SUGAR DERIVATIVE COMPOSITION FOR MODIFYING PROPERTIES OF CEMENT AND CEMENTITIOUS COMPOSITIONS AND PROCESSES FOR MANUFACTURING SAME

Exemplary compositions comprise a plurality of particles to be dispersed (e.g., calcium carbonate or a binder material such as Portland cement) and a compound for dispersing the plurality of particles. The compounds comprise a residue of a sugar or sugar derivative linked by an amine, amide, imide, or urea group to a non-sugar substituent comprising one or more alkyl, aryl, alkylaryl, oxyalkylene, polyoxalkylene groups, or a mixture thereof. Disclosed are exemplary compounds for dispersing particles and for modifying properties of hydratable compositions, such as cementsitious mixtures (e.g., concrete, masonry, mortar, or cement), as well as methods for making the compounds and for modifying particle-containing compositions. The compounds and methods are useful for increasing fluidity, strength, grinding performance, or other properties in cements and cementitious compositions. The invention is also believed to provide one or more of these qualities in aqueous environments wherein particles, such as cement particles, are dispersed (e.g., slurries).
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>Albania</td>
<td>ES</td>
<td>Spain</td>
<td>LS</td>
<td>Lesotho</td>
<td>SI</td>
<td>Slovenia</td>
</tr>
<tr>
<td>AM</td>
<td>Armenia</td>
<td>FI</td>
<td>Finland</td>
<td>LT</td>
<td>Lithuania</td>
<td>SK</td>
<td>Slovakia</td>
</tr>
<tr>
<td>AT</td>
<td>Austria</td>
<td>FR</td>
<td>France</td>
<td>LU</td>
<td>Luxembourg</td>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>GA</td>
<td>Gabon</td>
<td>LV</td>
<td>Latvia</td>
<td>SZ</td>
<td>Swaziland</td>
</tr>
<tr>
<td>AZ</td>
<td>Azerbaijan</td>
<td>GE</td>
<td>Georgia</td>
<td>MC</td>
<td>Monaco</td>
<td>TD</td>
<td>Chad</td>
</tr>
<tr>
<td>BA</td>
<td>Bosnia and Herzegovina</td>
<td>GH</td>
<td>Ghana</td>
<td>MD</td>
<td>Republic of Moldova</td>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>GN</td>
<td>Guinea</td>
<td>MG</td>
<td>Madagascar</td>
<td>TJ</td>
<td>Tajikistan</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>GR</td>
<td>Greece</td>
<td>MK</td>
<td>The former Yugoslavia</td>
<td>TM</td>
<td>Turkmenistan</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>HU</td>
<td>Hungary</td>
<td>ML</td>
<td>Mali</td>
<td>TR</td>
<td>Turkey</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>IE</td>
<td>Ireland</td>
<td>MN</td>
<td>Mongolia</td>
<td>TT</td>
<td>Trinidad and Tobago</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
<td>IL</td>
<td>Israel</td>
<td>MR</td>
<td>Mauritania</td>
<td>UA</td>
<td>Ukraine</td>
</tr>
<tr>
<td>BY</td>
<td>Belarus</td>
<td>IS</td>
<td>Iceland</td>
<td>MW</td>
<td>Malaysia</td>
<td>UG</td>
<td>Uganda</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>IT</td>
<td>Italy</td>
<td>MX</td>
<td>Mexico</td>
<td>US</td>
<td>United States of America</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>JP</td>
<td>Japan</td>
<td>NE</td>
<td>Niger</td>
<td>VN</td>
<td>Viet Nam</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>KE</td>
<td>Kenya</td>
<td>NL</td>
<td>Netherlands</td>
<td>YU</td>
<td>Yugoslavia</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>KG</td>
<td>Kyrgyzstan</td>
<td>NO</td>
<td>Norway</td>
<td>ZW</td>
<td>Zimbabwe</td>
</tr>
<tr>
<td>CI</td>
<td>Côte d’Ivoire</td>
<td>KP</td>
<td>Democratic People’s Republic of Korea</td>
<td>NZ</td>
<td>New Zealand</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>KR</td>
<td>Republic of Korea</td>
<td>PL</td>
<td>Poland</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN</td>
<td>China</td>
<td>LC</td>
<td>Saint Lucia</td>
<td>PT</td>
<td>Portugal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CU</td>
<td>Cuba</td>
<td>LJ</td>
<td>Liechtenstein</td>
<td>RO</td>
<td>Romania</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CZ</td>
<td>Czech Republic</td>
<td>LK</td>
<td>Sri Lanka</td>
<td>RU</td>
<td>Russian Federation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td>LR</td>
<td>Liberia</td>
<td>SD</td>
<td>Sudan</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td></td>
<td></td>
<td>SE</td>
<td>Sweden</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EE</td>
<td>Estonia</td>
<td></td>
<td></td>
<td>SG</td>
<td>Singapore</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
SUGAR DERIVATIVE COMPOSITION FOR MODIFYING PROPERTIES OF CEMENT AND CEMENTITIOUS COMPOSITIONS AND PROCESSES FOR MANUFACTURING SAME

Inventors: Ara Jeknavorian, Byong-Wa Chun, Hideo Koyata, Shawn Williams, Felek Jachimowicz, Ginevra Clark, Jyoti Seth, Paul Westgate, Brent Williams, and Lawrence R. Roberts

Field of the Invention

This invention relates to dispersing particles using a compound comprising a residue of a sugar or sugar derivative linked by an amine, amide, imide, or urea group to a non-sugar substituent comprising one or more alkyl, aryl, alkylaryl, oxyalkylene, or polyoxyalkylene groups, or a mixture thereof. The particles to be dispersed may be inorganic (e.g., calcium carbonate) and include hydratable cementitious binders such as Portland cement. More particularly, the invention involves methods for making the compounds, and methods for modifying properties of cementitious compositions.

Background of the Invention

While increased flowability in a hydrating cement composition can be attained by incorporating excess amounts of water, it is generally known that the building or civil engineering structure made from the resultant cementitious mixture will have less than desirable compressive strength or other disadvantageously altered characteristics such as reduced durability.

Various additives have been proposed to increase the flowability, or “slump,” in cement compositions such as mortar and concrete, without increasing the water content of the initially formed compositions. Such additives or admixtures are classified as chemical “superplasticizers” or “water reducers,” and include compounds such as naphthalene sulfonate formaldehyde condensates, lignin sulfonates, and the like.

Water reducing admixtures are disclosed in US Patent 5,393,343 of Darwin et al., which is owned by the common assignee hereof. The ‘343 Patent disclosed the use of a composition comprising an imidized acrylic polymer or copolymers thereof which were unexpectedly found to provide a high degree of slump in a cement
mixture over a sustained period of time while not having any significant set retardation. This was deemed an improvement, for example, over the alkenyl-ethers and acrylic acid or maleic anhydride based slump enhancers as proposed in Japanese Pat. Publ. Nos. 285140/88 and 163108/90; and over the copolymers formed from hydroxy-terminated allylethers and a salt, ester or amide derivative of maleic anhydride as disclosed in US Patent 4,471,100.

An early attempt to formulate a water reducing cement composition was disclosed in Japanese Patent Application Kokai No. S52-76327 (Kokai date: June 27, 1977) by Inoue et al. This patent taught that water reducers such as lignin sulfonates and hydroxycarboxylates caused poor hardening of concretes when used in excessive amounts, and sometimes resulted in accidents whereby the resultant concrete structures fell apart. To counteract this effect, Inoue et al. taught that poor hardening could be overcome by introducing into the cement mixture a composition formed by reacting C₂-C₃ alkylene oxides with gluconates or glucoheptonates using an alkali catalyst.

In Japanese Patent Application Kokai No. S58-15054 (Kokai date: January 28, 1983) of Takemoto Yushi Co., Ltd., Yamamoto et al. disclosed a concrete water reducer comprising a salt of naphthalenesulfonic acid-formaldehyde condensate and a gluconate-ethylene oxide adduct. This was said to offer high water-reducibility, to prevent deterioration of the concrete due to change of slump over time, and to avoid a set retarding effect that would hinder initial strength.

In Japanese Patent Application Kokai Nos. S58-135165 and S58-135167 (Kokai date: June 27, 1977) of Sanyo Chemical, Tanaka et al. disclosed a cement dispersing composition comprising a salt of naphthalenesulfonic acid-formalin condensate, a cement setting retarder such as an alkylene oxide adduct of a carboxycarboxylic acid or polyhydroxy compound (e.g., oxyalkylene adduct of gluconic acid), and an ester of glycol or glycerin and/or C₆ or lower aliphatic mono- or polycarboxylic acid.

In US Patent 4,432,801 of Tegiacchi et al., there was disclosed a process for modifying certain sugars, e.g., liquid glucose syrups into salts of the corresponding sugar acid or into the salts of the lower carboxylic acid. The resultant sugar material was then taught to be incorporated into concrete to modify its fluidity.
Summary of the Invention

This invention relates to modification of fluidity, strength, grinding efficiency, set retardation, and/or other properties of a cement, cementitious mixture, or other particle-containing composition. Exemplary compositions of the invention comprise a binder and a compound having a residue of a sugar or sugar derivative linked by an amine, amide, imide, or urea group to a non-sugar substituent comprising one or more alkyl, aryl, alkylaryl, oxyalkylene, polyoxyalkylene groups, or a mixture thereof.

The term "additive" is sometimes used to refer to agents that are incorporated during the manufacturing of cement (e.g., grinding), whereas the term "admixture" is sometimes used to refer to agents combined in a "cementitious composition," such as concrete or mortar. However, for purposes of the present invention, the term "cementitious composition" will encompass compositions having a binder (cement, other cementitious binders); optionally pozzolans, slag, clay, etc.; and at least one compound (whether termed an "additive" or "admixture" is not critically important) for modifying a property of the cementitious composition.

An exemplary compound of the invention for use in modifying cementitious (or other particle-containing compositions) thus comprises: (A) at least one residue of sugar or sugar derivative; (B) at least one non-sugar substituent, such as an alkyl group (preferably one C₁-C₈ alkyl group, substituted or unsubstituted, per sugar residue in component (A)), an aryl or alkylaryl group (preferably having one C₅-C₈ aryl or alkylaryl substituted or unsubstituted group per sugar residue in component (A)), and/or an oxyalkylene or polyoxyalkylene oligimer or polymer group (e.g., preferably having repeating C₂-C₄ oxyalkylene groups, or, more preferably, repeating ethylene oxide and propylene oxide groups, wherein the number of repeating units is 2-200); and (C) a linking group comprising an amide, amine, imide, urea, or mixture thereof, for linking the sugar residue of component (A) to the non-sugar substituent of component (B).

Exemplary sugar residues of component (A) may be derived from hydroxycarboxylic acids such as aldonic acid (e.g., gluconic acid, heptogluconic acid), aldaric acid (e.g., glycaric acid, heptoglutaric acid), and uronic acid (e.g., glucuronic acid, heptoglucuronic acid), or their salts or their lactones (i.e. anhydrides); or may
also be derived from aldoses or sugars (e.g., monosaccharides such as glucose, disaccharides such as sucrose, etc.), including corn syrup and molasses and their oxidized forms which could also serve as substrates for gluconamide formation.

Exemplary non-sugar substituents of component (B) comprise at least one substituted or unsubstituted alkyl group, aryl group, and/or alkylaryl group, and/or an oxyalkyl or polyoxyalkylene group. Substituted alkyl, aryl, or alkylaryl groups may comprise a functional group such as a hydroxy group, alkene group, alkyne group, halide group, ether group, carbonyl group, aldehyde group, ketone group, ester group, carboxylic acid group, amide group, amine group, nitrite group, nitro group, sulfide group, sulfoxide group, amino acid group, sulfonate group, phosphonate group, or a mixture thereof, without deviating from the present invention. When the sugar residue is derived from a monomeric sugar and the non-sugar substituent group is an alkyl group, the alkyl group should preferably have from 1 to 8 carbons so as to provide suitable solubility and surface activity to the overall sugar residue compound derived.

Among linking groups identified for component (C), amides are most preferred for connecting sugar residue group(s) to non-sugar substituent group(s).

A preferred exemplary compound of the invention for modifying cement, cemenitious compositions, or other particle-containing compositions, comprises at least one residue of sugar or sugar derivative; at least one non-sugar substituent comprising a C₂–C₄ oxyalkylene groups, or, more preferably, repeating ethylene oxide and propylene oxide groups, wherein the number of repeating units is 2-200 (and more preferably 2-100); and a linking member, preferably an amide group, for linking the sugar residue(s) to the ethoxylated non-sugar substituent group(s). This compound may, for example, be sold as a cement additive (e.g., grinding) or as an admixture for use in cemenitious compositions (e.g., concrete, mortar). The compound is also believed to be useful as a particle dispersant in non-hydratable particle-containing compositions (e.g., clay-containing mixes, latexes for paint; also patching, sealant, or coating compositions).

The present invention particularly includes cement and other cemenitious or other hydratable binder compositions (as well as nonhydratable compositions employing non-hydratable binders) comprising the above-described additive or
admixture compound. The present invention also pertains to processes for modifying such compositions, as well as to processes for making the above-described compound.

In addition to the ability to modify the fluidity of cement and cementitious compositions, the above-described compounds may be used to modify other properties of cementitious compositions as well. For example, the inventive compounds are useful as grinding aids for cement clinker; and thus a process of the invention involves introducing the compound during grinding of cement clinker. It is believed that when used as a grinding aid, the compounds of the invention are useful for increasing the strength of materials and structures made from the processed cement.

The above-described compounds are suitable for use as efficient water reducer additives or admixtures for use in or with cement, for use in the manufacture of cement, and for use in cementitious mixtures including concrete, mortar, or masonry. In addition to the ability to modify the fluidity of cement and cementitious compositions, the compounds may be used to modify other properties of cementitious compositions. For example, the compounds are believed to be useful as grinding aids for cement clinker; and, consequently, an exemplary process of the invention involves introducing the above-described additive compound during the grinding of cement clinker. It is believed that when used as a grinding aid, the compounds are useful for increasing the strength of materials and structures made from the processed cement.

In addition, the above-described compounds, when used as admixtures, are believed to provide benefits as water reducers for cement and cementitious compositions. Thus, exemplary methods of the involve incorporating the above-described compounds into an aqueous environment having a binder material. For example, the composition may be introduced into a concrete or mortar as an admixture, either with a hydratable and/or nonhydratable binder material (e.g., cement and/or clay), or it can be introduced using mix water.

On a general level, the compounds of the invention can be used as dispersants for a plurality of particles to be dispersed, such as calcium carbonate which is technically by itself not a hydratable binder. Thus, compositions of the invention include a plurality of particles to be dispersed and a compound for dispersing the
plurality of particles, the compound having at least one residue of sugar or sugar derivative, at least one non-sugar substituent, and a linking group.

The invention also pertains to a method of dispersing nonhydratable solids such as polymer particles (e.g., synthetic polymers for latexes) or minerals (e.g., calcium carbonate) in an aqueous system, comprising introducing to said nonhydratable solids the compound described herein having the sugar residue connected to the non-sugar substituents by the linking group, as described above. Thus, an exemplary composition comprises a plurality of particles to be dispersed and a compound for dispersing said plurality of particles, said compound comprising (A) at least one residue of sugar or sugar derivative; (B) at least one non-sugar substituent, such as an alkyl group (preferably one C_1-C_4 alkyl group, substituted or unsubstituted, per sugar residue in component (A)), an aryl or alkyaryl group (preferably having one C_6-C_4 aryl or alkyaryl substituted or unsubstituted group per sugar residue in component (A)), and/or an oxyalkylene or polyoxyalkylene oligimer or polymer group (e.g., preferably having repeating C_2-C_4 oxyalkylene groups, or, more preferably, repeating ethylene oxide and propylene oxide groups, wherein the number of repeating units is 2-200); and (C) a linking group comprising an amide, amine, imide, urea, or mixture thereof, for linking the sugar residue of component (A) to the non-sugar substituent of component (B).

Exemplary processes for manufacturing sugar amide compounds are also disclosed herein. An exemplary method comprises introducing into a mix tank a sugar derivative and an amine (and optionally a solvent) to form a reaction mixture; and forming a sugar amide reaction product. The sugar amide reaction product can then be separated from the reaction mixture solvent. The components may be added using conventional methods. For example, the sugar derivative component may be incorporated into a mixing tank using a bulk solids hopper and feed system.

Another exemplary process involves evaporating the reaction mixture solvent to isolate the sugar amide reaction product as a dry material. In another exemplary process, the evaporation may be achieved by decreasing pressure above the reaction mixture (e.g., applying a vacuum), whereby solvent is removed from the sugar amide reaction product. Solvent may also be removed by flowing a gas over or through the reaction mixture. In still further exemplary methods, the sugar amide reaction product
forms a precipitate. The reaction product may optionally be chilled, before removing the resulting crystals by filtration. A dry product can then be obtained by evaporating the residual solvent.

Another exemplary process of the invention involves the use of water to extract the sugar amide reaction product from the solvent. Thus, a water-immiscible solvent and reaction product are contacted with water, such as in a counter-current extraction, and the product is removed from the solvent phase resulting in an aqueous phase product. This exemplary approach provides advantages in terms of avoiding solids handling and eliminating the need to vaporize or distill solvents.

A still further exemplary process of the invention involves the use of water to replace solvent after the reaction is completed. After reaction is completed in a batch vessel, the solvent may be replaced with water using batch distillation. During replacement and/or solvent recovery, water is added, either continuously or all at once, to the mixture containing solvent and product. As with the extraction process described above, this solvent replacement process provides the advantage of eliminating solids handling and the need to condense solvent from a carrier stream. In a further exemplary process, the components may be added into a continuous in-line mixing tank to obtain the sugar amide reaction product which, with solvent (and any residual amine), can then be fed continuously into a distillation column. The solvent is replaced by water that is heated and vaporized into the distillation column, and the reaction product may be removed from the column in aqueous form while the solvent is condensed, optionally refluxed, and purified for reuse (along with any residual amine) in the process.

Further advantages and features of the present invention are discussed hereinafter.
Brief Drawings of the Invention

An appreciation of the various advantages and features of the present invention may be facilitated when the following detailed description of exemplary embodiments of the invention is contemplated in conjunction with appended drawings, wherein:

Fig. 1 is a graphic illustration of flow performance of cement compositions comprising various admixtures, including admixtures of the present invention;

Fig. 2 is a graphic illustration of set retarding performance of cement compositions comprising various admixtures, including admixtures of the present invention;

Fig. 3 is a diagram of an exemplary evaporation process of the invention for manufacturing a sugar amide composition of the present invention;

Fig. 4 is a diagram of an exemplary crystallization process of the invention for manufacturing a sugar amide composition of the present invention;

Fig. 5 is a diagram of an exemplary extraction process of the invention for manufacturing a sugar amide composition of the present invention;

Fig. 6 is a diagram of an exemplary solvent replacement process of the invention for manufacturing a sugar amide composition of the present invention; and

Fig. 7 is a diagram of another exemplary solvent replacement process of the invention for manufacturing a sugar amide composition of the present invention.
Detailed Description of the Invention

The present invention relates to compositions and methods involving particles to be dispersed (e.g., fillers such as calcium carbonate, binders such as cement, particles in slurries such as drilling mud) and compounds for dispersing or otherwise modifying the particles. In particular, the present invention pertains to cementitious compositions comprising a cement binder and a modifying compound.

The terms “cement” and “cementitious composition” (which may be synonymous with “cement composition”) may be used herein to refer to dry powders as well as to pastes, mortars, grouts such as oil well cementing grouts, and concrete compositions comprising a hydratable cement binder. The terms “paste”, “mortar” and “concrete” are terms of art: pastes are mixtures composed of a hydratable cement binder (usually, but not exclusively, Portland cement, masonry cement, or mortar cement and may also include limestone, hydrated lime, fly ash, blast furnace slag, pozzolans, and silica fume or other materials commonly included in such cements) and water; mortars are pastes additionally including fine aggregate (e.g., sand), and concrete are mortars additionally including coarse aggregate (e.g., crushed gravel, stone). The cementitious compositions tested in this invention may be formed by mixing required amounts of certain materials, e.g., a hydratable cement, water, and fine and/or coarse aggregate, as may be applicable to make the particular cement composition being formed.

Exemplary compounds for modifying one or more properties of cementitious compositions comprise, as summarized above, a residue of sugar or sugar derivative, a non-sugar substituent, and a linking member for connecting the sugar residue to the non-sugar substituent. Such a compound may be represented by the following formula

$$[G]_g[X]_x[Q]_q$$

wherein G represents at least one residue of sugar or sugar derivative; “g” is an integer of from 1 to 100, and more preferably “g” is from 1 to 50; X represents a linking group selected from amide, amine, imide, urea, or mixture thereof (preferably it is an amide); “x” is an integer of from 1 to 100 (and preferably equal to or less than “q”); Q represents a non-sugar substituent group selected from an alkyl (preferably having one
C₂-C₈ substituted or unsubstituted alkyl group per sugar residue in component (G), aryl or alkylaryl group (preferably having one C₆-C₈ aryl or alkylaryl substituted or unsubstituted groups per sugar residue in component (G)), and/or an oxyalkylene or polyoxyalkylene oligomer or polymer group (e.g., preferably having repeating C₂-C₄ oxyalkylene groups, or, more preferably, repeating ethylene oxide and propylene oxide groups, wherein the number of repeating units is 2-200); and “q” is an integer of from 1 to 100.

Where “g” is 1, it will follow that “[G]” will represent a monomeric sugar residue. Where “g” is greater than 1, it also follows that there are more than one “[G]” groups. In other words, there can be more than one [G] group attached to the linking group “X” or indirectly attached by being attached to other [G] groups. Consequently, the formula [G]ₙ[X]₁[Q]ₖ may encompass structures, for example, represented by the formulae

\[\text{G - G - G - X - Q} \quad \text{G - G - G - X - Q}\]

wherein a number of sugar residue groups (G) are attached to each other and one sugar residue group is attached to the linking group (X); and the formula [G]ₙ[X]₁[Q]ₖ may also be seen to encompass the structures, for example, shown below

\[\text{G} \quad \text{G - G} \quad \text{G - G - G - G - G} \]
\[\text{X - Q} \quad \text{X - Q} \quad \text{X} \quad \text{X}
\[\text{G} \quad \text{G - G} \quad \text{Q} \quad \text{Q}\]

and variations thereof. It is understood that “G,” “X,” and “Q” can represent the same or similar groups, units, or compounds.

Similarly, for the non-sugar substituent represented by [Q]ₖ, it will be seen that the formula can encompass various structures, such as those shown below:

\[\text{G - X - Q - Q - Q} \quad \text{G - X - Q - Q}\]
\[\text{Q} \quad \text{Q - Q} \quad \text{Q - Q - Q - Q - Q}\]
\[\text{X - G} \quad \text{X - G} \quad \text{X} \quad \text{X}\]
\[\text{Q} \quad \text{Q - Q} \quad \text{Q - Q} \quad \text{G}\]
and variations thereof.

In view of the present disclosure, it will be appreciated that the sugar residue and non-sugar substituent components may be connected to the linking member (X), as well as to other similar or identical groups or compounds, as in the following structures:

\[
\begin{align*}
G & \quad G & \quad G \\
\quad \quad X & \quad \quad X \\
\quad \quad \quad \quad Q & \quad \quad \quad \quad Q
\end{align*}
\]

and other variations. Other variations can be made wherein some of the “G” and/or “Q” groups above can be connected, in turn, to G, Q, GX, XQ, and/or GXQ containing groups.

The term “residue of sugar” as employed herein means and refers to a sugar molecule (e.g., monosaccharide, disaccharide, polysaccharide, etc. as further described hereinafter) or derivative thereof which is capable of chemically-bonding to the linking group.

A particularly preferred compound of the invention comprises a sugar amide (the “[G]_{s}[X]_{x}” component) for modifying the fluidity of cement, mortar, or concrete. This exemplary embodiment may be derived from a hydroxycarboxylic acid, such as a sugar acid, and an amine. For example, the sugar residue “G” may be derived from hydroxycarboxylic acids such as aldonic acid (e.g., gluconic acid, heptogluconic acid), aldonic acid (e.g., glycaric acid, heptoglucaric acid), and uronic acid (e.g., glucuronic acid, heptoglucuronic acid or, as it is otherwise sometimes called, glucoheptonic acid), or their salts or their lactones (i.e. anhydrides). The sugar residue may also be derived from aldoses or sugars (e.g., glucose, sucrose, tetrose, pentose, hexose, etc.),
including corn syrup and molasses and their oxidized forms which could also serve as substrates for gluconamide formation.

Preferred sugar residues are sugar acids having 3-10 carbons; more preferred are sugar acids having 4-8 carbons; and most preferred are those having 5-7 carbons. Sugar acids which are also preferred include D-gluconic acid, D-gluaric acid, and D-Glucuronic acid, and mixtures thereof.

As previously mentioned, the non-sugar substituent “Q” group may comprise substituted alkyl and aryl groups having functional groups such as a hydroxy group, alkene group, alkyne group, halide group, ether group, carbonyl group, aldehyde group, ketone group, ester group, carboxylic acid group, amide group, amine group, nitrite group, nitro group, sulfide group, sulfoxide group, amino acid group, sulfonate group, phosphonate group, or a mixture thereof.

Thus, an alkoxylated amine, which can be used for combining with the starting sugar acid to obtain the additive/admixture compounds of the invention, may be represented by the formula

\[
\begin{array}{c}
\text{H-N} \\
\text{AO}_n R^1
\end{array} \\
\text{AO}_p R^2
\]

wherein AO represents an alkoxy group, and preferably a C₂-C₃ ethylene oxide/propylene oxide group; “n” and “p” are integers whereby the sum of “n” and “p” are from 1 to 100, and “n” or “p” individually are integers of from 0 – 100; and R¹ and R² each represents hydrogen or a substituted or unsubstituted C₁-C₈ alkyl, aryl, or alkylaryl group; and, if “n” = 0, then the corresponding R¹ comprises an alkyl, aryl, or alkyaryl group (preferably up to 8 carbons). Also, R¹ can be connected to R² to form a cyclic polyoxyalkylene secondary amine, e.g. morpholine.

Thus, an alkylamine which can be used for combining with the starting sugar acid to obtain additive/admixture compounds of the invention may be represented by the formula
wherein R³ and R⁴ independently represented hydrogen or C₁-C₂₀ alkyl group, a
cycloalkyl group, or an aryl ring (e.g., as in benzyl amine). R³ and R⁴ may also form a
cyclic structure such as in a cyclic secondary amine, e.g. piperidine, etc. R³ and R⁴
can also contain additional amine or other functional groups.

The amine may be reacted with a sugar acid by thermal amidation with or
without an amidation catalyst. The reaction temperature is preferably in the range of
80 to 180°C (more preferably 100-145°C), and the reaction can be done in bulk or in
solution. An azeotropic agent, such as toluene, can be used to facilitate dehydration.
Lactone formation can be minimized by using a slight to modest excess of the amine,
and it is believed that any residual amine will not have an adverse effect upon
cementitious materials into which the sugar residue containing compounds are
incorporated.

The derived sugar amide can be represented by the general formula:

\[
\begin{align*}
\text{O} & \quad (AO)_nR^1 \\
\| & \quad / \\
\left[G^1\right]_g - C - N & \quad \downarrow \\
\| & \quad / \\
\left(G^1\right)_g - C - N & \quad \downarrow \\
\text{R}^2 & \quad (AO)_nR^2
\end{align*}
\]

\[(1)\]

\[
\begin{align*}
\text{O} & \quad R^3 \\
\| & \quad / \\
\left[G^1\right]_g - C - N & \quad \downarrow \\
\text{R}^4
\end{align*}
\]

\[(2)\]

wherein G¹ represents a monomeric sugar residue after amidation wherein the C=O
moiety participating in the amide linkage is originally derived from G and wherein
sugar acids are reacted with a non-sugar amine, and G¹ can be either linear or cyclic in
form depending on the amine species and/or surrounding environment; AO represents
C₂-C₄ alkoxyl group, and more preferably ethylene oxide and propylene oxide groups; R¹ and R² independently represent hydrogen or a C₁-C₃ alkyl group; “n” and “p” each independently represent an integer from 0 to 100; and the sum of “n” and “p” is an integer from 1 to 100, and R³ and R⁴ independently represent hydrogen or C₁-C₂₀ alkyl, cycloalkyl group, or an aryl ring (e.g., as in benzyl amine). R¹, R², R³, and R⁴ may also contain functional groups.

The amine may also be reacted with sugars or oligosaccharide having reactive aldehyde or ketone groups to form adducts. The reaction temperature is in the range of 0 to 120°C, preferably 20°C to 100°C. The reaction can be done practically in bulk with a small amount of water (fusing a sugar with an amine), alcohols, alcohols containing water or in water. Acid catalysts, such as hydrochloric acid, acetic acid, oxalic acid, etc., can be used to rearrange the sugar amine adducts into more stable form, known as Amadori derivatives (in the case of reaction of aldoses with an amine) or Heyns compounds (in the case of the reaction of ketoses with an amine).

Exemplary sugar-amine adducts, after being rearranged with an acid catalyst, can be represented by the general formulae:

\[
\begin{align*}
\text{(3) or} \\
\begin{array}{c}
O \\
\| \\
\text{[G₂]ₙ - C - CH₂ - N} \\
\| \\
\text{(AO)ₙR¹} \\
\text{[G₂]ₚ - C - CH₂ - N} \\
\| \\
\text{(AO)ₚR²} \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{(4)} \\
\begin{array}{c}
O \\
\| \\
\text{[G₂]ₚ - C - CH₂ - N} \\
\| \\
\text{R³} \\
\end{array}
\end{align*}
\]

wherein G² represents a monomeric sugar residue after amination reaction of sugar with non-sugar amine; wherein AO represents an alkoxy group, and preferably C₂-C₃ ethylene oxide and propylene oxide groups; “n” and “p” are integers whereby the sum
of “n” and “p” are from 1 to 100, and “n” or “p” individually are integers of from 0 –
100; and R¹ and R² each represents hydrogen or a (substituted or unsubstituted) C₁-C₈
alkyl, aryl, or alkylaryl group; and, if “n” = 0, then the corresponding R¹ comprises an
alkyl, aryl, or alkylaryl group (preferably up to 8 carbons). Also, R¹ can be connected
to R² to form a cyclic poloyoxyalkylene secondary amine, e.g. morpholine. R³ and R⁴
independently represented hydrogen or C₁-C₂₀ alkyl, cycloalkyl group, or aryl group
(e.g., benzyl amine). R¹, R², R³, or R⁴ may also contain other functional groups.

Hydrogenation of the sugar amine adducts may also be done to stabilize the
compounds as well as to improve their dispersing performance. Hydrogenation can
be done simultaneously with amine adduct formation with or without a catalyst. The
derived hydrogenated sugar-amine adducts can be represented by the general
formulae:

\[
\begin{align*}
&\text{(AO)}_n R^1 \\
&/ \\
&[G^3]_g - \text{CH}_2 - N \\
&\backslash \\
&\text{(AO)}_p R^2 \\
&\text{R}^3 \\
&/ \\
&[G^3]_g - \text{CH}_2 - N \\
&\backslash \\
&\text{R}^4
\end{align*}
\]

\[(5) \text{ or } (6)\]

wherein G³ represents a monomeric sugar residue after amination followed by
hydration; AO represents an alkoxy group, and preferably a C₂-C₃ ethylene
oxide/propylene oxide group; “n” and “p” are integers whereby the sum of “n” and
“p” are from 1 to 100, and “n” or “p” individually are integers of from 0 – 100; and R¹
and R² each represents hydrogen or a substituted or unsubstituted C₁-C₈ alkyl, aryl, or
alkylaryl group; and, if “n” = 0, then the corresponding R¹ comprises an alkyl, aryl, or
alkyaryl group (preferably up to 8 carbons). Also, R¹ can be connected to R² to form a
cyclic poloyoxyalkylene secondary amine, e.g. morpholine. R³ and R⁴ independently
represented hydrogen or C₁-C₂₀ alkyl, cycloalkyl group, or aryl group (e.g., benzyl
amine). R¹, R², R³, or R⁴ may also contain other functional groups.
Cements and cement compositions of the invention comprise a mixture of a hydratable cement, or other cementitious binder, and from 0.001 to 5.0 weight percent based on the weight of the hydratable cement of the above-described sugar-amine derivative compound. More preferably, the amount of the sugar-amine derivative compound in the cement or cement composition is 0.0005 to 0.5 weight percent based on the weight of the hydratable cement or cementitious binder.

Without being confined by theoretical speculation, the inventors proffer herein their belief that, for cementitious compositions, the exemplary \([G]_k[X]_l[Q]_q\) compounds provide a particle attachment group (e.g., the sugar residue component \(G\) connected by an intervening linking group \(X\) to a non-sugar substituent component \(Q\) to provide steric hindrance and/or repulsion for enhancing the dispersion ability of the compounds and providing a beneficial adsorption rate relative to the cement particles being attached and dispersed within the aqueous matrix of a cementitious slurry. It is believed that such compounds described herein become uniformly dispersed throughout cementitious compositions, such as mortar or concrete, before being attached by, or entirely adsorbed onto, the cement.

The present invention also provides novel processes for making compounds of the present invention, such as a sugar amide derivatives, useful for modifying hydratable compositions (e.g., mortar, concrete) and non-hydratable particle-containing compositions alike.

As shown in Fig. 3, an exemplary process for producing a sugar amide derivative involves combining an amine component 10, a derivative of a sugar 12, and optionally a solvent 14 in a mix tank 20 to initiate a reaction wherein the amine component 10 and sugar derivative are linked by means of an amide bond.

After the product is formed, it must then be separated or removed from the solvent, which acts to provide sufficient contact between the two reactants to facilitate formation of sugar amide derivative product, which is designated as at 22 in the solvent removed from mix tank 20.

The amine component 10 can comprise a wide variety of primary alkyl amines, secondary alkyl amines, or aromatic amines. The amine may be added at about a 1:1 molar ratio to the sugar derivative component 12. A small excess of the amine (e.g., 3 mol %) may be added to drive the reaction to completion. Amines of
particular interest include primary and secondary amines as well as primary or secondary amines containing functional groups.

The sugar derivative component 12 may consist of an acid derivative of a sugar or its salt or lactone (e.g., glucono-delta lactone). The solvent acts to provide adequate contact between the two reactants for the reaction to occur.

The solvent 14 may be preferably selected so that it is miscible with the amine component 10. Dissolution of the sugar derivative 12, although not believed to be essential for product formation, may be advantageous in increasing the rate of reaction. Further, it may be advantageous in some isolation schemes if the nature of the solvent is such that, under reaction conditions, the reaction product is soluble in the solvent, but upon cooling (to room temperature or below) the product may precipitate or crystallize from the reaction solvent. Sufficient quantities of solvent 14 should be used to dissolve completely the amine component 10, and to dissolve or wet the sugar derivative 12. Solvents that are contemplated for use include alcohols and other polar organic solvents (such as chlorinated hydrocarbons, ethers, amides, nitriles), aromatic hydrocarbons, tertiary amines (e.g., triethylamine, triethanolamine, methylthiethanolamine, trisopropanolamine, etc.), and the amine that is used as a reactant (e.g., as incorporated in the amine component 10). Methanol is most a preferred solvent in terms of facilitating the reaction. However, other solvents are also suitable and may facilitate the isolation step, as further discussed below.

The mixing step (as designated at 20) may be conducted using at room temperature, or, more preferably, at slightly higher temperatures and/or atmospheric pressures. It is believed that the reaction itself gives rise to a temperature increase within the mixing tank 20 because the reaction is exothermic in nature. This may advantageously increase the rate of reaction/production. In some cases, gentle heating may be applied to increase the rate (e.g., in mix tank 20). It is contemplated that the reaction may be run using refluxing methanol, although this is not essential for the reaction to occur.

Product isolation, such as the drying step, designated as at 28 in Fig. 3, will be the step having the largest effect on the process scheme. As shown in Fig. 3, the isolation of product 30 occurs by driving off the residual solvent, such as by using any known direct or indirect heating methods, and then applying a vacuum and/or sweep
gas (designated as at 29) to remove solvent and obtain the separated dry reaction product 30. Preferably, the solvent would then be condensed 32, and possibly purified 34 such as through distillation, filtration through activated carbon, or other known methods, before being returned to a solvent recovery tank 14 which is also used as a feed into the mixing tank 20. Off gases 35 from the condensor 32 are preferably recovered (e.g., scrubbed) and reused, as well, in the process. Solvent selection in this case is dictated by the ability of the process to evaporate off readily the residual material. Solvents of interest can include lower molecular weight alkyl alcohols, and in particular methanol, as mentioned above.

Another exemplary process for product isolation is shown in Fig. 4 wherein, after the reaction is initiated in the mixing tank 20, the sugar amide derivative reaction product-in-solvent is then crystallized, preferably in a separate tank as shown at 26, and optionally but preferably by using conventional cooling means in the separate crystallization tank 26 (or alternatively through cooling coils (designated at 24)). The crystallized or precipitated reaction product can then be filtered 27 from the bulk of the solvent, which can be returned to the solvent tank 14, preferably after purification 34. Filtration can be accomplished by a wide range of approaches, such as batch cake filtering (e.g., pressure leaf or nutsche filters), continuous cake filtering (e.g., disk or horizontal vacuum filters), or centrifugation filtering (e.g., basket, peeler, or pusher). The resulting cake can undergo further drying using the standard approaches described above. Filtered solvent 27 can then be purified 34 such as by filtration using activated carbon, and reused in the process (by feeding back to the solvent tank 14). The residual solvent remaining with the filtered reaction product is subjected to the drying step 28, wherein the residual solvent may be driven off by direct or indirect heating 28 to obtain the separated reaction product 30. A sweep gas, vacuum, or both 29 can be used to facilitate removal of the residual solvent, which then can be condensed 32, optionally purified 34 (as described above), and returned to the solvent tank 14 for reuse in the process. Off gas 35 may be recovered (e.g., scrubbed using condensers) and reused in the process as well.

The crystallization approach provides advantages including significant reduction of the quantity of solvent condensed from the carrier stream. The number of solvent return steps illustrated for example in Fig. 4 illustrates this advantage. Solvent
selection is important since the product should be soluble at reaction temperatures, but the reaction product is preferably nearly insoluble at the crystallization temperatures. Isopropanol and methanol are particularly useful solvents, providing nearly complete recovery of the product at ambient temperatures (e.g., about 70° Fahrenheit).

Thus, an exemplary process for making a sugar amide derivative of the present invention comprises: introducing into a mix tank a sugar derivative, an amine, and a solvent to form a reaction mixture; forming a sugar amide reaction product; and separating said sugar amide reaction product from said reaction mixture solvent. The sugar derivative may, for example, comprise a sugar acid derivative of a sugar or its salt or its lactone. The amine component may comprise a primary amine, a secondary amine, or mixture thereof comprising a group selected from an aromatic, hydroxy, etheric, halogen, unsaturated alkyl, carbonyl, ester, amino, nitro, carboxylic, nitrilo, thio, or sulfone functional group. In exemplary processes, the solvent may comprise an alcohol, polar organic solvent (e.g., a chlorinated hydrocarbon, ether, amide, nitrile, or mixture thereof), aromatic hydrocarbon, an amine (e.g., preferably a tertiary amine, or mixture thereof. The mix tank 20, moreover, may comprise a batch mix tank, wherein a valve and/or pipe is opened after reaction is substantially completed (and/or periodically) whereby reaction-product/solvent (22) can be conveyed to the drying step 28; and the mix tank 20 may also be a continuous in-line tank, from the bottom of which the crystallized or precipitated reaction product is flowed in solvent to the drying step 28 on a continuous basis.

The drying of the sugar amide reaction product, shown at 28, may be accomplished, as aforesaid, by heating (e.g., direct heat source applied such as by thermal energy, or by exposure to heated pipes), but it is advisable that sugar amide derivative not be charred by overheating or unnecessarily high thermal energy. In further exemplary processes, the solvent is removed from sugar amide reaction product by flowing a gas through said reaction mixture, and/or by applying a vacuum.

In further exemplary processes of the invention, a cooling step 24 is preferably employed, after mixing together the amine 10, sugar derivative 12, and solvent 14, to crystallize or precipitate a reaction product. This facilitates the subsequent filtering of the reaction mixture solvent to separate the sugar amide reaction product from the solvent.
Another exemplary process of the invention for manufacturing a sugar amide derivative involves the use of water to extract the product from the solvent. As diagrammatically illustrated in Fig. 5, the amine component 10, sugar derivative component 12, and solvent 14 are mixed together 20, and the resultant reaction product in solvent are fed to an extraction column or vessel 40. In the extraction column 40, the solvent containing reaction product is contacted with water which is flowed into the column 40 such that the reaction product flows in a direction that is counter-current to the direction of water flow. The reaction product may be removed as an aqueous product 44 from the bottom of the extraction column 40, and the solvent is then collected at the top of the extraction column 40 and returned, after optional purification step 34, to the solvent recovery tank 14 for reuse in the process.

The solvent 14 used in the reaction step 20 must be immiscible in water to enable the extraction to work. A suitable solvent for this purpose is toluene. Other exemplary solvents that are also believed to be suitable include anisole, benzene, acetonitrile, xylene, and methyl butyl ether (preferably methyl-t-butyl ether).

One important consideration in the exemplary extraction approach illustrated in Fig. 5 is that residual amine may degrade the reaction product in the presence of water. This may be overcome by adding a buffer, with the water 42 introduced into the extraction column 40, to control the pH. Examples of buffers and pH modifiers include conventional (commercially available buffer solutions), ionic polymers, acetic acid, hydrochloric acid, nitric acid, mineral and carboxylic acids, ammonium chloride, or a mixture thereof.

A still further process for manufacturing a sugar amide derivative involves solvent replacement distillation. As with the extraction process, the solvent replacement distillation process, as seen in Fig. 6, provides the advantage of eliminating solids handling and the need to condense solvent from a carrier stream. As illustrated in Fig. 6, the solvent 14 and amine component 10 are combined with the sugar derivative component 12 in the mixing tank 20, which in this case is a batch vessel. After the reaction is complete, solvent is replaced with water 42, preferably along with a pH buffer, that is introduced continuously or in one dose directly into the mix tank 20 containing the solvent and reaction product. Solvent is driven off by heating, such as by employing a distillation column 50 connected to the mix tank 20,
and is separated from the water using batch distillation. The reaction product is then
recovered as an aqueous product 30. Solvent which travels through the distillation
column 50 is condensed using a condensor apparatus 32 and may be refluxed in the
column 50. Ultimately, recovered solvent may optionally (and preferably) undergo
purification using activated carbon or other filtration methods before being reused in
future batches. Solvent selection is important because the separation from water must
be nearly complete for reuse in subsequent reactions. A solvent such as methanol is
preferred since it does not form an azeotrope with water. Other alcohols can be
utilized, but the reaction rate is inhibited because a small amount of water tends to be
recycled with the solvent.

As in the extraction process, an important consideration in the solvent
replacement approach is that residual amine will degrade the product in the presence
of water and also high temperatures. This can be overcome by adding a buffer with
the water to control the pH, as previously mentioned. Alternatively, drawing a
vacuum over the mixing tank (to lower the pressure) also helps to reduce degradation
since the operating temperature decreases.

Another exemplary solvent replacement process is illustrated by diagram in
Fig. 7. In this case, a continuous reactor (e.g., an in-line, continually stirred mix tank
22 is used for reacting continuously fed amine component 10, sugar derivative
component 12, and solvent 14 together. The reaction product in solvent (20) is
continuously fed to a distillation column 50 where water 42 replaces the solvent. The
water 42 (optionally with one or more pH buffers) is introduced at or near the bottom
of the distillation column 50 where a heating element or "reboiler" 52 is used to heat
the distillation column. The water functions to replace the solvent, and the reaction
product is removed in an aqueous form. The solvent is then condensed using a
condenser 32 and optionally purified 34, using activated carbon filtration for example,
and then solvent (with any unreacted amine) is recovered 14 and may be reused in the
process. This approach (Fig. 7) has an additional advantage over the batch process (as
shown in Fig. 6) since residual amine is removed before combining with significant
amounts of water. This reduces degradation and may eliminate the need for a buffer
or vacuum operation.
The aforementioned compounds of the invention may be combined with conventional admixtures, such as alkoxylated polycarboxylates (such as “comb” type polymers used as water reducers or superplasticizers; e.g., superplasticizers commercially available from Grace Construction Products, Cambridge, Massachusetts, under the tradename “ADVA®”), naphthalene sulfonate formaldehyde condensate, melamine sulfonate formaldehyde condensate, calcium or sodium lignosulfonate, alkali or alkaline earth metal nitrates or nitrate (e.g., calcium nitrite and/or calcium nitrate such as commercially available from Grace Construction Products under the tradename “DCI®,” sodium nitrite and/or sodium nitrate, potassium nitrite and/or nitrate, etc.); or shrinkage-reduction admixtures such as those containing alkyl ether oxyalkylene adducts and/or oxyalkylene glycols (e.g., such as commercially available from Grace Construction Products under the tradename “ECLIPSE®”).

The following examples may further enhance an appreciation of the advantages or features of the present invention.

**Example 1**

Preparation of \(N\)-methoxypropyl gluconamide

Twenty grams of an aqueous solution of gluconic acid (50 wt%; obtained from Aldrich Chemical)(51mM) and 4.54 grams (51mM) of methoxypropylamine (available as “MOPA” from Huntsman Chemical) are mixed in a four-neck flask fitted with a mechanical stirrer, a DEAN-STARK™ trap with condenser, a dry nitrogen inlet, and a thermocouple at room temperature. The homogeneous mixture was then heated to 145°C under slow continuous flow of nitrogen. The solvent water was removed during the heating process. The reaction mixture continued to be stirred for two hours after the temperature reached 145°C. A viscous syrup, dark brown to black in color, was obtained. The product was dissolved to give 10% aqueous solution. The resultant solution pH was 4-6.
Example 2
Preparation of \(N\)-methoxy oxypropylene-2-propyl gluconamide

The procedure of example 1 was followed except that the amine used was 7.49 grams (51mM) of methoxy oxypropylene-2-propanamine (available from Huntsman Chemical). The resultant solution pH was 4-6.

Example 3
Preparation of \(N\)-polyoxyalkyl (MW=715) gluconamide

The procedure of example 1 was followed except that the amine used was 35.7 grams (51mM) of a monomethoxypolyalkyleneoxidemonoamine available from Huntsman Chemical under the tradename JEFFAMINE® M715 (MW=ca. 715, EO/PO molar ratio = 13/2). The resultant solution pH was 5-6.

Example 4
Preparation of \(N\)-polyoxyalkyl (MW=2000) gluconamide

The procedure of example 1 was followed except that the amine used was 102 grams (51mM) of monomethoxypolyalkyleneoxidemonoamine available from Huntsman under the tradename JEFFAMINE® M2070 (MW=ca. 2000, EO/PO molar ratio = 32/10). The resultant solution pH was 4-6.

Example 5
Preparation of \(N\)-polyoxyalkyl (MW=3000) gluconamide

The procedure of example 1 was followed except that the amine used was 153 grams (51mM) of monomethoxypolyalkyleneoxidemonoamine available from BASF under the tradename POLYETHERAMINE M3000 (MW=ca. 3000, EO/PO weight ratio = 0.85). The resultant solution pH was 4-6.

Example 6
Preparation of \(N\)-2-hydroxyethyl gluconamide (Gluconic acid/ethanolamine)

A 6.1 g (100 mM) sample of ethanolamine was dissolved in about 250 mL of toluene in a round-bottomed flask fitted with mechanical stirrer and a DEAN-STARK™ trap with condenser. A 39.2 g sample of the aqueous solution of gluconic acid (50 wt.%(100 mM) was added. The mixture was then heated to reflux until
water ceased to be evolved. The toluene was removed by decanting. The residue, a sticky, brown solid, was dissolved in water. The product was dissolved to give 48% aqueous solution. The resultant solution pH was 4.7.

**Example 7**
Preparation of N-methoxypropyl heptogluconamide (Sodium glucoheptonate/MOPA)

An 8.9 g (100 mM) sample of methoxypropylamine (MOPA, Huntsman Chemical) was dissolved in about 250 mL of toluene in a round-bottomed flask fitted with mechanical stirrer and a DEAN-STARK™ trap with condenser. A 8.3 mL (100mM) sample of hydrochloric acid (12.1M) was added with stirring. A 75.2 g sample of the aqueous solution of sodium glucoheptonate (50wt%)(100 mM) was added. The mixture was then heated to reflux until water ceased to be evolved. The toluene was removed by decanting. The residue, a sticky, brown solid, was dissolved in water. The product was dissolved to give 45% aqueous solution. The resultant solution pH was 4.7.

**Example 8**
Preparation of N-hexyl gluconamide (delta-gluconolactone/hexylamine)

A 6 gram (33.7 mM, Aldrich Chemical Company) sample of delta-gluconolactone was dissolved in 115 mL of refluxing methanol in a round-bottomed flask with magnetic stirrer and reflux condenser. A 3.5 gram sample of hexylamine (33.7 mM, Aldrich Chemical Company) was added and the mixture was allowed reflux with stirring for 90 minutes. The reaction mixture was cooled to room temperature and the solvent was removed by rotary evaporation. The product, a white, crystalline solid, was recrystallized in a solution of methanol: tetrahydrofuran. The product was dissolved in water to give 1 % aqueous solution. The solution pH was 7-9.

**Example 9**
Preparation of N-butyl gluconamide (a-gluconolactone/butylamine)

A 10.0 gram (56.2 mM, Aldrich Chemical Company) sample of a-gluconolactone was dissolved in 200 mL of refluxing methanol in a round-bottomed flask with magnetic stirrer and reflux condenser. A 4.10 gram sample of butylamine (56.2 mM, Aldrich Chemical Company) was added and the mixture was allowed reflux with stirring for 90 minutes. The reaction mixture was cooled to room
temperature and the solvent was removed by rotary evaporation. The product was a white crystalline solid. The product was dissolved in water to give 10% aqueous solution. The solution pH was 4-6.

**Example 10**
**Mortar Testing Procedure**

The mortar mix containing 760 g of Ordinary Portland Cement (Type I) with 1575 g of sand (SSD condition of masonry sand, SG = 2.65), and 334 g of water was formulated. Admixture dosage is reported as a percentage (by wt. of cement). The mortar was mixed for 5 minutes using a HOBART™ mixer, then slump, slump-flow, and air content were measured. Slump was measured by placing the mortar mix into a slump cone and casting a cone-shaped sample on a table, removing the cone, and then measuring the drop in height of the cone-shaped sample. The cone size used was in accordance with Japanese Industrial Standard (JIS) A1173 (cone height = 150 mm; upper diameter = 50 mm; bottom diameter = 100 mm). At the same time, slump-flow (diameter of spread) was measured. Air content was measured in accordance with ASTM C185. After the test, the mortar mix was used for the measurement of setting time. Setting time was measured with an automatic penetrometer developed by W. R Grace & Co.-Conn. so that the measured setting time is equal to the initial set time defined by ASTM C 403/C403M-95.

Results are provided below in Tables 1-4 below and Figures 1 & 2. In Figure 1, the fluidity performance (flow (mm)) of Examples 1 and 5 is compared, as a function of dosage, to that of gluconic acid. In Figure 2, the set retarding performance in terms of set time (hrs) as a function of dosage is shown for Examples 1, 5, and unmodified gluconic acid.

**Table 1**
*Mortar testing results (1)*

<table>
<thead>
<tr>
<th>#</th>
<th>SAMPLE</th>
<th>Dosage (%/c)</th>
<th>Slump (mm)</th>
<th>Flow (mm)</th>
<th>Air (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Blank</td>
<td>0</td>
<td>72</td>
<td>124</td>
<td>2.7</td>
</tr>
<tr>
<td>6</td>
<td>Gluconic acid</td>
<td>0.12</td>
<td>104</td>
<td>166</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>Example 2</td>
<td>0.12</td>
<td>113</td>
<td>182</td>
<td>2.2</td>
</tr>
<tr>
<td>4</td>
<td>Example 3</td>
<td>0.12</td>
<td>118</td>
<td>200</td>
<td>1.9</td>
</tr>
<tr>
<td>9</td>
<td>Example 1</td>
<td>0.12</td>
<td>115</td>
<td>191</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Table 2
Mortar testing results (2)

<table>
<thead>
<tr>
<th>ADMIXTURE</th>
<th>Dosage (%s/c)</th>
<th>Slump (mm)</th>
<th>Flow (mm)</th>
<th>Air %</th>
<th>Set time hrs/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>n/a</td>
<td>89</td>
<td>138</td>
<td>2.5</td>
<td>5h08m</td>
</tr>
<tr>
<td>Gluconic acid</td>
<td>0.12</td>
<td>118</td>
<td>222</td>
<td>1.0</td>
<td>18h00m</td>
</tr>
<tr>
<td>Example 2</td>
<td>0.12</td>
<td>116</td>
<td>198</td>
<td>2.4</td>
<td>7h40m</td>
</tr>
<tr>
<td>Example 3</td>
<td>0.12</td>
<td>118</td>
<td>208</td>
<td>1.6</td>
<td>6h03m</td>
</tr>
</tbody>
</table>

Table 3
Mortar testing results (3)

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Dosage (%s/c)</th>
<th>Slump (mm)</th>
<th>Flow (mm)</th>
<th>Air (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>n/a</td>
<td>87</td>
<td>131</td>
<td>2.7</td>
</tr>
<tr>
<td>Gluconic acid</td>
<td>0.12</td>
<td>112</td>
<td>187</td>
<td>2.3</td>
</tr>
<tr>
<td>Example 2</td>
<td>0.12</td>
<td>118</td>
<td>207</td>
<td>2.1</td>
</tr>
<tr>
<td>Example 4</td>
<td>0.12</td>
<td>114</td>
<td>195</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 4
Mortar testing results (4)

<table>
<thead>
<tr>
<th>ADMIXTURE</th>
<th>Dosage (%s/c)</th>
<th>Slump (mm)</th>
<th>Flow (mm)</th>
<th>Air (%)</th>
<th>Set time hrs/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>N/a</td>
<td>81</td>
<td>141</td>
<td>3.2</td>
<td>3h27m</td>
</tr>
<tr>
<td>Gluconic acid</td>
<td>0.04</td>
<td>82</td>
<td>143</td>
<td>3.4</td>
<td>4h23m</td>
</tr>
<tr>
<td>Example 8</td>
<td>0.04</td>
<td>116</td>
<td>201</td>
<td>3.3</td>
<td>5h51m</td>
</tr>
<tr>
<td>Example 9</td>
<td>0.04</td>
<td>110</td>
<td>188</td>
<td>3.4</td>
<td>5h08m</td>
</tr>
</tbody>
</table>

Example 11
Concrete Testing Procedure

The concrete test was carried out using the following mix design units are provided in pounds per cubic yard, lbs/cyd) (Table 5). 30 liters of concrete was mixed with a drum mixer for 9 minutes. Admixture was added to concrete with mixing water. Admixture dosage is reported as a percentage (by wt. of cement).
Table 5
Concrete Test Mix Design

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Cement</th>
<th>Sand</th>
<th>Stone</th>
<th>W/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain</td>
<td>307</td>
<td>517</td>
<td>1418</td>
<td>1653</td>
<td>0.594</td>
</tr>
<tr>
<td>Concrete Test</td>
<td>290</td>
<td>517</td>
<td>1418</td>
<td>1700</td>
<td>0.591</td>
</tr>
</tbody>
</table>

The test results are shown in Table 6 below. For a given dosage, the gluconamide or glucoheptonamide showed less retardation than gluconic acid and equivalent or improved slump.

Table 6
Concrete Test results

<table>
<thead>
<tr>
<th>Exp</th>
<th>Admix</th>
<th>Dosage (%)</th>
<th>Slump (inches)</th>
<th>Air (%)</th>
<th>Initial Set Time (hrs/mins)</th>
<th>Final Set Time (hrs/mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>0</td>
<td>7.00</td>
<td>1.9</td>
<td>4h 12m</td>
<td>5h 50m</td>
</tr>
<tr>
<td></td>
<td>Ca-lignin</td>
<td>0.22</td>
<td>6.75</td>
<td>1.4</td>
<td>7h 09m</td>
<td>8h 48m</td>
</tr>
<tr>
<td></td>
<td>Gluconic Acid</td>
<td>0.11</td>
<td>7.50</td>
<td>1.0</td>
<td>10h 13m</td>
<td>12h 15m</td>
</tr>
<tr>
<td></td>
<td>Example 3</td>
<td>0.11</td>
<td>7.00</td>
<td>1.3</td>
<td>6h 50m</td>
<td>7h 33m</td>
</tr>
<tr>
<td>2</td>
<td>None</td>
<td>0</td>
<td>7.50</td>
<td>1.9</td>
<td>4h 16m</td>
<td>6h 00m</td>
</tr>
<tr>
<td></td>
<td>Ca-lignin</td>
<td>0.22</td>
<td>8.00</td>
<td>1.5</td>
<td>7h 03m</td>
<td>8h 54m</td>
</tr>
<tr>
<td></td>
<td>Gluconic Acid</td>
<td>0.10</td>
<td>8.00</td>
<td>1.4</td>
<td>9h 20m</td>
<td>11h 32m</td>
</tr>
<tr>
<td></td>
<td>Example 1</td>
<td>0.10</td>
<td>7.50</td>
<td>1.8</td>
<td>6h 47m</td>
<td>8h 38m</td>
</tr>
<tr>
<td></td>
<td>Example 2</td>
<td>0.10</td>
<td>8.00</td>
<td>1.6</td>
<td>6h 45m</td>
<td>8h 38m</td>
</tr>
<tr>
<td>3</td>
<td>None</td>
<td>0</td>
<td>6.00</td>
<td>2.6</td>
<td>4h 18m</td>
<td>6h 21m</td>
</tr>
<tr>
<td></td>
<td>Ca-lignin</td>
<td>0.20</td>
<td>7.00</td>
<td>2.5</td>
<td>6h 10m</td>
<td>8h 30m</td>
</tr>
<tr>
<td></td>
<td>Example 1</td>
<td>0.10</td>
<td>8.00</td>
<td>2.5</td>
<td>7h 03m</td>
<td>9h 04m</td>
</tr>
<tr>
<td></td>
<td>Example 2</td>
<td>0.10</td>
<td>7.00</td>
<td>2.7</td>
<td>6h 18m</td>
<td>8h 07m</td>
</tr>
<tr>
<td></td>
<td>Example 5</td>
<td>0.10</td>
<td>7.25</td>
<td>2.1</td>
<td>7h 27m</td>
<td>9h 03m</td>
</tr>
<tr>
<td></td>
<td>Example 6</td>
<td>0.10</td>
<td>7.00</td>
<td>2.5</td>
<td>6h 13m</td>
<td>8h 05m</td>
</tr>
<tr>
<td>4</td>
<td>None</td>
<td>0</td>
<td>5.00</td>
<td>2.8</td>
<td>3h 52m</td>
<td>5h 39m</td>
</tr>
<tr>
<td></td>
<td>Ca-lignin</td>
<td>0.20</td>
<td>7.00</td>
<td>2.5</td>
<td>6h 24m</td>
<td>8h 12m</td>
</tr>
<tr>
<td></td>
<td>Example 1</td>
<td>0.08</td>
<td>7.00</td>
<td>3.4</td>
<td>6h 18m</td>
<td>7h 35m</td>
</tr>
<tr>
<td></td>
<td>Example 5</td>
<td>0.08</td>
<td>7.00</td>
<td>3.1</td>
<td>6h 41m</td>
<td>8h 33m</td>
</tr>
</tbody>
</table>
Example 12
Preparation of N-polyoxalkyl (MW=700) - glucamine

A 10 gram sample of glucose was dissolved in 10 grams of water in a four-neck flask fitted with a mechanical stirrer, a DEAN-STARK™ trap with condenser, and a dry nitrogen inlet at 60 to 80°C. A homogenous syrup was obtained in less than 20 min. To the syrup, 0.19 mL of 5N HCl aqueous solution were added followed by the addition of 38 grams (mM) of a monomethoxypolyalkyleneoxidemonoamine available from Huntsman Chemical under the tradename JEFFAMINE® M715 (MW=ca. 715, EO/PO molar ratio = 13/2). The homogeneous mixture was then heated in an oil bath at 110°C for 3 hours under slow continuous flow of nitrogen. The color of the homogenous mixture quickly turned into yellow to greenish, and then a dark yellow color was obtained. The mortar testing results of the material appear in Table 7 along with that of D-glucose. The mortar testing procedure was the same as is described in Example 10.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dose (%)</th>
<th>Slump (mm)</th>
<th>Flow (mm)</th>
<th>Air (%)</th>
<th>Initial/Finish Set Time (hours minutes/hours minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Mix</td>
<td>Na</td>
<td>88</td>
<td>155</td>
<td>2.8</td>
<td>4h 08m / 5h 47m</td>
</tr>
<tr>
<td>D-Glucose</td>
<td>0.10</td>
<td>62</td>
<td>123</td>
<td>3.6</td>
<td>&gt;8:00</td>
</tr>
<tr>
<td>Example 12</td>
<td>0.10</td>
<td>105</td>
<td>185</td>
<td>3.4</td>
<td>5h 10m / 6h 39m</td>
</tr>
</tbody>
</table>

Example 13
Preparation of glucose - ethanolamine adduct

A 20 gram sample of glucose (111 mM), 6.78 grams of ethanolamine (111 mM), 6.67 grams of acetic acid (111 mM), and 2.5 grams of water were fused in a four-neck flask that had been fitted with a mechanical stirrer, a DEAN-STARK™ trap with condenser, and a dry nitrogen inlet at 60 to 80°C. The homogeneous mixture was then heated in an oil bath at 110°C for 30 min. under slow continuous flow of nitrogen. The pressure in the flask was then reduced to 35 - 50 mm Hg for 40 min. to
remove water. The very viscous black syrup was obtained. The mortar testing results of the material are shown in Table 8 along with that for D-glucose. The mortar testing procedure is the same as is described in Example 10.

**Example 14**

*Preparation of glucose-ethanolamine adduct hydrogenated*

A 20.0 gram sample of glucose (111 mM) was dissolved in 20 grams of water in a four-neck flask that was fitted with a mechanical stirrer, a DEAN-STARK™ trap with condenser, and a dry nitrogen inlet at 60°C. A 0.19 mL aliquot of 5N HCl aqueous solution are added. After 15 min., 6.97 grams (114 mM) of monoethanolamine was added to the flask. The temperature was kept at 80°C for 1 hour 30 min. The flask was taken out from the oil bath and cooled down to 30 - 40°C. A 2.1 grams of NaBH₄ was dissolved in 30 mL of methanol, and the solution was added to the flask drop-wise so that the temperature was kept below 50°C (took 30 to 45 min.). The flask was then placed in the oil bath at 80°C for 1 hour. Methanol was removed by reducing the pressure. Dark red to black colored viscous syrup was obtained. The mortar testing results of the material is shown in Table 8.

**TABLE 8**

*Mortar test result (6)*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dose (mm)</th>
<th>Slump (mm)</th>
<th>Flow (mm)</th>
<th>Air (%)</th>
<th>Set Time (hrs min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Mix</td>
<td>Na</td>
<td>63</td>
<td>121</td>
<td>2.9</td>
<td>4h 52m</td>
</tr>
<tr>
<td>D-Glucose</td>
<td>0.10</td>
<td>45</td>
<td>110</td>
<td>3.2</td>
<td>8h 00m</td>
</tr>
<tr>
<td>Example 14</td>
<td>0.10</td>
<td>94</td>
<td>162</td>
<td>2.9</td>
<td>5h 25m</td>
</tr>
<tr>
<td>Example 154</td>
<td>0.10</td>
<td>100</td>
<td>172</td>
<td>2.4</td>
<td>5h 29m</td>
</tr>
</tbody>
</table>

**Example 15**

*Preparation of glucose - hexylamine adduct*

A 9.0 gram sample of glucose (50 mM) was fused with 3.0 grams of acetic acid (50 mM), and 2.0 grams of water in a four-neck flask fitted with a mechanical stirrer, a DEAN-STARK™ trap with condenser, and a dry nitrogen inlet at 60 to 80°C. A 5.06 grams of hexylamine (50 mM) was slowly added with 7 mL of methanol. The temperature was held at 65 - 68°C for 2 hours under a slow continuous nitrogen flow. Methanol was removed by rotary evaporation. A viscous, black syrup
was obtained. The mortar testing procedure is the same as is described in Example 10.

**Example 16**

*Preparation of corn syrup ethanolamine adduct*

A 54 gram sample of corn syrup (dextrose equivalence 35%) was placed in a four-neck flask that was fitted with a mechanical stirrer, a DEAN-STARK™ trap with condenser, and a dry nitrogen inlet. The temperature was raised to 80°C and a 0.38 mL aliquot of 5N HCl aqueous solution were added to the syrup. 7.0 grams of monoethanolamine was then slowly added to the flask. The solution was continued to stirred for another 1 hour under slow nitrogen flow. A viscous, black syrup was obtained. The mortar testing results of the material are shown in Table 9 along with that from corn syrup. The mortar testing procedure is the same as is described in Example 10.

**TABLE 9**

*Mortar result (7)*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dose (%)</th>
<th>Slump (mm)</th>
<th>Flow (mm)</th>
<th>Air (%)</th>
<th>Set Time hrs min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn Syrup (DE* = 35%)</td>
<td>0.10</td>
<td>93</td>
<td>155</td>
<td>1.9</td>
<td>9h 13m</td>
</tr>
<tr>
<td>Example 16</td>
<td>0.10</td>
<td>98</td>
<td>162</td>
<td>2.5</td>
<td>7h 35m</td>
</tr>
</tbody>
</table>

* dextrose equivalence

**Example 17**

*Preparation of corn syrup ethanolamine adduct hydrogenated*

A 36.6 gram sample of corn syrup (dextrose equivalence of 62%), 6.4 grams of monoethanolamine was placed in a four-neck flask that was fitted with a mechanical stirrer, a DEAN-STARK™ trap with condenser, and a dry nitrogen inlet. The solution was mixed at room temperature for 20 min. A 1.99 grams of NaBH₄ was dissolved in 30 mL of methanol, and the solution was added to the flask drop-wise over the period of 45 min. The temperature was about 35°C. The flask was then place in the oil bath at 60°C for another 1 hour. The flask was taken out from the bath and 40 mL of water were added. A transparent, golden-colored solution was obtained. The mortar testing results of the material are shown in Table 10 along with
that of corn syrup (dextrose equivalence of 35%). The mortar testing procedure is the same as is described in Example 10.

**Table 10**

**Mortar result (8)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dose (%)</th>
<th>Slump (mm)</th>
<th>Flow (mm)</th>
<th>Air (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Mix</td>
<td>NA</td>
<td>81</td>
<td>147</td>
<td>2.9</td>
</tr>
<tr>
<td>Corn Syrup (DE*=35%)</td>
<td>0.10</td>
<td>90</td>
<td>160</td>
<td>1.9</td>
</tr>
<tr>
<td>Example 17</td>
<td>0.10</td>
<td>96</td>
<td>172</td>
<td>1.9</td>
</tr>
</tbody>
</table>

* dextrose equivalence

**Example 18**

*Use of hexyl gluconamide as a grinding aid for cement*

A 3325 g sample of cement clinker from Scancem (SiO₂ 21.62 %; Al₂O₃ 3.42 %; Fe₂O₃ 3.00 %; CaO 65.15 %; MgO 2.64 %; SO₃ 1.49 %; Na₂O 0.23 %; K₂O 1.21 %; TiO₂ 0.19 %; P₂O₅ 0.04 %; Mn₂O₃ 0.05 %; SrO 0.03 %; L.O.I. (950 °C) 0.31 %; C3S 69; C2S 10 C3A 4; C4AF 9) was blended with 175 g of Terra Alba gypsum and 2.8 g of hexyl gluconamide. The materials were put in a rotating ball mill and ground. The blaine surface area (BSA) was measured periodically as described by ASTM C 204. This process was repeated for a control sample.

**Table 11**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grinding time (hr:min)</th>
<th>Final BSA (m²/kg)</th>
<th>grinding efficiency (BSA/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>3:15</td>
<td>382</td>
<td>2.0</td>
</tr>
<tr>
<td>Example 18</td>
<td>2:40</td>
<td>401</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The flow of mortar (6% water cut) was tested. The mortar testing procedure is the same as described in Example 10. The 3 day strength of cured samples of this mortar were tested according to the procedure put forward in ASTM C 109.
Table 12
Mortar result

<table>
<thead>
<tr>
<th>Sample</th>
<th>Strength (Mpa)</th>
<th>Flow (mm)</th>
<th>Air (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Mix</td>
<td>38.4</td>
<td>122</td>
<td>2.3</td>
</tr>
<tr>
<td>Example 18</td>
<td>65.9</td>
<td>199</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Example 19
Calcium carbonate sedimentation experiment

A sedimentation experiment was conducted wherein a dilute suspension of calcium carbonate powder (about .079 volume percent fraction) was made. (CaCO₃ powder from Aldrich, 10 micron ave. diameter). A small dosage of N-pentyl gluconamide (preparation was analogous to that of Example 9) was dosed into the suspension (0.75-1.60 % by wt based on calcium carbonate powder). The suspension was treated by ultrasonic exposure for precisely 5 minutes and then dispersed again by agitation. The suspension was then quickly transferred to a capped volumetric cylinder and left to stand for the sedimentation observation. The volume of the sediment was measured after 20 minutes, and the powder volume fraction in the sediment was calculated. The higher powder volume fraction in the sediment indicated that the sediment was more compact, suggesting better dispersion of the powder.

The sedimentation results are shown in Table 13 below. N-Pentyl gluconamide had higher powder volume fraction in the final sediment, which indicated that the compound had the ability to disperse the powder.

Table 13
Calcium Carbonate Powder sedimentation

<table>
<thead>
<tr>
<th></th>
<th>Blank</th>
<th>Example ## gluconamide</th>
<th>Example ## gluconamide</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃ (grams)</td>
<td>3.00</td>
<td>2.99</td>
<td>3.00</td>
</tr>
<tr>
<td>Dosage applied (solid wt%)</td>
<td>NA</td>
<td>1.60%</td>
<td>0.75%</td>
</tr>
<tr>
<td>Total Water (grams)</td>
<td>12.01</td>
<td>12.00</td>
<td>12.02</td>
</tr>
<tr>
<td>Initial Powder Volume Fraction in the Suspension (cc/cc)</td>
<td>0.0786</td>
<td>0.0784</td>
<td>0.0785</td>
</tr>
<tr>
<td>Final Powder Volume Fraction in the Sediment (cc/cc)</td>
<td>0.2067</td>
<td>0.2528</td>
<td>0.2661</td>
</tr>
</tbody>
</table>
Example 20

Preparation of butyl N-methyl glucamide

To a dry round bottom flask charged with 3.85 g of NaHCO₃ and a magnetic
stir bar was added 100 ml of anhydrous THF and 5 ml of butyric anhydride. N-methyl
glucamine (6 g) was added in small portions as solid. The mixture was stirred for
extra five minutes after the addition was completed. Dropwise addition of 1 ml of
methanol resulted in heavy white precipitate. The mixture was stirred for 2 h.
Additional ethanol (30 ml) was added and the mixture was stirred for 30 min. The
white solid was filtered off. The clear filtrate was concentrated on a rotovap. Acetone
(15 ml) was added to the clear liquid. The solution was heated gently which leads to
sudden formation of white precipitate. The white solid was washed with acetone
dried under vacuum.

Table 14

<table>
<thead>
<tr>
<th></th>
<th>Dose (%)</th>
<th>Slump (mm)</th>
<th>Flow (mm)</th>
<th>Air (%)</th>
<th>Set time (hr min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Mix</td>
<td>NA</td>
<td>81</td>
<td>147</td>
<td>2.9</td>
<td>4 h 36 m</td>
</tr>
<tr>
<td>Example 20</td>
<td>0.04</td>
<td>98</td>
<td>171</td>
<td>1.5</td>
<td>4 h 40 m</td>
</tr>
</tbody>
</table>

The foregoing examples are provided for illustration only and are not intended
to limit the scope of the invention.
We claim:

1. A composition comprising: a plurality of particles to be dispersed and a compound for dispersing said plurality of particles, said compound comprising (A) at least one residue of sugar or sugar derivative; (B) at least one non-sugar substituent; and (C) a linking group comprising an amide, amine, imide, urea, or mixture thereof, for linking the sugar residue of component (A) to the non-sugar substituent of component (B).

2. The composition of claim 1 wherein said plurality of particles to be dispersed comprises at least one hydratable binder.

3. The composition of claim 2 wherein said hydratable binder comprises Portland cement, limestone, hydrated lime, fly ash, blast furnace slag, pozzolans, silica fume, or a mixture thereof.

4. The composition of claim 3 wherein said binder comprises Portland cement.

5. The composition of claim 4 wherein said composition, in addition to comprising Portland cement, further comprises a hydratable binder selected from limestone, hydrated lime, fly ash, blast furnace slag, pozzolans, silica fume.

6. The composition of claim 2 wherein said plurality of particles to be dispersed comprises a non-hydratable mineral.

7. The composition of claim 1 wherein, in said compound, said sugar residue of said compound is derived from a hydroxycarboxylic acid or its salt.

8. The composition of claim 1 wherein, in said compound, said sugar residue is derived from a sugar comprising an aldonic acid or its lactone or salt; an aldaric acid or its lactone or salt; a uronic acid or its lactone or salt; an aldose; a ketose; or mixture thereof.

9. The composition of claim 8 wherein, in said compound, said sugar residue is derived from an aldonic acid selected from gluconic acid (or its salts or lactones), heptogluconic acid (or its salts or lactones), or mixture thereof.
10. The composition of claim 8 wherein, in said compound, said sugar residue is derived from an aldaric acid selected from glucaric acid or its lactone or salt, heptoglucaric acid or its lactone or salt, or mixture thereof.

11. The composition of claim 8 wherein, in said compound, said sugar residue is derived from a uronic acid selected from glucuronic acid or its lactone or salt, heptoglucuronic acid or its lactone or salt.

12. The composition of claim 9 wherein, in said compound, said sugar residue is derived from an aldose or ketose sugar selected from a glucose sugar, an aldohexose sugar, a sucrose sugar, a tetrose sugar, a pentose sugar, or mixture thereof.

13. The composition of claim 8 wherein, in said compound, said sugar residue is derived from corn syrup, molasses, or their oxidized forms.

14. The composition of claim 8 wherein, in said compound, said sugar residue is derived from a polyhydroxy alcohol selected from glucitol, sorbitol, mannitol, reduced corn syrup, or mixture thereof.

15. The composition of claim 1 wherein, in said compound, said non-sugar substituent is substituted or nonsubstituted.

16. The composition of claim 15 wherein, in said compound, said non-sugar substituent comprises at least one alkyl having attached thereto an oxyalkylene group, hydroxy group, amino acid group, sulfonate group, phosphonate group, or mixture thereof.

17. The composition of claim 1 wherein, in said compound, said sugar residue is a C₅-C₇ sugar acid derivative; said linking group is an amide; and said non-sugar substituent is at least one (AO)ₙ-R¹ oxyalkylene group wherein AO represents a C₂-C₃ alkoxy group, R¹ represents hydrogen or a C₁-C₃ alkyl group; and “n” represents an integer from 1 to 100.

18. The composition of claim 1 wherein, in said compound, said non-sugar substituent comprises at least two alkyl, aryl, or alkyaryl groups connected to said linking group.

19. The composition of claim 18 wherein, in said non-sugar substituents, said at least two alkyl, aryl, or alkyaryl groups are connected to said linking group by at least one oxyalkylene group.
20. The composition of claim 19 wherein each of said at least one oxyalkylene group comprises ethylene oxide and propylene oxide groups.

21. The composition of claim 1 wherein said compound has the structural formula

\[ [G]_g[X]_x[Q]_q \]

wherein \( G \) represents at least one residue of sugar or sugar derivative; “\( g \)” is an integer of from 1 to 100; \( X \) represents a linking group selected from amide, amine, imide, urea, or mixture thereof; “\( x \)” is an integer of from 1 to 100; \( Q \) represents a non-sugar substituent group selected from an alkyl, aryl or alkylaryl group, an oxyalkylene oligomer or polymer group, a polyoxyalkylene oligomer or polymer group, or mixture thereof; and “\( q \)” is an integer of from 1 to 100.

22. The composition of claim 21 wherein, in said compound, “\( g \)” is from 1 to 50; \( X \) is an amide; “\( x \)” is equal to or less than “\( q \)” ; \( Q \) represents a non-sugar substituent group selected from an alkyl group having one \( C_1-C_8 \) substituted or unsubstituted alkyl group per sugar residue, or aryl or alkylaryl group having one \( C_1-C_8 \) aryl or alkylaryl substituted or unsubstituted groups per sugar residue, or an oxyalkylene or polyoxyalkylene oligomer or polymer group having repeating ethylene oxide and propylene oxide groups, wherein the number of repeating units is 2-200; and “\( q \)” is an integer of from 1 to 100.

23. The composition of claim 1 wherein said compound can be represented by the general formula:

\[
\begin{align*}
\text{O} & \quad (AO)_nR^1 \\
\text{\|} & \quad / \\
[G']_s - C - N & \quad \text{\|} \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\end{align*}
\]

(1) or

\[
\begin{align*}
\text{O} & \quad (AO)_nR^2 \\
\text{\|} & \quad / \\
[G']_s - C - N & \quad \text{\|} \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\text{\|} & \quad / \\
\end{align*}
\]

(2)

35

-36-
wherein G\(^1\) represents a monomeric sugar residue after amidation wherein sugar acids are reacted with a non-sugar amine, and G\(^1\) is linear or cyclic in form; AO represents a C\(_2\)-C\(_4\) alkoxy; R\(^1\) and R\(^2\) independently represent hydrogen or a C\(_1\)-C\(_8\) alkyl group; “n” and “p” each independently represent an integer from 0 to 100; and the sum of “n” and “p” is an integer from 1 to 100, and R\(^3\) and R\(^4\) independently represent hydrogen or C\(_1\)-C\(_8\) alkyl group, a alkylaryl group, or an aryl ring.

24. The composition of claim 23 wherein, in said compound, said C\(_2\)-C\(_4\) alkoxy group comprises ethylene oxide and propylene oxide groups.

25. The composition of claim 24 wherein at least one of said R\(^1\), R\(^2\), R\(^3\), and R\(^4\) groups contains at least one substituted group.

26. The composition of claim 21 wherein, in said compound, said “[G]” comprises a derivative of a C\(_3\)-C\(_7\) sugar acid or its salt; X is an amine; and Q comprises at least one (AO)\(_n\)-R oxyalkylene group wherein AO represents a C\(_2\)-C\(_3\) alkoxy group, R represents hydrogen or a C\(_1\)-C\(_3\) alkyl group or C\(_7\)-C\(_{20}\) aryl group; and “n” represents an integer from 1 to 100.

27. The composition of claim 1 wherein said composition is in the form of a dry powder.

28. The composition of claim 1 wherein said binder is cement and said composition further comprises a fine aggregate.

29. The composition of claim 28 wherein said composition further comprises a coarse aggregate.

30. The composition of claim 1 further comprising water.

31. A process for modifying a particle-containing composition comprising combining said particles with a compound comprising (A) at least one residue of sugar or sugar derivative; (B) at least one non-sugar substituent; and (C) a linking group comprising an amide, amine, imide, urea, or mixture thereof, for linking the sugar residue of component (A) to the non-sugar substituent of component (B).

32. The process of claim 31 wherein, in said compound, said at least one non-sugar substituent comprises a group having the formula (AO)\(_n\)-R wherein AO represents a C\(_2\)-C\(_3\) alkoxy group, and R represents hydrogen or a C\(_1\)-C\(_3\) alkyl group; and n represents an integer from 1 to 100.
33. The process of claim 31 wherein said particles are cement, and said compound is combined with said cement during the manufacture of said cement or after the manufacture of said cement.

34. The process of claim 33 wherein said compound is combined with said cement in an amount of 0.005 to 0.5 weight percent, based on the weight of said cement.

35. A process for manufacturing a compound for dispersing particles in an aqueous environment comprising reacting a residue of a sugar with an amine or diamine to provide a compound comprising (A) at least one residue of sugar or sugar derivative; (B) at least one non-sugar substituent; and (C) a linking group comprising an amide, amine, imide, urea, or mixture thereof, for linking the sugar residue of component (A) to the non-sugar substituent of component (B).

36. A process for making a sugar amide derivative, comprising: introducing into a mix tank a sugar derivative, an amine, and a solvent to form a reaction mixture; forming a sugar amide reaction product; and separating said sugar amide reaction product from said reaction mixture solvent.

37. The process of claim 36 wherein said sugar derivative comprises a sugar acid derivative of a sugar or its salt or its lactone.

38. The process of claim 36 wherein said amine comprises a primary amine, a secondary amine, or mixture thereof.

39. The process of claim 36 wherein said amine is substituted with a group selected from an aromatic, hydroxy, etheric, halogen, unsaturated alkyl, carbonyl, ester, amino, nitro, carboxylic, nitrilo, thio, or sulfone functional group.

40. The process of claim 36 wherein said solvent comprises an alcohol, polar organic solvent, aromatic hydrocarbon, an amine, or mixture thereof.

41. The process of claim 36 wherein said solvent comprises a polar organic solvent is chlorinated hydrocarbon, ether, amide, nitrile, or mixture thereof.

42. The process of claim 40 wherein said solvent comprises an amine solvent having a tertiary amine.

43. The process of claim 36 wherein said mix tank is a batch mix tank or in-line tank.

44. The process of claim 43 wherein said mix tank is an in-line tank.
45. The process of claim 36 wherein said separating step is accomplished by evaporating said reaction mixture solvent.

46. The process of claim 36 wherein said separating step is accomplished by heating said reaction mixture to a temperature below the char temperature of said sugar amide derivative.

47. The process of claim 36 further comprising decreasing pressure above said reaction mixture whereby solvent is removed from said sugar amide reaction product.

48. The process of claim 36 further comprising removing solvent from said sugar amide reaction product by flowing a gas over or through said reaction mixture.

49. The process of claim 36 wherein, in said separating step, said sugar amide reaction product forms a precipitate.

50. The process of claim 36 comprising chilling of said sugar amide reaction product in said reaction mixture solvent to precipitate said reaction product from said reaction mixture solvent.

51. The process of claim 36 further comprising filtering said reaction mixture solvent to remove said sugar amide reaction product.

52. The process of claim 36 wherein said separating step comprises extracting said reaction product from solvent using water.

53. The process of claim 47 wherein said separating step includes the steps of flowing said sugar amide reaction product and solvent in a first flow direction and flowing water in a second flow direction that is counter-current to said first flow direction.

54. The process of claim 36 wherein said solvent comprises toluene, anisole, benzene, acetonitrile, xylene, a methyl butyl ether, or mixture thereof.

55. The process of claim 54 wherein said solvent comprises toluene or xylene or xylenes.

56. The process of claim 36 further comprises flowing a water and at least one buffer in a second flow direction counter-current to said first flow direction.

57. The process of claim 36 wherein, after said step of forming a sugar amide reaction product, said step of separating said sugar amide reaction product from said reaction mixture solvent comprises replacing solvent with water.
58. The process of claim 36 wherein said step of replacing solvent with water occurs by introducing water into said mix tank, removing sugar amide reaction product in an aqueous form from said mix tank, and employing a distillation column connected to said mix tank.

59. The process of claim 58 further comprising condensing and refluxing solvent after distillation.

60. The process of claim 59 further comprising returning distilled solvent to said mixing tank.

61. The process of claim 36 wherein said solvent replacing step includes the steps of providing a continuous in-line mixing tank for combining said amine component, said sugar derivative component, and solvent together to obtain a sugar amide reaction product in solvent; and flowing said reaction product in solvent to a distillation column.

62. The process of claim 57 further comprising heating water to create a vapor within said distillation column.

63. The process of claim 57 wherein solvent is separated from said reaction product and reused in said solvent replacing step.

64. The process of claim 36 wherein a solvent is employed comprising an amine.

65. A compound for modifying a particle containing composition, said compound comprising: (A) at least one residue of sugar or sugar derivative; (B) at least one non-sugar substituent; and (C) a linking group comprising an amide, amine, imide, urea, or mixture thereof, for linking the sugar residue of component (A) to the non-sugar substituent of component (B).

66. The compound of claim 65 wherein said at least one non-sugar substituent comprises an oxyalkylene or polyoxyalkylene oligimer or polymer group (e.g., preferably having repeating C$_2$–C$_4$ oxyalkylene groups, or, more preferably, repeating ethylene oxide and propylene oxide groups, wherein the number of repeating units is 2-200).

67. A method of dispersing nonhydratable solids in an aqueous system comprising introducing to said nonhydratable solids a compound comprising: (A) at least one residue of sugar or sugar derivative; (B) at least one non-sugar substituent;
and (C) a linking group comprising an amide, amine, imide, urea, or mixture thereof, for linking the sugar residue of component (A) to the non-sugar substituent of component (B).
Fig. 1

Fig. 2
Fig. 7
A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : B01F 17/56; C04B 24/12
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)
U.S. : 516/88, 203, 914, 915; 252/363.5; 106/707, 708, 709, 710, 714, 725, 727, 790, 795, 804, 217.9, 162.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 5,565,420 A [STEARNS] 15 October 1996, see column 4, lines 50+, examples 1 and 20</td>
<td>1, 7-12, 14-16, 18, 19, 21, 22, 27, 30, 31 and 35</td>
</tr>
</tbody>
</table>

Date of the actual completion of the international search: 30 MARCH 2000
Date of mailing of the international search report: 24 APR 2000

* 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 document 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

"I"*": 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

"M"*: document member of the same patent family

Authorized officer: [Signature]
Telephone No.: (703) 308-0661
A. CLASSIFICATION OF SUBJECT MATTER:
US CL:

516/88, 203, 914, 915; 252/363.5; 106/707, 708, 709, 710, 714, 725, 727, 790, 795, 804, 217.9, 162.1