) added to the first mix or 2) added to the second mix; or 3) is co-added with the amorphous silica to the first mix, wherein the amorphous silica and the tailwater are, optionally, added optionally intercombined; and wherein 1) the first mix is agitated for a time t_{11} prior to the addition of the tailwater, for a time t_{12} after the addition of the tailwater but before the addition of the amorphous silica, and for a time t_{13} after the addition of the amorphous silica; or 2) the second mix is agitated for a time t_{21} prior to the addition of the amorphous silica, for a time t_{22} after the addition of the amorphous silica but before the addition of the tailwater, and for a time t_{23} after the addition of the tailwater; or 3) the second mix is agitated for a time t_{31} prior to co-addition of the amorphous silica and the tailwater, and whereupon the concrete mix is then agitated for a time t_{32} ;

OR

C) wherein the quantity of water is added to a) and the components of d) to form a mix, whereupon said mix is agitated for a time t_a prior to the addition of the amorphous silica, whereupon the concrete mix is then agitated for a time t_b ;

D) pouring the concrete mix of B) or C) to form a concrete installation' said concrete installation comprising an upper surface;

E) floating the upper surface;

F) applying, to the upper surface, a formulation comprising water; an alpha-hydroxy acid, a glycol alkyl ether, and a polyethylene glycol with an average molecular weight in the range of from about 500 to about 1500 mw to the concrete surface preferably at a rate of between about 200 and about 2000 sq ft per gallon;

G) performing a combination step on the upper surface;

H) optionally, final finishing the upper surface such that its glossiness improves, and is, optionally, Grade 1;

I) if step H), then, optionally, burnishing the upper surface, and if the surface at the final finishing of step H) is Grade 1, then, optionally, improving the surface to Grade 2 by burnishing.

- 2) A process as in claim 1 wherein the initial portion of water comprises at least 30, 40, 50, 60, 70, 80, 90, or 99 wt% of the quantity of water.
- 3) A process as in claim 1, wherein upon combination of the dry cement mix of a) with the water of b), the water/cement ratio is:
equal to or greater than the suggested value in i), but less than the value corresponding to 30% greater than the suggested value; or
equal to or greater than the upper value of the suggested range in ii), but not greater than the value corresponding to 30% greater than the upper value; or
with respect to iii) at least 0.35, but not greater than 0.65.
- 4) A process as in claim 1 wherein the amorphous silica is introduced into the first mix as a colloidal silica solution and wherein the solution comprises between about 50 and about 95 wt % silica, and between about 5 to about 50 wt % water.
- 5) A process as in claim 4 wherein the silica comprises between about 75 and about 90 wt % silica and between about 10 and about 25 wt% water.
- 6) A process as in claim 5 wherein the amorphous silica is added in an amount in the range of from about 2.5 to about 5.5 ounces per hundredweight cement.
- 7) A process as in claim 6 wherein the amorphous silica is added in an amount in the range of from about 3.5 to about 4.5 ounces per hundredweight cement.
- 8) A process as in claim 1 wherein the colloidal silica is added after the tailwater.
- 9) A process as in claim 1 wherein the concrete is poured into slab or a footing.
- 10) A process as in claims 1 or 4, wherein the process is conducted in a Ready-mix; wherein the tailwater is added to the first mix after the first mix is agitated at a speed in the range of from about 2 rpm to about 18 rpm for a time in the range of from 15 seconds to 5 minutes; wherein after the tailwater addition, the mix is agitated at a speed in the range of from about 5 rpm to about 18 rpm, for a time in the range of from about 1 minute to about 18 minutes, after which the silica is added, as colloidal silica, to the Ready-mix, and the mix is agitated for a time in the range of from about 1 to about 15 minutes at a speed in the range of from about 2 to about 18 rpm; wherein the concrete is then poured as a slab form.

- 11) A process as in claim 1 wherein the formulation is applied at a rate of from about 500 to about 1500 sq ft per gallon.
- 12) A process as in claim 1 wherein the formulation comprises is a Korkay dilution in the range of from about 6 to about 8 parts water per part Korkay and the application rate is between about 800 and 1200 sq ft per gallon.
- 13) A process as in claim 1 wherein the formulation comprises an alpha-hydroxy acid present in the formulation in the range of from about 5 to about 20 weight percent; a glycol alkyl ether present in the range of from about 5 to about 20 weight percent; a polyethylene glycol present in the range of from about 1 to about 15 weight percent; water present in the range of from about 70 to about 80 weight percent.
- 14) A process as in claim 13 wherein the formulation comprises an alpha-hydroxy acid present in the formulation in the range of from about 10 to about 15 weight percent; a glycol alkyl ether present in the range of from about 10 to about 15 weight percent; a polyethylene glycol present in the range of from about 1 to about 9 weight percent; water present in the range of from about 70 to about 80 weight percent.
- 15) A concrete installation prepared by the processes of claims 1, 3, 5, 7, 8, 9 or 10.



Fig. 1
SUBSTITUTE SHEET (RULE 26)



Fig. 2
SUBSTITUTE SHEET (RULE 26)



Fig. 3
SUBSTITUTE SHEET (RULE 26)



Fig. 4
SUBSTITUTE SHEET (RULE 26)



Fig. 5
SUBSTITUTE SHEET (RULE 26)



Fig. 6
SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/00013

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C04B 28/02; C04B 28/04; C04B 40/00 (2019.01)
 CPC - C04B 28/02; C04B 28/04; C04B 40/0028; Y02W 30/92

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)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2002/0014187 A1 (Greenwood et al.) 7 February 2002 (07.02.2002) Abstract, para [0012], [0014], [0016], [0026], [0029], [0031].	1-14
A	US 4,740,348 A (Lawrence K. Rose) 26 April 1988 (26.04.1988) Abstract, col 1 ln 29-60.	1-14
A	US 2015/0038389 A1 (Eastman Chemical Company) 5 February 2015 (05.02.2015) Abstract, para [0048], [0070]-[0071], [0101].	1-14
A	US 2015/0299041 A1 (Multiquip, Inc.) 22 October 2015 (22.10.2015) Entire Document.	1-14
A	WO 1998/012149 A1 (EKA Chemicals AB) 26 March 1998 (26.03.1998) Entire Document.	1-14

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

12 August 2019

Date of mailing of the international search report

22 AUG 2019

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/00013

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 15
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.