

ADMIXTURE FOR HYDRAULIC CEMENT COMPOSITIONS

This invention relates to admixtures for hydraulic cement compositions and more particularly to water-reducing admixtures which provide improved slump and slump retention in hydraulic cement compositions with relatively minimal increases in initial and final setting times.

The use of various water-reducing admixtures in hydraulic cement compositions, e.g., mortars, grouts, and concrete, is well known. These admixtures allow the use of lesser amounts of water to achieve a desired plasticity or workability. The admixture also provides higher compressive strengths in the cement composition after setting, due either to the use of less water in the mix or to a more complete dispersion of the cement particles in the plastic cement mix by the admixture.

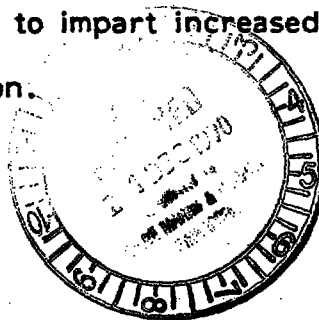
A major problem associated with the use of conventional water-reducing admixtures is that the length of time during which the admixture is able to maintain a desired high level of plasticity or workability in the cement mix is relatively short, lasting an average of 25 to 45 minutes after addition of the admixture. In most job situations, this generally requires that the admixture be added just prior to placement, i.e., at the job site, thus requiring the equipping of delivery trucks with specially designed dispensing equipment. In addition to the expense associated with the installation and maintenance of this equipment, its use can be problematic where local work specifications or conditions prohibit on site addition of admixtures. In addition, the relatively short duration of increased plasticity limits the amount of time the applicator has to place and work the mixture. This can be a particularly troublesome constraint under difficult placement or job conditions.

The problem of a relatively short duration of increased plasticity can sometimes be lessened by a high dosage of the water-reducing admixture. However, this tends to provide too fluid a mix immediately following addition and generally results in excessive set retardation.

- 5 This latter disadvantage, in turn, can delay strength gain in the cement mix after setting.

There is accordingly a continuing desire in the art to develop new water-reducing admixture compositions which can provide a high degree of plasticity to hydraulic cement compositions without undue adverse
10 effect on the cement setting time. There is, furthermore, a continuing desire to develop such admixtures which are also capable of maintaining the plasticity for more extended periods of times, again without undue adverse effect on the setting time.

The plasticity of a hydraulic cement mixture is normally evaluated
15 by slump measurement, e.g., in accordance with ASTM C143. The slump is measured by filling a truncated cone with the mixture, removing the cone, and measuring the drop in height of the unsupported mixture. As a measure of the decrease in plasticity of the mixture over time, slump measurements are made on the aging mixture
20 at spaced time intervals. The decreasing plasticity is thus quantified as the decrease in slump with time. A lesser decrease in slump with time i.e., increased slump retention, indicates a greater ability on the part of a water-reducing admixture to impart increased plasticity to the cement mixture for a longer duration.



SUMMARY OF THE INVENTION

The present invention is directed to cement admixture compositions which are capable of providing significant water reduction in hydraulic cement compositions without excessive increases in set retardation.

- 5 These admixtures are effective water-reducing agents at relatively low dosages in hydraulic cements and the ability to utilize these materials at such low dosage levels provides substantial control in minimizing the set retardation associated with use of the admixtures.

- The present invention is accordingly directed to admixture
10 compositions which comprise a borate ester of a polyhydroxy compound. The borate ester is generally prepared by reaction of boric acid with an esterifying polyhydroxy compound or salt thereof. It has been found that, in general, the esterification or complexation of the polyhydroxy compound with the boron moiety substantially reduces the set
15 retardation associated with the use of the polyhydroxy compound alone i.e., not esterified, in a hydraulic cement mix, while providing a level of water-reduction which compares favorably with that obtained using the polyhydroxy compound alone.

- The preferred admixture compositions of this invention, which can
20 provide levels of water reduction which are at least as great as those provided by conventional water-reducing agents and, in addition, provide substantially increased levels of slump retention, are blends or mixtures comprising a borate ester of a polyhydroxy compound and a hydraulic cement water-reducing agent. A particular advantage of
25 these preferred admixtures is that they can be formulated to provide significant and substantial increases in slump retention with only relatively minimal increases in the initial and final setting times of the cementitious mix.

These preferred admixture compositions can comprise the borate ester component in combination with a single water-reducing agent or, preferably, in combination with two or more water-reducing agents. Preferred water-reducing agents for use in these admixtures are

5 aromatic sulfonic acid-aldehyde condensate salts and lignosulfonic acid salts. Most preferably, both of these preferred water-reducing agents are present in the admixture together with the borate ester.

The relative quantity of each of the admixture components can vary over a wide range such that a variety of admixture formulations

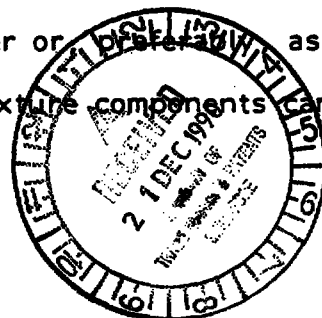
10 can be provided to meet different requirements of slump retention or set retardation. This flexibility in formulating the admixture can also be used to compensate for variations in reactivity of different cements to the admixture. This flexibility is significantly increased by the use of two or more different water-reducing agents in the admixture,

15 inasmuch as the ratio of the water-reducing agents to each other, as well as to the borate ester, can be adjusted. Thus, a wider variety of formulations, with a correspondingly broader range of properties in hydraulic cement mixes, can be provided.

In the admixtures of the present invention, it is preferred to

20 employ amine salts of the borate esters, inasmuch as these salts can provide especially favorable early compressive strengths in the set cement product. These amine salts may also provide less retardation than that provided by the corresponding ester either existing in its free acid form or neutralized with a metal cation.

25 The admixtures of this invention can be provided and used as neat formulations in the form of a dry powder or, preferably, as aqueous-based solutions, i.e., the admixture components can be dissolved in an aqueous-based solvent.



The present invention is further directed to hydraulic cement compositions comprising the admixture compositions of this invention.

DETAILED DESCRIPTION OF THE INVENTION

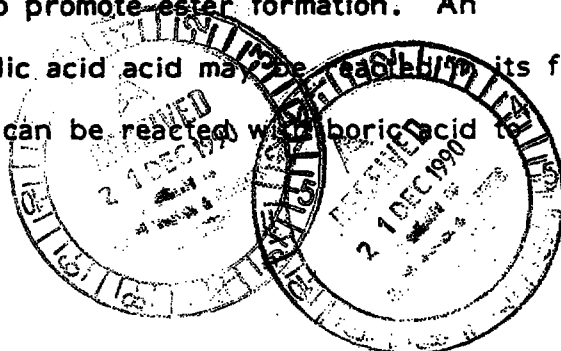
As used herein, the term "hydraulic cement composition" is intended to refer to any composition containing a hydraulic cement binder, e.g., an ASTM Type I, II, III, IV, or V Portland cement, inclusive of both dry cement compositions and wet cement slurries or pastes. Included within the term are concretes, grouts, mortars, cement pastes, and the like. The admixtures of this invention are particularly useful in Portland cement concretes, and especially in larger scale Portland cement concrete preparations where the concrete is prepared at a mixing plant and transported to the job site.

As used herein, the term "polyhydroxy compound" refers to diols and polyhydric compounds, i.e., compounds containing more than two hydroxy groups. The polyhydroxy compound can be an aromatic compound, such as a catechol, or an aliphatic compound, with the latter being preferred from the standpoint of attaining lower levels of set retardation. The aliphatic polyhydroxy compound can be an aliphatic diol such as ethylene glycol, 1,2-propanediol, or 1,3-propanediol; an aliphatic polyhydric alcohol such as glycerol, glucose, or mannose; an aliphatic diol carboxylic acid such as 2,3-dihydroxypropionic acid or tartaric acid; or, most preferably, an aliphatic polyhydric carboxylic acid such as a glucaric acid. Particularly preferred aliphatic polyhydric carboxylic acids are the glyconic acids, with gluconic acid and glucoheptonic acid being especially preferred. The stereospecificity

of the polyhydroxy esterifying compound must, of course, be such as to permit formation of the cyclic borate ester. The stereospecific molecular requirements relating to borate ester formation are well known. An early study of this subject is provided by J. Boeseken, 5 Advances in Carbohydrate Chemistry, 4, 189-210 (1949).

The borate esters present in the admixtures of this invention are cyclic esters which are believed to involve complexation or bonding of a boron moiety to two hydroxyl groups within an esterifying polyhydroxy compound so as to form a cyclic structure. The borate esters generally 10 used herein are believed to be mono-esters involving the complexation or bonding of one molecule of esterifying compound to one boron moiety, with the third valence position of the boron moiety occupied by a hydroxy group. However, although the mono-ester is believed to be the species generally used herein, the present invention broadly 15 contemplates the employment of bis esters, involving complexation or bonding of two polyhydroxy compounds to one boron moiety. The hydroxy group of the mono-esters of this invention can be neutralized with a cation, as discussed hereinafter.

The borate esters of the invention can be prepared by known 20 methods. Thus, boric acid can be reacted with the esterifying compound in an aqueous medium, using mild heating to facilitate completion of the reaction. Where the esterifying compound is not readily reactive with boric acid, it may prove desirable to employ an anhydrous polar reaction solvent, e.g., tetrahydrofuran, or higher 25 reaction temperatures in order to promote ester formation. An esterifying polyhydroxy carboxylic acid may be reacted with its free acidic form, e.g., gluconic acid can be reacted with boric acid to



provide an ester, or it may be reacted in its salt form, e.g., calcium gluconate may be reacted with boric acid to provide the correspondingly neutralized calcium borogluconate. A precursor to the carboxylic acid esterifying compound, e.g., a precursor lactone, may also be utilized as
5 an esterifying reagent.

After formation of the ester, a base may be added to the reaction solution to neutralize the ester or as desired for cation exchange. However, the pH of the solution should be maintained at less than pH 10-11, and preferably less than about pH 8, in order to
10 provide a stable solution which can be stored for extended periods.

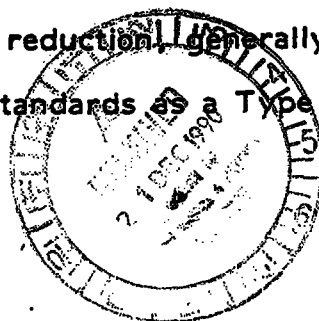
Preparation of the mono-ester is normally facilitated by reacting approximately equimolar amounts of boron and the esterifying compound. However, the mono-ester may also be prepared using a molar excess of the esterifying compound, as may prove necessary where stereospecific
15 or steric factors hamper the reaction of the esterifying compound with the boron moiety. Conversely, where the esterifying compound is readily reacted with the boron moiety, bis esters may be formed using a molar excess of the esterifying compound and the present invention broadly contemplates the use of bis borate esters as well.

20 The borate esters may be prepared and used in the free acid form, i.e. with an -OH group on the boron and -COOH group on an esterifying carboxylic acid compound. However, the salt form of the ester can provide less set retardation in concrete formulations and is thus generally preferred for use herein. Where the esterifying
25 polyhydroxy compound is a polyhydroxy alcohol, the salt form incorporates a cation which displaces the hydrogen of the remaining hydroxyl group on the boron moiety. Where the esterifying

polyhydroxy compound is a polyhydroxy carboxylic acid, this salt form incorporates a cation associated with the carboxyl group(s) of the esterifying compound and, optionally, a cation which displaces the hydrogen of the remaining hydroxyl group on the boron moiety. The cation can be an alkali metal, e.g., sodium or potassium, or an alkaline earth metal, e.g., calcium or magnesium. Preferably, however, the cation is an amine cation such as ammonium; alkylammonium, e.g., triethylammonium; alkanolammonium, e.g. diethanolammonium, triethanolammonium; or mixtures of the same. Utilization of alkanolammonium borate ester salts in particular has been found to result in admixtures which provide lesser increases in initial and final setting times as compared, for example, to similar admixtures comprising alkaline earth ester salts. A particularly preferred borate ester salt comprises a mixture of alkanolamines as a cationic grouping, and more particularly a mixture of diethanolammonium, and triethanolammonium cations. Monoethanolammonium cation may also be included in this mixture.

The esters may also be prepared by reaction of a borate salt such as zinc borate or calcium borate with the esterifying compound, e.g., as described in U. S. Patent No. 3,053,674.

The borate esters present in the admixtures of this invention can provide significant water reduction in hydraulic cement compositions when used at a relatively low dosage. Thus, for example, when added to Portland cement concretes in an amount of less than 0.075% weight, based on the weight of Portland cement binder in the concrete, the borate esters can provide effective water reduction. Generally at a level which is sufficient to meet ASTM C494 standards as a Type D



water-reducing agent. These water reduction levels are approximately equal to or greater than those provided by an equivalent amount of the non-esterified polyhydroxy compound added to the same concrete.

However, the retardation associated with the use of the borate ester is

5 generally significantly less than that associated with use of an equivalent amount of the non-esterified polyhydroxy compound. For

Example, at the above dosage levels, the initial setting time of the concrete is normally retarded about 1/2 hour to 2 1/2 hours as

compared to the initial setting time of the same concrete without the

10 admixture added. The early compressive strengths of the concretes containing the admixture at these dosage levels, e.g., 1 day and 7 day strengths as determined in accordance with ASTM C192, generally equal or exceed those of the same concrete without the admixture present.

As indicated above, the preferred admixtures of this invention
15 comprise a hydraulic cement water-reducing agent in combination with a borate ester of a polyhydroxy compound. These preferred admixtures provide a longer slump life, i.e., increased slump retention, in

hydraulic cement compositions. For many larger scale applications

using Portland cement concrete, the increased slump retention permits

20 addition of the admixture to the concrete at the mixing plant, rather than at the job site. This option can be advantageous where local work specifications or conditions prohibit on site addition of admixtures.

Moreover, it facilitates mixing during transportation to the job site and provides greater flexibility in terms of the time allowed for pouring, placing, and working the concrete at the job site. However, since the admixtures can be formulated to provide the increased slump retention while causing only a relatively minimal increase in the initial setting time, (as compared, for example, to the initial setting time obtained with a conventional water-reducing agent) the cement mix will generally thereafter set up in sufficient time to permit the applicator to gain access onto the concrete and finish it within the time constraints of the average work day.

An additional unexpected advantage provided by the preferred admixtures is the generally excellent finishing characteristics imparted to hydraulic cement compositions, whereby the composition assumes a smooth, creamy consistency, for an extended duration, without stickiness, and thus can be surface finished easily and with highly satisfactory results. The borate esters used in the preferred admixtures of this invention are believed to provide the improved finishing characteristics and slump retention which have been observed in hydraulic cement compositions containing the preferred admixtures.

Any of the known hydraulic cement water-reducing agents, can be used in the preferred admixtures. It is preferred to use as the water-reducing agent component either an aromatic sulfonic acid-aldehyde condensate salt or a lignosulfonic acid salt. Most preferably, the admixture comprises both of these preferred water-reducing agents. The aromatic sulfonic acid-aldehyde condensate salt which can be used in the preferred admixtures can be any such polymeric condensate which meets the ASTM C494 standard for a Type



A or Type F water-reducer. Such condensates and their use as dispersants or water-reducers in hydraulic cements are disclosed, for example, in U. S. Patent Nos. 2,141,569; 2,690,975; 3,359,225; 3,582,375; 4,125,410; 4,391,645; and 4,424,074.

5 Exemplary aromatic moieties which can be present in the condensate polymer are phenyl, tolyl, xylyl, benzoic acid, phthalic acid, phenol, melamine, diphenyl, naphthalene, methylnaphthalene or anthracene moieties. The condensate polymer may contain a single aromatic moiety or two or more different aromatic moieties in the polymer chain.

10 The aldehyde used in preparation of the condensate is an alkylaldehyde, e.g. acetaldehyde, or preferably formaldehyde. The formaldehyde condensates are particularly well known water-reducing agents and are generally preferred from an availability, cost, and performance standpoint.

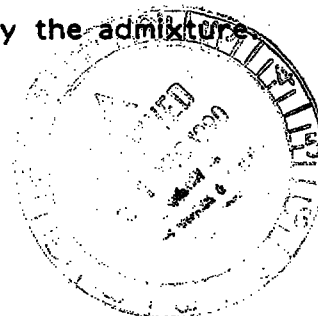
15 The condensates can be prepared by reaction of an aromatic sulfonic acid with an aldehyde to form a condensation polymer, followed by neutralization with a basic material, e.g., sodium hydroxide, or they can be prepared by condensation of an aromatic compound with the aldehyde followed by sulfonation of the condensation product and
20 neutralization of the sulfonated material. Processes for preparing the condensates are disclosed in U. S. Patent Nos. 2,141,589; 3,067,243; 3,193,575; 3,277,162; and 4,125,410.

The condensates used in the preferred admixtures are in the salt form, so as to possess desired water solubility, and can comprise, as
25 the salt forming cation, sodium, potassium, calcium, zinc, aluminum, magnesium, manganese, ferrous, ferric, or ammonium cations. Alkylammonium or alkanolammonium cations can also be used such as methylammonium, dimethylammonium, ethanolammonium or diethanolammonium cations.

Naphthalenesulfonic acid-formaldehyde condensate salt is the preferred condensate polymer for use in the preferred admixtures of this invention. A commercial naphthalenesulfonic acid-formaldehyde condensate which has been found particularly useful in the inventive
5 admixtures is that sold under the trademark "WRDA-19" by W. R. Grace & Co., Cambridge, Massachusetts.

With respect to the the use of a lignosulfonate component in the preferred admixtures, lignosulfonates, as a class, are well known materials which have been used as water-reducing agents, plasticizers,
10 and set-retarding agents in Portland cement compositions. Lignosulfonates are commonly obtained as water-soluble salt derivatives of conventional sulfite wood-pulping processes. These derivatives may be subsequently treated to provide "desugarized" lignosulfonates and these desugarized materials are preferred for use herein. The
15 lignosulfonate used herein can be a salt of any alkali metal such as sodium or potassium or any alkaline earth metal such as calcium or magnesium.

As previously indicated, the relative quantity of each component in the preferred admixtures can be varied as appropriate to meet different
20 requirements of slump retention or set retardation or to compensate for variations in reactivity of different cements to the admixture. Accordingly, any ratio of the aforementioned components can be employed, as necessary for particular applications. In general, it is preferred to employ less than about 30% by weight of the borate ester
25 component, based on the total weight of admixture components, in order to minimize any set retardation imparted by the admixture.



The set retardation encountered by use of the preferred admixtures can be modulated by adjustment in the relative proportion of the borate ester in the admixture, with a lower proportion generally resulting in a lesser degree of set retardation; by use and adjustment of the relative proportion of a set retarding water-reducing agent, e.g., lignosulfonate; by use of differently neutralized borate esters, with ammonium, alkylammonium, and alkanolammonium neutralized borate esters tending to provide lesser degrees of set retardation than alkali metal and alkaline earth metal neutralized borate esters; and by adjustment of the concentration or "dosage" of the admixture in the cementitious mix.

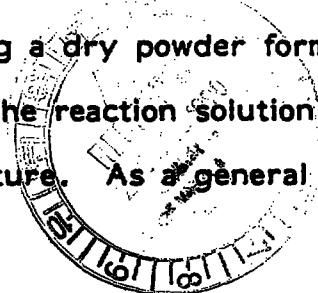
The initial slump and the slump retention obtained by use of the preferred admixtures can be modulated by adjustment in the relative proportion of the borate ester, with a higher proportion generally providing a higher initial slump and increased slump retention; and by adjustment of the dosage of admixture in the cementitious mix.

For most applications, it will be desired to obtain a maximal increase in slump retention with minimal set retardation. Any of the above methods of modulating set retardation and slump retention may be used, either individually or in combination, to obtain the desired performance. In general, optimal combinations of slump retention and set retardation are most readily obtained utilizing the preferred admixtures of this invention comprising both the naphthalene sulfonic acid-formaldehyde condensate polymer salt and lignosulfonic acid salt. Most preferably, from the standpoint of minimizing set retardation, these preferred admixtures should comprise as the borate ester component an ammonium, alkylammonium, or alkanolammonium neutralized borate ester.

Although it is generally preferred to formulate the admixture so as to provide minimal set retardation, for some applications, such as hot weather applications, a greater degree of set retardation may be desired and adjustments can be made in the admixture formulation or dosage, as described above, in order to meet this need.

A particularly preferred admixture of this invention comprises 30 to 90 percent by weight of an aromatic sulfonic acid-aldehyde condensate, 15 to 80 percent by weight of a lignosulfonic acid salt, and 1 to 15 percent by weight of borate ester, where the percentage is of the total weight of the three components. A more preferred admixture formulation comprises 50 to 70 percent by weight of the condensate, 25 to 45 percent by weight of the lignosulfonate, and 3 to 10 percent by weight of the borate ester. In general, it is desirable to employ less than about 10 percent by weight of the borate ester in the admixture compositions containing both the condensate and lignosulfonic acid salt in order to provide desirably low levels of set retardation, although higher proportions of the borate ester may be employed where the admixture is to be used at a low concentration in the cementitious mix.

The admixture compositions of this invention may be provided in dry powder form, generally by simple evaporation of the reaction solvent used in preparation of the admixture. Preferably, for purposes of facilitating addition to hydraulic cement compositions the admixture is provided in aqueous solution, i.e., the admixture is dissolved in an aqueous-based solvent. The admixture solution can be prepared at any suitable concentration, either by re-dissolving a dry powder form of the admixture or by adjustment as necessary of the reaction solution product obtained in preparation of the admixture. As a general rule,



admixture solutions containing about 10% to about 70% by weight of the borate ester are used in this invention. The admixture solution should have a pH of less than pH 10 or 11, and more preferably less than about pH8, in order to provide a stable solution which can be
5 stored for extended periods.

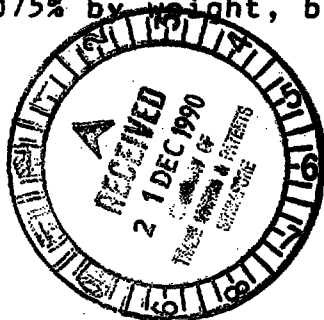
The preferred admixtures of this invention can be provided as a dry powder mixture of the aforementioned components but preferably, for purposes of easy dispensing into cement formulations, is provided in an aqueous solution, generally at a concentration of 30 to 50 percent by
10 weight of the admixture, based on the total weight of the solution. The admixture can be dissolved in water at these concentration levels at a pH ranging between 3 to 10 to provide a stable, homogeneous solution.

The preferred admixtures of this invention can be used as either
15 low range water-reducing agents, as defined by ASTM C494, Type A, or as high range water-reducers, defined by ASTM C494, Type F or Type G. In general, the functioning of the admixture as a low range or high range water-reducer is dependent on the dosage level, although performance in this regard may also be dependent on the particular
20 admixture formulation and hydraulic cement type. As a general guide for Portland cement concretes, the admixture will function as a low range water-reducer at dosage levels of less than 0.20% solids of the admixture, based on the weight of Portland cement binder in the concrete, and as a high range water-reducer at dosage levels
25 above 0.20%, similarly based. It is generally preferred to employ the admixture as a high range water-reducer in Portland cement concretes utilizing dosage levels in the range of about 0.20% to 0.50%.

At these levels, the preferred admixtures have been found to provide initial slumps in the desired range of approximately 8 to 10 inches (20 to 25 cm) (ASTM C143) and improved slump retention (as quantified in the following Examples), while retarding initial setting times by approximately 1/2 hour to 2 hours as compared to the initial setting time of the same concrete containing comparable dosages of conventional water-reducing agents. Accordingly, a high slump concrete is provided which retains its slump for longer durations but is generally capable of setting and being surface finished within the time constrictions of a typical work day.

The admixtures of the invention may be added to the dry cementitious mixture or to the wet cement slurry. In general, the admixture will be added in its dry powder form to a dry cementitious mix while an aqueous solution of the admixture is used in the case of addition to a wet cement slurry. While the admixture may be dissolved in the mix water used to prepare the cement slurry, it preferably is added as a separate solution following preparation of the slurry. After addition, sufficient mixing should be provided to assure a substantially uniform distribution of the admixture throughout the cement composition.

Consistent with the foregoing, the present invention is further directed toward hydraulic cement compositions comprising a hydraulic cement binder and a borate ester of a polyhydroxy compound. The total amount of the borate ester in the cement composition is less than 0.075% by weight, based on the weight of hydraulic



cement binder, in order to minimize the set retardation.

The cement composition can be in an essentially dry, free-flowing powder form or a wet slurry form. The preferred hydraulic cement compositions of the invention comprise a Portland cement binder. Fine
5 or course aggregate or additional admixtures may be present in the inventive cement compositions.

The present invention is further directed toward preferred hydraulic cement compositions comprising a hydraulic cement binder and the preferred admixtures of this invention. In these cement
10 compositions, the total amount of the admixture components is preferably 0.05% to 0.50% by weight, based on the weight of hydraulic cement binder. These preferred cement compositions can be in an essentially dry, free-flowing powder form or a wet slurry form. The cement composition can be formed by individual addition of
15 each of the admixture components to the hydraulic cement binder or by addition the multicomponent admixture, either in dry form, or, preferably, in solution. The preferred hydraulic cement binder is Portland cement and the inventive cement compositions may comprise additional materials such as fine or course aggregate or additional
20 admixture materials. Consistent with the foregoing, in preferred Portland cement concretes the admixture components, in total, will generally be present in a weight concentration of 0.50% to 0.20%, based on the weight of Portland cement binder, where performance of the admixture as a low range water-reducer is desired
25 and in a weight concentration of 0.20% to 0.50%, where performance as a high range water-reducer is desired.

The preferred admixtures of this invention can be prepared by mixing the respective components in dry form or, preferably, by

blending aqueous solutions of the respective components followed by adjustment of the blended solution to a desired concentration by water addition.

In the Examples which follow, 8 to 14 further describe and illustrate the present invention whilst 1 to 7 are included for reference. The Examples are illustrative only and are not intended to limit the present invention in any sense. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

10 Preparation of calcium borogluconate solution:

860.5 grams of calcium gluconate monohydrate and 244 grams of technical grade boric acid were added to 1100 grams of water at room temperature. The resultant mixture was stirred and warmed to a temperature of about 50°C until a dark brown solution was obtained.

15 The solution was allowed to cool to room temperature. The solution can be used as is or the water can be evaporated to provide the calcium borogluconate as a brownish solid.

EXAMPLE 2

Preparation of calcium borogluconate solution:

20 28 grams of calcium oxide were added to water to form a thick slurry. This slurry was slowly added with stirring to 392 grams of a 50% aqueous solution of technical grade gluconic acid. After all of the slurry was added the resultant mixture was cooled and 61.8 grams of technical grade boric acid added. The mixture was stirred until a dark
25 brown solution was obtained and then adjusted by water addition to provide a 40% solids solution.



EXAMPLE 3

Preparation of sodium boroglucoheptonate solution:

123.7 grams of technical grade boric acid were added slowly to 1417 grams of a 35% aqueous solution of technical grade sodium glucoheptonate. The mixture was stirred at room temperature until a dark brown solution was obtained.

EXAMPLE 4

Preparation of triethanolammonium borogluconate solution:

35.6 grams of gluconolactone and 12.2 grams of technical grade boric acid were added to 50 ml. of water at room temperature. The resultant mixture was stirred and heated at about 50°C. for about 4 hours and the water allowed to evaporate to reduce the mixture volume to about 45 ml. The mixture was then cooled to room temperature and 28 grams of triethanolamine were added with stirring.

EXAMPLE 5

2584 grams of a 35% solids aqueous solution of technical grade sodium glucoheptonate were adjusted to about pH 6 by addition of 20.5 grams of an 88% formic acid solution. 226 grams of technical grade boric acid were then added to the pH adjusted solution and the resultant mixture stirred overnight at room temperature. 476 grams of a mixture of monoethanolamine, diethanolamine, and triethanolamine were then added with stirring, bringing the pH of the resultant solution to pH 8. The alkanol amine mixture was reported by the supplier to contain 0-15% monoethanolamine, 13-45% diethanolamine, 55-76% triethanolamine, and 0-5% of other materials.

The borate ester prepared in this Example is hereinafter referred to as sodium-mixed alkanolamine boroglucoheptonate and is believed to comprise a mixture of both the sodium and alkanolamine borate ester salts.

EXAMPLE 6

Preparation of mixed alkanolamine borogluconate solution:

500 grams of gluconolactone and 173.6 grams of technical grade boric acid were added to 500 ml. of water and the resultant mixture stirred and warmed until a dark brown solution was obtained. The solution was cooled to room temperature and 418 grams of the alkanolamine mixture of Example 5 were added with cooling. The resultant solution was diluted with water to a total weight of 1980.4 grams to provide a 50% solids solution of the mixed alkanolamine borogluconate.

EXAMPLE 7

The following admixtures were prepared by blending a 40% solids aqueous solution of naphthalene sulfonic acid-formaldehyde condensate salt ("WRDA-19", available from W. R. Grace & Co., Cambridge, Massachusetts), a 50% solids aqueous solution of sodium lignosulfonate, and an aqueous solution of a borate ester, as indicated below. The weight ratios given below are solids weight ratios of the condensate: lignosulfonate: borate ester. The resultant blends were adjusted to a concentration of 40% solids by addition of water to provide a final admixture solution.

<u>Admixture</u>	<u>Weight Ratio</u>	<u>Borate Ester</u>
A	65:25:10	Mixed alkanolamine borogluconate (Example 6)
B	65:25:10	Calcium borogluconate
C	65:30:5	Mixed alkanolamine borogluconate (Example 6)
25 D	65:30:5	Sodium-mixed alkanolamine boroglucoheptonate (Example 5)
E	65:30:5	Calcium borogluconate
F	65:30:7	Mixed alkanolamine borogluconate (Example 6)
G	65:30:7	Triethanolammonium borogluconate (Example 4)
H	15:80:5	Mixed alkanolamine borogluconate (Example 6)

EXAMPLE 8

Admixtures A and B were added to individual batches of a Type II Portland cement concrete slurry which had been prepared with a water/cement ratio of 0.49 and mixed for about 11 minutes prior to addition of the admixture. The amount of admixture added to the cement in this and the following Examples is given in terms of the total weight of solid admixture components expressed as a percentage of the weight of Portland cement binder present in the concrete formulation, hereinafter termed "percent solids on solids" (% s/s). In this Example, each of the admixture solutions was added to the individual concrete batches in an amount sufficient to provide an admixture concentration of 0.40% s/s.

The concrete of this Example and the concretes of the following Examples 9-13 were prepared at a cement factor of 611 lbs/yd. (362.5 kg/m³)

To provide a reference sample, an individual portion of the concrete was also admixed with WRDA-19 alone at a concentration of 0.40% s/s. This commercial material has been widely used as a high range water-reducer.

Slump measurements were carried out on the concrete before and after addition of the admixtures in accordance with ASTM C143. The measured slumps are presented in Table I. The times given in Table I and in the following Examples are the times at which slump measurements were made and denote the total mixing time of the concrete. As noted above, the admixtures were added at about 11 minutes into the mix cycle.

Table I

<u>Admixture</u>	<u>Slump (inches) (cms)</u>				
	<u>9 Min.</u>	<u>15 Min.</u>	<u>30 Min.</u>	<u>45 Min.</u>	<u>60 Min.</u>
Reference	4.25 (10.8)	10.00 (25.4)	8.25 (21.0)	5.25 (13.3)	3.25 (8.3)
A	4.00 (10.2)	10.50 (26.7)	8.75 (22.2)	7.25 (18.4)	4.50 (11.4)
B	4.25 (10.8)	10.25 (26.0)	8.75 (22.2)	7.50 (19.0)	5.50 (14.0)

The results presented in Table I indicate approximately equal initial (15 Min.) slumps among the three samples and substantially improved slump retention in the samples containing the admixtures of this invention.

The concretes of this Example and of the following Examples were also measured for air content (ASTM C231), initial and final setting times (ASTM C403), and compressive strength (ASTM C192) at 1, 7, and 28 days (average of two cylinders). These measurements on the concretes of this Example are presented in Table II.

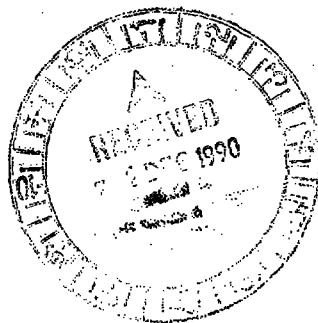


Table II

Admixture Reference	Air %	Initial Setting Time (hr:min)	Final setting Time (hr:min)	Compressive Strength (psi) (kPa)		
				1 day	7 day	28 day
	1.7	4:00	5:16	1894 (13060)	4522 (31180)	6031 (41580)
A	1.8	5:58	7:02	1840 (12690)	4943 (34080)	5833 (40220)
B	2.1	6:24	7:28	1861 (12830)	4868 (33560)	6415 (44230)

Table II indicates the generally observed result of lesser increases in setting time where the borate ester is neutralized with an alkanolamine (Admixture A) rather than an alkaline earth metal (Admixture B).

EXAMPLE 9

Admixture solutions A and C were added to individual batches of a Type I/II Portland cement concrete slurry in amounts sufficient to provide admixture solids concentrations of 0.40% s/s, 0.33% s/s, and 0.25% s/s. The concrete was prepared with a water/cement ratio of 10 0.48 and the admixtures were added at 11 minutes as in Example 8.

Reference samples were prepared by addition of WRDA-19 alone at the three different concentration levels. Measurements were taken as in Example 8 and are presented in Tables III and IV.



Table III

Admixture	Admixture Concentration (%s/g)	Slump (inches) (cms.)			
		9 Min.	15 Min.	30 Min.	45 Min. 60 Min.
Reference	0.40	3.00(7.6)	9.75(24.8)	8.00(20.3)	6.00(15.2) 3.50(8.9)
A	0.40	2.75(7.0)	9.50(24.1)	7.00(17.8)	5.75(14.6) 4.25(10.8)
C	0.40	3.25(8.3)	9.50(24.1)	7.50(19.1)	7.00(17.8) 5.00(12.7)
Reference	0.33	2.25(5.7)	9.75(24.8)	6.00(15.2)	3.75(9.5) 2.50(6.35)
A	0.33	3.50(8.9)	9.75(24.8)	6.50(16.5)	5.00(12.7) 4.00(10.2)
C	0.33	2.50(6.4)	9.00(22.9)	7.75(19.7)	4.50(11.4) 3.50(8.9)
Reference	0.25	3.25(8.3)	8.25(21.0)	4.50(11.4)	3.50(8.9) 3.00(7.6)
A	0.25	3.75(9.5)	8.25(21.0)	6.00(15.2)	4.75(12.1) 3.50(8.9)
C	0.25	3.00(7.6)	8.00(20.3)	6.00(15.2)	3.50(8.9) 3.50(8.9)

Table IV

Admixture	Admixture Concentration (%s/s)	Air %	Initial Setting Time (hr:min)	Final Setting Time (hr:min)	Compressive Strength (psi)				(k Pa)	
					1 day	7 day	28 day	1 day	7 day	28 day
Reference	0.40	1.6	4:36	5:35	2974	5361	6655	20500	36960	45880
A	0.40	2.0	6:19	7:18	3077	5912	6461	21210	40760	44550
C	0.40	1.8	6:00	7:11	2968	5556	6640	20460	38310	45780
Reference	0.33	1.9	4:32	5:28	2857	6104	6937	19700	42090	47830
A	0.33	1.6	5:32	6:29	3128	5825	6905	21570	40160	47610
C	0.33	2.0	5:49	6:50	2951	5746	7066	20350	39620	48720
Reference	0.25	1.7	4:28	5:24	2527	4948	6891	17420	34110	47510
A	0.25	1.9	4:25	5:32	2631	5286	6753	18140	36450	46560
C	0.25	1.9	4:55	6:04	2749	5228	6494	18950	36050	44770



The results presented in Tables III and IV indicate increased slump retention over the reference at all admixture concentration levels. Compressive strengths and air content are close to those of the reference samples at all admixture concentration levels. The increases in initial and final setting times resulting from use of the admixtures decreases with decreasing concentration, with the setting time with Admixture A at 0.25% s/s being about equal to that of the reference.

EXAMPLE 10

Admixtures solutions C and D were each added to batches of two concretes which respectively contained Type I/II and Type II Portland cement binders, respectively designated as Concretes I and II. Admixture concentration was 0.33% s/s for all batches and the admixtures were added at 11 minutes into the mix cycle. The concretes were each prepared at a water/cement ratio of 0.57.

For comparison, reference samples were prepared as in Examples 8 and 9 (WRDA-19 alone) at an admixture concentration of 0.33% s/s ("Reference 1"). In addition, a second reference ("Reference 2") was prepared in which WRDA-19 was added at 11 minutes into the mix cycle to Concretes I and II which contained 0.1% s/s of a commercial low range water-reducer sold under the tradename "Hycol" by W. R. Grace & Co. The combined concentration of the water-reducers was thus 0.43% s/s.

Slump measurements were conducted as in Examples 8 and 9 and are presented in Table V.

Table V

<u>Concrete</u>	<u>Admixture</u>	<u>Slump (inches) (Cms)</u>				
		<u>9 Min.</u>	<u>15 Min.</u>	<u>30 Min.</u>	<u>45 Min.</u>	<u>60 Min.</u>
I	Reference 1	2.25(5.7)	8.50(21.6)	5.50(14.0)	3.25(8.3)	2.25(5.7)
I	Reference 2	5.75(14.6)	10.00(25.4)	7.75(19.7)	4.75(12.1)	4.25(10.8)
I	C	3.50(8.9)	9.50(24.1)	8.00(20.3)	6.25(15.9)	4.50(11.4)
I	D	3.50(8.9)	9.75(24.8)	8.00(20.3)	6.25(15.9)	4.50(11.4)
II	Reference 1	2.00(5.1)	5.50(14.0)	3.50(8.9)	2.50(6.35)	2.50(6.3)
II	Reference 2	2.50(6.3)	8.00(20.3)	3.50(8.9)	2.75(7.0)	2.50(6.3)
II	C	1.75(4.4)	7.50(19.0)	3.50(8.9)	2.75(7.0)	2.00(5.1)
II	D	2.25(5.7)	6.75(17.1)	4.25(10.8)	3.25(8.3)	2.75(7.0)

The results of Table V indicate improved slump retention over Reference 1 in both concretes by both admixtures. The slump retention provided by both admixtures is comparable to or better than that provided by Reference 2 notwithstanding the higher total concentration of water-reducers in Reference 2, with this result being more pronounced in Concrete I.

The air content, setting times, and compressive strengths of the concretes were measured as in Example 8 and are provided in Table VI.



Table VI

<u>Concrete</u>	<u>Admixture</u>	<u>Air %</u>	<u>Initial Setting Time (hr:min)</u>	<u>Final Setting Time (hr:min)</u>	<u>Compressive Strength (psi)</u>				<u>kPa</u>	
					<u>1 day</u>	<u>7 day</u>	<u>28 day</u>	<u>1 day</u>	<u>7 day</u>	<u>28 day</u>
I	Reference 1	1.8	4:46	5:58	1817	4249	5678	12530	29300	39150
I	Reference 2	1.5	5:14	6:14	1971	4432	5920	13590	30560	40820
I	C	1.6	5:30	6:48	1928	4604	5975	13290	31740	41200
I	D	1.4	5:51	7:11	1606	4196	5484	11070	28930	37810
II	Reference 1	1.7	4:59	6:34	1500	4339	6323	10340	29920	43600
II	Reference 2	1.9	5:48	7:08	1533	4568	6499	10570	31500	44810
II	C	1.5	6:02	7:19	1537	4850	6619	10600	33440	45640
II	D	1.6	6:19	7:39	1501	4678	6455	10350	32250	44510

Example II

Admixtures E, F, and G were added to concrete batches at a concentration of 0.40% s/s at 11 minutes into the mix cycle. The concrete was prepared using the Type I/II Portland cement binder of Example 9 at a water/cement ratio of about 0.48. Slump retention measurements are presented in Table VII.

Table VII

<u>Admixture</u>	<u>Slump (inches) (cms.)</u>				
	<u>9 min.</u>	<u>15 min.</u>	<u>30 min.</u>	<u>45 min.</u>	<u>60 min.</u>
E	3.00 (7.6)	10.00 (25.4)	8.50 (21.6)	7.00 (17.8)	5.25 (13.3)
F	3.50 (8.9)	10.25 (26.0)	8.50 (21.6)	6.75 (17.1)	4.75 (12.1)
G	3.50 (8.9)	9.75 (24.8)	8.75 (22.2)	7.75 (19.7)	5.00 (12.7)

Measurement of air content, setting times, and compressive strengths are given in Table VIII.

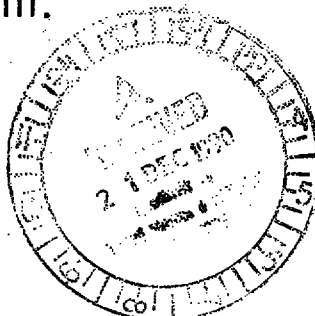


Table VIII

<u>Admixture</u>	<u>Air %</u>	<u>Initial Setting Time (hr:min)</u>	<u>Final Setting Time (hr:min)</u>	<u>Compressive Strength (psi) (kPa)</u>		
				<u>1 day</u>	<u>7 day</u>	<u>28 day</u>
E	1.6	7:01	8:15	2699(18610)	(5542(38210)	6801(46890)
F	1.5	6:08	7:02	2513(17330)	4828(33290)	6499(44810)
G	1.8	7:11	8:10	4736*(32650)	5430(37440)	7106(48990)

31

*Compressive strength at 3 days

As shown in Table VIII, setting times are less using the mixed alkanolamine borogluconate (Admixture F) rather than calcium borogluconate (Admixture E), notwithstanding the higher dosage of the borogluconate component in Admixture F. Admixture F also provides lower setting times than Admixture G, which is consistent with a generally observed trend of lower setting times using a borate ester neutralized with the alkanolamine mixture, as opposed to a borate ester neutralized solely with triethanolamine. However, the setting times provided with Admixture G are still approximately equal to those provided with Admixture E, notwithstanding a higher dosage of the borogluconate component.

Example 12

In order to demonstrate a water-reducing capability at low dosage, admixtures C and H were each added to concrete slurry batches in concentrations of 0.10% s/s and 0.16% s/s. The admixtures were added with the mix water used to prepare the slurries and slump measurements were taken at 9 minutes into the mix cycle. The concrete was prepared using the Type I/II Portland cement binder of Example 9 at a water/cement ratio of about 0.49.

The experimental concretes were compared against a batch with no admixture added ("Blank") and a batch to which were added the same dosages of the commercial low range water-reducing agent "Hycol". The 9 minute slumps and results of similar measurements as in the above Examples are provided in Table IX.

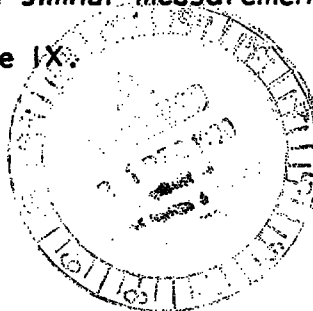


Table IX

Admixture	Admixture Concentration (%s/s)	Slump (Inches)(cms.)	Air %	Initial Setting Time (hr:min)	Final Setting Time (hr:min)
Blank	-	4.00 (10.2)	2.1	4:35	6:03
Hycol	0.10	5.00 (12.7)	2.5	6:20	7:37
C	0.10	4.75 (12.1)	2.1	5:17	6:44
H	0.10	5.25 (13.3)	2.2	5:47	7:03
Hycol	0.16	7.50 (19.0)	3.1	8:07	9:39
C	0.16	5.75 (14.6)	2.2	5:51	7:06
H	0.16	6.00 (15.2)	2.4	6:29	7:52

Admixture	Compressive Strength (psi)			kPa		
	1 day	7 day	28 day	1 day	7 day	28 day
Blank	2103	4920	6126	14500	33920	42240
Hycol	2384	5162	6332	16440	35590	43660
C	2195	4887	6095	15130	33690	42020
H	2136	4590	6255	14730	31650	43130
Hycol	2114	5030	6205	14580	34680	42780
C	2227	6251	6251	15350	43100	43100
H	2306	5305	6358	15900	36580	43840

As shown by Table IX, significant water reduction was provided by both Admixtures C and H. The increases in setting time over the blank sample were least with Admixture C and greatest with the Hycol samples.

Example 13

5 Two 40% solids admixture solutions of this invention were prepared by blending WRDA-19 and an aqueous solution of calcium borogluconate at WRDA-19: calcium borogluconate solids weight ratios of 50:50 and 75:25 and adjusting the final concentration with water. These admixtures were added to concrete batches at 11 minutes into the mix
10 cycle at a dosage of 0.2% s/s and compared against a reference concrete dosed with 0.2% s/s WRDA-19 alone. The concretes were prepared using the Type II Portland cement binder of Example 8 at a water/cement ratio of 0.51. Slump retention measurements and air content, setting times, and compressive strengths are provided in Tables X and XI.

Table X

<u>Admixture</u>	<u>Slump (inches) (cms.)</u>				
	<u>9 min.</u>	<u>15 min.</u>	<u>30 min.</u>	<u>45 min.</u>	<u>60 min.</u>
Reference	3.00(7.6)	6.25(15.9)	4.00(10.2)	3.00(7.6)	2.25(5.7)
75:25	2.50(6.3)	8.50(21.6)	5.00(12.7)	4.00(10.2)	3.00(7.6)
50:50	4.00(10.2)	8.00(20.3)	5.25(13.3)	4.00(10.2)	2.75(7.0)

Table XI

<u>Admixture</u>	<u>Air %</u>	<u>Initial Setting Time (hr:min)</u>	<u>Final Setting Time (hr:min)</u>	<u>Compressive Strength (psi) (kPa)</u>		
				<u>1 day</u>	<u>7 day</u>	<u>28 day</u>
Reference	2.2	4:22	5:22	1442 (9942)	4699 (32400)	4355 (30030)
75:25	1.8	5:07	6:15	1846 (12730)	5084 (35050)	6377 (43970)
50:50	2.1	7:08	8:38	1788 (12330)	5448 (37560)	7087 (48860)

EXAMPLE 14

A 69% by weight aqueous solution of the alkanolamine borogluconate of Example 6 was added to two concretes containing different Type I Portland cement binders, respectively designated Concretes I and II.

- 5 The mixed alkanol amine borogluconate was added with the mix water in an amount of about 0.07% by weight, based on the weight of Portland cement binder.

Also added to separate batches of Concretes I and II was a 58.7% aqueous solution of a non-neutralized borogluconate ester prepared by
10 reaction of approximately equimolar amounts of gluconolactone and technical grade boric acid in water at ambient temperature. The non-neutralized borogluconate was added with the mix water in an amount of about .044% by weight, based on the weight of the Portland cement binder.

- 15 The above respective weight concentrations of 0.07% and 0.044% provided approximately equivalent molar amounts of the mixed alkanolamine borogluconate and non-neutralized borogluconate in the concretes. For purposes of calculating this molar quantity, the mixed alkanolamine borogluconate was assumed to be neutralized with a 50:50
20 mixture of diethanolamine and triethanolamine so as to arrive at an assumed molecular weight of 351. The amount of mixed alkanolamine borogluconate used in this Example (5.98 grams of the mixed alkanolamine borogluconate were added to concrete containing about 8600 grams of Portland cement binder) was thus assumed to be .017 moles.

- 25 Each of the above concretes was prepared at a water/cement ratio of 0.58 and with a cement factor of 517 lbs./yd. (307 kg/m^3)

Slump measurements of the resultant concrete slurries were made at about 9 minutes after addition of the admixtures in accordance with ASTM C143. The concretes were also measured for air content (ASTM

C231), initial and final setting times (ASTM C403), and compressive strength (ASTM C192) at 1, 7, and 28 days (average of two cylinders).

The above concretes were compared against batches of the same concretes without any admixture added and against batches of the same
5 concretes to which were added about .017 moles of, respectively, boric acid, gluconic acid, the alkanolamine mixture used to prepare the mixed alkanolamine borogluconate, this being the same alkanolamine mixture as described in Example 5 but assumed to be a 50:50 mixture of
10 diethanolamine and triethanolamine, and boric acid and gluconic acid (.017 moles of each) added separately to the same concrete. Slump, air content, initial and final setting times, and compressive strengths of the comparative concretes were measured as above. The results of all measurements made on the various Concretes I and II are presented in Tables XII and XIII, respectively.

Table XII

Concrete	Admixture	Air %	Slump (in.)(cm.)	Initial Setting Final Setting		
				Time (hr:min)	Time (hr:min)	
I	None	1.8	3.75 (9.5)	4:49	6:29	
I	Boric Acid	1.7	5.50 (14)	5:05	6:39	
I	Gluconic Acid	1.7	7.00 (17.8)	8:00	9:39	
I	Boric Acid Gluconic Acid	2.0	4.25 (10.8)	6:42	8:27	
I	Alkanolamine Mixture	2.3	4.50 (11.4)	5:11	6:39	
I	Mixed alkanolamine Borogluconate	2.2	7.50 (19)	7:12	8:45	
I	Non-neutralized Borogluconate	1.7	6.50 (16.5)	7:24	9:21	
Concrete	Admixture	Compressive Strength psi			(kPa)	
		1 day	7 day	28 day	1 day	7 day 28 day
I	None	1215	4179	5549	8377	28810 38260
I	Boric Acid	1225	4199	6010	8446	28950 41440
I	Gluconic Acid	1004	4309	6249	6922	29710 43090
I	Boric Acid Gluconic Acid	1064	4622	5903	7336	31870 40700
I	Alkanolamine Mixture	1512	4695	6254	10420	32370 43120
I	Mixed alkanolamine Borogluconate	1272	4615	6472	8770	31820 44620
I	Non-neutralized Borogluconate	1053	4480	6043	7260	30890 41670

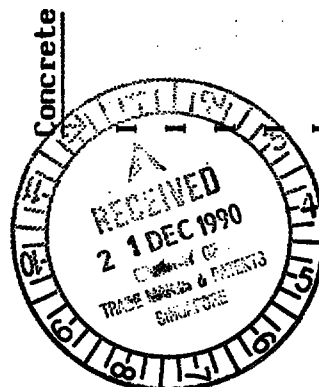


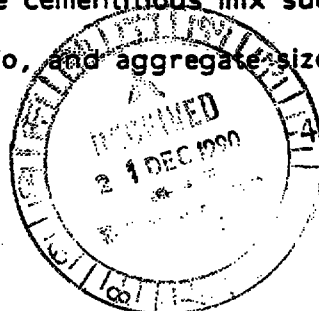
Table XIII

Concrete	Admixture	Air %	Slump (in.)(cm.)	Initial Setting Time (hr:min)		Final Setting Time (hr:min)
II	None	1.8	4.50 (11.4)	4:01		5:12
II	Boric Acid	1.8	5.00 (12.7)	4:09		5:19
II	Gluconic Acid	1.8	5.25 (13.3)	5:50		7:23
II	Boric Acid Gluconic Acid	1.9	4.25 (10.8)	5:17		6:42
II	Alkanolamine Mixture	1.9	4.50 (11.4)	4:01		5:15
II	Mixed Alkanolamine Borogluconate	2.0	5.25 (13.3)	5:09		6:30
II	Non-neutralized Borogluconate	1.4	5.25 (13.3)	5:22		6:52
Concrete	Admixture	Compressive Strength (psi)			(kPa)	
		1 day	7 day	28 day	1 day	28 day
II	None	1742	4193	6191	12010	28910 42680
II	Boric Acid	1593	3926	5727	10980	27070 39490
II	Gluconic Acid	1612	4416	6448	11110	30450 44460
II	Boric Acid Gluconic Acid	1644	4115	5970	11330	28370 41160
II	Alkanolamine Mixture	1843	4700	6364	12710	32400 43880
II	Mixed Alkanolamine Borogluconate	1699	4738	5903	11710	32670 40700
II	Non-neutralized Borogluconate	1661	4076	6139	11450	28100 42330

As shown in Tables XII and XIII, the mixed alkanolamine borogluconate admixture provided the best combination of slump and set retardation in both Concretes I and II. Significant increases in slump over the concretes containing no admixture were observed, with initial and final setting time increases of 2:24 and 2:26, respectively, in Concrete I and 1:08 and 1:17, respectively, in Concrete II. The mixed alkanolamine borogluconate containing samples exhibited less set retardation than the concretes containing either the gluconic acid alone or the boric acid and gluconic acid mixture, while providing slump increases approximately equal to or greater than those provided in these comparative concretes. While the boric acid and mixed alkanolamine samples had lower setting times than the mixed alkanolamine borogluconate samples, the borogluconate samples exhibited higher slumps, with this tendency being more pronounced in Concrete I.

The non-neutralized borogluconate also provided significant increases in slump over the concretes containing no admixture, with initial and final setting time increases of 2:35 and 2:52, respectively, in Concrete I and 1:22 and 1:39, respectively, in Concrete II. The set retardation provided by the non-neutralized borogluconate was greater than that provided by the mixed alkanolamine borogluconate or gluconic acid, but was less than that provided by an equivalent molar amount of gluconic acid alone.

The results provided in the above Examples should be taken as exemplifying the performance which can be obtained employing the admixtures of this invention. As previously indicated, the admixture performance will vary as a function of admixture composition and the variables associated with formulation of the cementitious mix such as cement type and source, water/cement ratio, and aggregate size and amount.





CLAIMS

1. A hydraulic cement composition as hereinbefore defined comprising a hydraulic cement binder and less than 0.075% by weight, based on the weight of said hydraulic cement binder, of a borate ester of a polyhydroxy compound as hereinbefore defined.
- 5 2. A composition of Claim 1 wherein said hydraulic cement binder is Portland cement.
3. A hydraulic cement composition comprising a hydraulic cement binder and an ammonium or amine salt of a borate ester of a polyhydroxy compound.
- 10 4. A composition according to any one of Claims 1 to 3 wherein said borate ester is a salt comprising an ammonium, alkylammonium, or alkanolammonium cation.
- 15 5. A hydraulic cement water-reducing admixture composition comprising a hydraulic cement water-reducing agent and a borate ester of a polyhydroxy compound.
- 20 6. A composition of Claim 5 wherein the said borate ester is a salt comprising an alkali cation, alkaline earth metal cation, ammonium cation, alkylammonium cation, or alkanolammonium cation.
7. A composition of Claim 5 or 6 wherein said hydraulic cement water-reducing agent comprises a salt of an aromatic sulfonic acid-aldehyde condensate polymer or a lignosulfonic acid salt.



8. A composition of Claim 5, 6 or 7 comprising, as the water-reducing agent component, at least two different hydraulic cement water-reducing agents.

9. A composition of Claim 8 comprising a salt of an aromatic sulfonic acid-aldehyde condensate polymer and a lignosulfonic acid salt.

10. A composition according to any one of Claims 5 to 9 comprising less than about 30% by weight of said borate ester, based on the total weight of the admixture.

11. A composition of Claim 9 comprising about 30 to 90% by weight of said condensate polymer, about 15 to 80% by weight of said lignosulfonic acid salt, and about 1 to 15% by weight of said borate ester, based on the total weight of said condensate polymer, lignosulfonic acid salt, and borate ester.

12. A hydraulic cement composition comprising a hydraulic cement binder, a hydraulic cement water-reducing agent, and less than 0.075% by weight, based on the weight of said hydraulic cement binder, of a borate ester of a polyhydroxy compound.

13. A cement composition of Claim 12 wherein the total amount of said water reducing agent and said borate ester is about 0.05% to 0.50% by weight, based on the weight of said hydraulic cement binder.

14. A cement composition of Claim 12 or 13 wherein said water-reducing agent comprises a salt of an aromatic sulfonic acid-aldehyde condensate polymer and a lignosulfonic acid salt.

15. A cement composition substantially as described in any one of Examples 8 to 14, but excluding the compositions quoted for comparative or reference purposes.

