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(54) Titre : DEMOUSSEURS SOLUBILISES POUR COMPOSITIONS A BASE DE CIMENT
(54) Title: SOLUBILIZED DEFOAMERS FOR CEMENTITIOUS COMPOSITIONS

(57) Abrégé/Abstract:
Solubilizing agents are mixed with water-insoluble defoamers and a dispersant for cementitious compositions to provide an admixture for cementitious compositions that is stable over time. Suitable solubilizing agents include alkoxylated moieties or particles. A cementitious composition is provided that includes cement, water, a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent that solubilizes the water-insoluble defoamer. A method is provided for making a cementitious composition that includes mixing cement, water, a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent that solubilizes the water-insoluble defoamer.
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SOLUBILIZED DEFOAMERS FOR CEMENTITIOUS COMPOSITIONS

FIELD OF THE INVENTION

The present invention is directed to a combination of solubilizing agents and defoamers that are used in conjunction with a dispersant for cementitious compositions to control air contents in cementitious compositions. Particularly, the present invention is directed to a combination of solubilizing agents with water-insoluble defoamers that are used in conjunction with dispersant for cementitious compositions to control air contents in cementitious compositions.

BACKGROUND OF THE INVENTION

Hydraulic cements, such as Portland cement, are used to form structural formations. Hydraulic cements can be mixed with aggregate to form mortars, or with coarse aggregate to form concretes.

When working with hydraulic cements, it is desired to increase the slump properties of the initially-formed hydraulic cement composition to aid in placement of the composition and to extend the period of flowability in order to provide working time to finish the placement of the structure. Admixtures can be added to hydraulic cement which increase the slump. Additionally, admixtures can be added which also reduce the amount of water required to produce flowable cementitious compositions. The reduced water content increases the strength of the resulting hydraulic cement formation.

One type of admixture for increasing the flowability and reducing the water content is a polycarboxylate dispersant. Polycarboxylate dispersants are polymers with a carbon backbone with pendant side chains, wherein at least a portion of the side chains are attached to the backbone through a carboxyl group or an ether group. Polycarboxylate dispersants are very effective at dispersing and reducing the water content in hydraulic cements.
One drawback of polycarboxylate dispersants is that they have a tendency to entrain air in the cementitious composition during mixing. While some entrained air may be desired for particular applications, such as providing freeze-thaw durability to the cement, an excess of entrained air is detrimental to the compressive strength of the resulting hydraulic formation.

Generally in the construction industry, non-air-entrained cementitious compositions having an air content of less than 3% is desired, with an air content of less than 2% being preferred. Air-entraining admixtures are sometimes used to provide air contents of 5-8% which improves the freeze-thaw durability of the cementitious mixture. When this is the case, it is desirable to be able to adjust the air content by changing the air entrainer dosage and to have the resulting air remain stable over time.

To overcome the excess entraining of air in cementitious compositions, defoamers have been added to the cementitious mix to reduce the air content to a desired level. Defoamers typically have been included with the polycarboxylate admixture. However, the defoamers used in the prior art have been non-water-soluble compositions used alone. The problem with non-water-soluble defoamers is that they give an inadequate long term storage stability to the admixture, resulting in phase separation. The polycarboxylate dispersant is generally a water-soluble dispersant. When a non-water-soluble defoamer is used in conjunction with a water-soluble dispersant, the mixture separates over time. This requires that the mixture be mixed prior to use. In addition, some insoluble defoamers can cause unpredictable air contents over time.

Commercial defoamers typically contain a mixture of materials. The major part is an oil or organic liquid (up to 95 parts by weight), small particulate (up to 15 parts by weight), and a surfactant (up to 5 parts by weight).

Another technique used in the prior art has been the grafting of the defoamer on to the dispersant molecule.
The prior art, however, has not shown the combination of a defoamer that is not chemically combined with the polycarboxylate dispersant that is used in conjunction with a solubilizing agent.

What is needed in the industry is a combination of a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent that solubilizes the water-insoluble defoamer that produces controllable air contents in non-air entrained and air-entrained cementitious compositions.

It is therefore an object of the invention to provide a combination of a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent that solubilizes the water-insoluble defoamer that produces controllable air contents in non-air-entrained and air-entrained cementitious compositions.

It is another object of the invention to provide an admixture containing a dispersant for cementitious compositions, a solubilizing agent, and a water-insoluble defoamer that is stable over time.

**SUMMARY OF THE INVENTION**

Solubilizing agents can be combined with water-insoluble defoamers and dispersants for cementitious compositions to provide an admixture for cementitious compositions that is stable over time. The resulting admixture has long-term storage stability, so that the admixture does not need to be mixed prior to use at the work site.

The present invention provides an admixture for cementitious compositions comprising a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent that solubilizes the water-insoluble defoamer.

The present invention also provides a cementitious composition comprising cement, water, a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent that solubilizes the water-insoluble defoamer.
The present invention also provides a method of making a cementitious composition comprising mixing cement, water, a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent that solubilizes the water-insoluble defoamer.

In one particular embodiment the dispersant is a polycarboxylate dispersant and the solubilizing agent is present in an amount from 0.25 wt.% to 40 wt.% based on the weight of the polycarboxylate dispersant to form a stable microemulsion having a particle size of 0.01 to 0.05 μm.

DETAILED DESCRIPTION OF THE INVENTION

The “term solubilizing agent” refers to a material that can solubilize insoluble material. Solubilization is defined as a mode of bringing into solution substances that are otherwise insoluble in a given medium. Solubilization involves the previous presence of a colloidal (organized) solution whose particles take up and incorporate within or upon themselves the otherwise insoluble material. (M.E.L. McBain and E. Hutchinson, Solubilization and Related Phenomena, Academic Press, New York (1955). Generally, a solubilizing agent is a solubilizing surfactant.

The term “dispersant for cementitious compositions” throughout this specification includes polycarboxylate dispersants and oligomeric dispersants.

The term “polycarboxylate dispersant” throughout this specification refers to polymers with a carbon backbone with pendant side chains, wherein at least a portion of the side chains are attached to the backbone through a carboxyl group or an ether group. The term dispersant is also meant to include those chemicals which also function as a plasticizer, water reducer, fluidizer, antiflocculating agent, or superplasticizer for cementitious compositions.

A number of different polycarboxylate dispersants are useful in the working of this invention. Examples of suitable dispersants may be found in United States Patents 5,158,996, 5,494,516, 5,612,396, 5,162,402, 5,660,626, 6,063,184, 5,668,195 and 5,798,425, and European Patent Application 0 753 488.

A preferred example of a polycarboxylate dispersant is a polymer comprising units derived from at least a substituted carboxylic acid monomer or substituted
ethylenically-unsaturated monomer, and optionally including at least one of an unsaturated hydrocarbon, an N-polyoxyalkylene maleimide, and a condensation product of an unsubstituted carboxylic acid monomer and an alkoxypolyoxyalkylene primary amine-substituted carboxylic acid monomer. The polycarboxylate dispersant preferably has the general structure shown below:

where:

- **D** = a component selected from the group consisting of the structure d1, the structure d2, and mixtures thereof;
- **X** = H, CH$_3$, C$_2$ to C$_6$ alkyl, phenyl, substituted phenyl such as p-methyl phenyl, sulfonated phenyl;
- **Y** = H, -COOM;
- **R** = H, CH$_3$;
- **Z** = H, -SO$_3$M, -PO$_3$M, -COOM, -OR$_3$, -COOR$_3$, -CH$_2$OR$_3$, -CONHR$_3$, -CONHC(CH$_3$)$_2$ CH$_2$SO$_3$M, -COO(CHR$_4$)$_n$OH where n=2 to 6;
- **R$_1$, R$_2$, R$_3$, R$_5$** are each independently -(CH$_2$CHRO)$_m$R$_4$ random copolymer of oxyethylene units and oxypropylene units where m=10 to 500 and wherein the amount of oxyethylene in the random copolymer is from 60% to 100% and the amount of oxypropylene in the random copolymer is from 0% to 40%;
- **R$_4$** = H, methyl, C$_2$ to C$_6$ alkyl, C$_6$ to C$_{10}$ aryl;
M = H, alkali metal, alkaline earth metal, ammonia, amine, substituted amine such as triethanolamine, methyl, C₂ to C₆ alkyl;

a = 0 to 0.8, preferably 0 to 0.6, and most preferably 0 to 0.5;

b = 0.2 to 1.0, preferably 0.3 to 1.0, and most preferably 0.4 to 1.0;

c = 0 to 0.5, preferably 0 to 0.3, and most preferably 0 to 0.1;

d = 0 to 0.5, preferably 0 to 0.3, and most preferably 0 to 0.1; and

wherein a, b, c, and d represent the mole fraction of each unit and the sum of a, b, c, and d is 1.0.

Representative monomers for the "a" component include, but are not limited to, styrene, ethylene, propylene, or sulfonated styrene. Representative monomers for the "b" component include, but are not limited to, acrylic acid, methacrylic acid, alkyl esters of acrylic acid, alkyl esters of methacrylic acid, alkoxypolyoxyalkylene esters of acrylic acid, aryloxypolyoxyalkylene esters of acrylic acid, alkoxypolyoxyalkylene esters of methacrylic acid, aryloxypolyoxyalkylene esters of methacrylic acid, maleic acid, maleic anhydride, vinyl sulfonic acid, methoxypolyoxyalkylene vinyl ether, methoxypolyoxyalkylene allyl ether, alkoxypolyoxyalkylene vinyl ether, aryloxypolyoxyalkylene vinyl ether, or aryloxypolyoxyalkylene allyl ether.

Components "c" and "d" can be formed from a post-reaction from the grafting of the side chains on to the polymer backbone such as a polyacrylate maleic anhydride copolymer. The reaction to form component "c" and/or "d" is related to the temperature of the grafting reaction. If the temperature is high enough, the imide components "c" and "d" are formed. Component "c" is formed from a single monomer which is a component "b" with Y being COOH and Z being CONHR₃. A condensation reaction occurs wherein water condenses and the ring closes to form component "c".

Component "d" is formed by a condensation of two monomers such as acrylic acid (component "b" with Y being COOH and Z being H) and an acrylic acid derivatized with an alkoxypolyoxyalkylene primary amine, that is a component "b" with Y being H and Z being CONHR₃. A condensation reaction occurs wherein water
condenses and the ring closes to form component "d1" or "d2". Component "d2" is formed by a head-to-head reaction of the two monomers. Component "d1" is formed by a head-to-tail reaction of the two monomers.

Component “b” can also be maleic anhydride when Y and Z are selected to be -COOH in the anhydride form.

The term “oligomeric dispersant” throughout this specification refers to oligomers that are a reaction product of a component A, optionally component B, and component C;

wherein each component A is independently a nonpolymeric, functional moiety that adsorbs on to a cementitious particle, and contains at least one residue derived from a first component selected from the group consisting of phosphates, phosphonates, phosphinites, hypophosphites, sulfates, sulfonates, sulfinites, alkyl trialkoxy silanes, alkyl triacyloxy silanes, alkyl triaryloxy silanes, borates, boronates, boroxines, phosphoramides, amines, amides, quaternary ammonium groups, carboxylic acids, carboxylic acid esters, alcohols, carbohydrates, phosphate esters of sugars, borate esters of sugars, sulfate esters of sugars, salts of any of the preceding moieties, and mixtures thereof;

wherein component B is an optional moiety, where if present, each component B is independently a nonpolymeric moiety that is disposed between the component A moiety and the component C moiety, and is derived from a second component selected from the group consisting of linear saturated hydrocarbons, linear unsaturated hydrocarbons, saturated branched hydrocarbons, unsaturated branched hydrocarbons, aryl, phosphoester, nitrogen-containing compounds, and mixtures thereof; and

wherein component C is at least one moiety that is a linear or branched water-soluble, nonionic polymer substantially non-adsorbing to cement particles, and is selected from the group consisting of poly(oxyalkylene glycol), poly(oxyalkylene amine), poly(oxyalkylene diamine), monoalkoxy poly(oxyalkylene amine), monoaryloxy poly(oxyalkylene amine), monoalkoxy poly(oxyalkylene glycol), monoaryloxy poly(oxyalkylene glycol) poly(vinyl
pyrrolidones), poly(methyl vinyl ethers), poly(ethylene imines), poly(acrylamides), polyoxazoles, and mixtures thereof.

Another preferred class of polycarboxylate polymer functioning as a polymer dispersant comprises a functionalized polyimide or polyamide main chain polymer on to which are grafted at least some proportion of oligomeric or polymeric hydrophilic side chains. The grafted side chains may include linking amides, esters, and thioesters. This polymer dispersant having a hydrophilic side chain substituted backbone has the general formula:

\[
\begin{align*}
\text{COOX} & \quad \text{O} \quad \text{C} \quad \text{Q} \quad (\text{R}_1) \quad \text{Y} \\
\text{(CH}_2\text{)}_{\text{m}} & \quad \text{(CH}_2\text{)}_{\text{m'}} & \quad \text{(CH}_2\text{)}_{\text{m}} & \quad \text{(CH}_2\text{)}_{\text{m'}} \\
\text{NH} & \quad \text{CH} & \quad \text{C} & \quad \text{NH} & \quad \text{CH} & \quad \text{C} & \quad \text{Z} \\
\end{align*}
\]

wherein \(X\) is at least one of hydrogen, an alkali earth metal ion, an alkaline earth metal ion, ammonium ion, and amine; \(R\) is at least one of \(C_1\) to \(C_6\) alkyl(ene) ether and mixtures thereof and \(C_1\) to \(C_6\) alkyl(ene) imine and mixtures thereof; \(Q\) is at least one of oxygen, nitrogen, and sulfur; \(p\) is a number from 1 to 300 resulting in at least one of a linear side chain and branched side chain; \(R_1\) is at least one of hydrogen, \(C_1\) to \(C_{20}\) hydrocarbon, and functionalized hydrocarbon containing at least one of -OH, -COOH, a derivative of -COOH, sulfonic acid, a derivative of sulfonic acid, amine, and epoxy; \(Y\) is a hydrophobic hydrocarbon or polyalkylene oxide moiety; \(m, m', m'', n, n'\) and \(n''\) are each independently 0 or an integer between 1 and 20; \(Z\) is a moiety containing at least one of i) at least one amine and one acid group, ii) two functional groups capable of being incorporated into the backbone selected from the group consisting of dianhydrides, dialdehydes, and di-acid chlorides, and iii) a succinimide residue; and wherein \(a, b, c\) and \(d\) reflect the mole fraction of each unit wherein the sum of \(a, b, c\) and \(d\) equals one, wherein \(a, b, c\) and \(d\) are each greater than or equal to zero and less than one, and at least two of \(a, b, c\) and \(d\) are greater than zero.
More particularly, Y is at least one of a hydrophobic polyalkylene glycol block polymer and a hydrophobic polyalkylene glycol random polymer; and Z is at least one of an imide moiety, a succinimide residue, the residue of a natural amino acid, a derived amino acid, H2N(CH2)kCOOH or a derivative thereof, the residue of aminobenzoic acid or a derivative thereof, the residue of H2N(CH2)kSO3H or a derivative thereof, and the residue of sulfanilic acid or a derivative thereof, where k is an integer between 1 and 20. Most preferably R1 is a C1 to C4 alkyl; and m, m', m", n, n' and n" are each independently an integer between 0 and 2.

In a preferred embodiment, the grafted polymer dispersant has the general formula:

\[
\begin{align*}
\text{COO} & \quad X_3 \\
\text{CH}_2 & \quad \text{CO} \\
\text{NH} & \quad \text{C} \\
\text{CH}_2 & \quad \text{O} \\
\text{NH} & \quad \text{C} \\
\text{C} & \quad \text{O} \\
\text{NH} & \quad \text{C} \\
\text{CH}_2 & \quad \text{O} \\
\text{CH}_2 & \quad \text{O} \\
\text{NH} & \quad \text{C} \\
\text{CH}_2 & \quad \text{O} \\
\text{CH}_2 & \quad \text{O} \\
\text{NH} & \quad \text{C} \\
\text{CH}_2 & \quad \text{O} \\
\end{align*}
\]

wherein a, b, c, d and g reflect the mole fraction of each unit wherein the sum of a, b, c, d, and g equal one, wherein a, b, c, d and g are each greater than or equal to zero and less than one, and at least two of a, b, c, and d are greater than zero; X3 is at least one of i) a moiety which will neutralize the negative charge on the carboxyl (COO⁻) ion, and ii) a hydrophobic hydrocarbon or polyalkylene oxide moiety, which if present, replaces no more than 20 mole% of X3. By way of example but not limitation, the neutralizing moiety can be an ammonium ion, ions of sodium, potassium, lithium, calcium, and the like. X2 is a hydrophilic side chain having the structure:

\[
\begin{align*}
\text{R}_2 \\
\text{CH} \\
\text{R}_5 \\
\text{O} \\
(R_3)_e \\
(R_4)_f \\
\text{CH}_3
\end{align*}
\]

wherein R2 is H, a C1 to C4 linear or branched alkyl, such as methyl, ethyl, propyl, or butyl, or phenyl; R5 is a C1 to C4 linear or branched alkyl, such as methylene, an alkylene, or phenylene; R3 is a residue derived from ethylene oxide, and R3 is present randomly or in block form; e is 1 to 300, preferably 11 to 300; R4 is a residue derived from propylene oxide, and R4 is present randomly or in block form; f is 0 to 180,
preferably with a mole ratio of R₃:R₄ of 100:0 to 40:60. Z is an imide group such as, but not limited to, a succinimide moiety. It is noted that the higher the proportion of propylene oxide present in the side chain, the less hydrophilic the side chain will be.

The a and c units of the preferred grafted polymer dispersant each represent an α-linkage and the b and d units each represent a β-linkage of the reacted unit of the reactant N-succinimide polymer. While it is possible to have 100% α or β, preferably the proportion of α to β linkage is 1:100 to 100:1.

The grafted polymer dispersant may contain an imide located at the point of attachment of the side chain with the polymer, or located in the backbone of the polymer. The grafted polymer dispersant has a molecular weight average of 1,000 to 1,000,000. More preferably, the grafted polymer dispersant has a molecular weight average of 2,000 to 100,000. Most preferably, the grafted polymer dispersant has a molecular weight average of 3,000 to 50,000. The units comprising the polymer may be present randomly or in block form. The polymer backbone is substantially linear, but could have slight branching, such as every 10th residue.

As used herein, the term “cement” refers to any hydraulic cement. Hydraulic cements are materials which set when mixed with water. Suitable examples of hydraulic cements include, but are not limited to, portland cement, masonry cement, alumina cement, refractory cement, magnesia cement, calcium sulfoaluminate cement, and mixtures thereof.

“Pastes” are defined as mixtures composed of a hydraulic cement binder, either alone or in combination with pozzolans such as fly ash, silica fume, or blast furnace slag, and water. Mortars are defined as pastes that additionally include fine aggregate. Concretes additionally include coarse aggregate.

A solubilizing agent can be combined with a water-insoluble defoamer and a dispersant for cementitious compositions to form an admixture for cementitious compositions. The combination of a solubilizing agent with a water-insoluble defoamer
and a dispersant for cementitious compositions provides an admixture that is stable over time in that there is little or no phase separation between the dispersant and defoamers.

Without being limited to theory, it is theorized that some combinations of a solubilizing agent with a water-insoluble defoamer form a microemulsion. A microemulsion is a single, thermodynamically stable, equilibrium phase; as compared to a macroemulsion, which is a dispersion of droplets that contain two or more phases, which are liquids or liquid crystals. (Smith, D. "Microemulsions", Kirk Othmer Encyclopedia of Chemical Technology, 4th ed 1999.) Emulsions typically are opaque, unstable, and macro-disperse systems of 0.5 to 10 micron droplet size. Microemulsions are typically transparent, oil-in-water systems stabilized by an interfacial layer of surfactants and have a particle size of 0.01 to 0.05 microns. The smaller particle size provides for the optical transparency. Further definition of microemulsions can be found in Microemulsions: Theory and Practice, by L.M. Prince, Academic Press, New York (1977).

Solubilizing agents can increase the total aqueous solubilization of oil in an aqueous phase. When a sufficient amount of solubilizer is present in a solution (reaching the critical micelle concentration), the solubilizer molecules aggregate into micelles. The micelle-water partition coefficient and the molar solubilization ratio can characterize the degree of solubility enhancement achieved by a solubilizing agent. The solubilization of the defoamer increases after the solubilizing agent reaches the critical micelle concentration. The defoamer diffuses through the aqueous phase to the micelles and dissolves in the core of the micelle. As more solubilizer is added, the shape of the micelles will change to cylinder form. As even more solubilizer is added, the shape will eventually change to lamellar. However, the number of micelles will remain about the same throughout these changes.

Solubilized refers to the aggregation or self-assembly micellization. Soluble refers to the interaction of an individual molecule with water.
Solubilizing agents according to the present invention preferably are at least partially effective themselves as defoamers for cementitious compositions.

The amount of the dispersant for cementitious compositions that is present in a cementitious mixture ranges from 0.01 wt.% to 2.0 wt.% based on the weight of cement. Preferably, the amount of dispersant for cementitious compositions that is present in a cementitious mixture ranges from 0.05 wt.% to 0.5 wt.% based on the weight of cement.

The amount of solubilizing agent that is present in the admixture is at least the amount sufficient to obtain a stable microemulsion. Preferably the amount of solubilizing agent that is present in the admixture is from 0.25 wt.% to 40 wt.% based on the weight of the polycarboxylate dispersant.

The amount of water-insoluble defoamer that is present in the admixture ranges from 0.01% to 25% based on the weight of the dispersant for cementitious compositions. Preferably, the amount of water-insoluble defoamer that is present in the admixture ranges from 0.25% to 10% based on the weight of the dispersant for cementitious compositions.

The ratio of insoluble defoamer to solubilizing agent ranges from an amount effective to solubilize the insoluble defoamer up to 100, preferably up to 0.27.

Examples of water-insoluble defoamers useful to control the air content in cementitious compositions include, but are not limited to, chemicals based on mineral or vegetable oils, fats and oils, fatty acids, fatty acid esters, any chemical with -OH (hydroxyl) functionality (such as alcohols, particularly fatty alcohols), amides, phosphoric esters, metal soaps, silicones, oxyalkylenes, polymers containing propylene oxide moieties, hydrocarbons, and acetylenic diol derivatives.

Suitable examples of the water-insoluble defoamers useful to control the air content in cementitious compositions include DYNOL™ 604, SURFYNOL® 440, nonyl phenol, castor oil, and polypropylene oxide.
Further examples of water-insoluble defoamers include the following: kerosene, liquid paraffin; animal oil, vegetable oil, sesame oil, castor oil, alkylene oxide adducts thereof; oleic acid, stearic acid and alkylene oxide adducts thereof; diethylene glycol laurate, glycerin monorecinolate, alkenyl succinic acid derivatives, sorbitol monolaurate, sorbitol trioleate, polyoxyethylene monolaurate, polyoxyethylene sorbitol monolaurate, natural wax; linear or branched fatty alcohol and alkoxylated derivatives thereof, acetylene alcohol, glycols, polyoxyalkylene glycol; polyoxyalkylene amide, acrylate polyamine; tributyl phosphate, sodium octyl phosphate; aluminum stearate, calcium oleate; silicone oil, silicone paste, silicone emulsion, organic-modified polysiloxane, fluorosilicone oil; and polyoxyethylene-polyoxypropylene adducts. To the extent that the defoamers in the preceding list contain alkylene oxides, reference is made to those that are water insoluble.

Examples of the solubilizing agent include, but are not limited to, compounds of alkoxylated R, carboxylated alkoxylated R, sulfated alkoxylated R, sulfonated alkoxylated R, styrene-maleic copolymer, and derivatized styrene-maleic copolymer, where R could be: a hydrocarbon, sorbitan, polypropylene oxide, fatty acid, fatty alcohol, isononanol, C₈-C₂₂ alkyl amine, styrene maleic copolymer, or derivatized styrene-maleic copolymer. The hydrocarbon preferably contains from 1 to 22 carbons, and the fatty acid and fatty alcohol preferably contain from 8 to 22 carbon atoms. Preferred alkoxylation are molecules containing ethylene oxide and/or propylene oxide. Most preferred alkoxylation are molecules containing ethylene oxide. The solubilizing agents can be used in combination with other solubilizing agents. Preferred derivatized groups for the derivatized styrene-maleic copolymers include, but are not limited to, sulfonated, hydroxy alkyl ester, and dimethyl amino propyl. A preferred derivatized styrene-maleic copolymer is alkoxylated styrene-maleic copolymer.

Preferred alkyl-ether sulfonates are given by the following formula: \( R_{1}-(O\text{CH}_{2}\text{CH}_{2})_{n}-\text{SO}_{3}\text{M} \), wherein \( R_{1} \) is an alkyl with 6 to 18 carbon atoms, and \( n \) is an integer from 1 to 15. Preferred alkyl-ether sulfonates are AVANEL™ products from BASF. AVANEL S-74 has \( R_{1} \) as \( \text{C}_{8} \) alkyl and \( n=3 \) in the above formula. AVANEL S-
70 has R₁ as C₁₂ alkyl and n=7. AVANEL S-150CG has R₁ as C₁₅ alkyl and n=15. AVANEL S-74 is most preferred.

Preferred alkyl-ether carboxylates are R₁O(CHR₂CH₂O)ₓCH₂CH₂COOM, wherein R₁ is a C₄-C₁₈ hydrocarbon, R₂=H or CH₃, n=1-30, m=H, Na, K, Li, Ca, Mg, amine, or ammonia. Preferred alkyl-ether carboxylates are available from Hickson DanChem under the trademark NEODOX.

Preferred styrene-maleic copolymers are given by the following formula:

```
    CH₂-CH
   [   ]

    CH-CH
   [   ]

    C=O C=O
   [   ]

    X X
   [   ]

    M M
   [   ]
```

wherein M is independently at least one of H, Na, K, Ca, Mg, alkyl, substituted alkyl, aryl, substituted aryl, or an oxyalkylene group (R₂O)ₓ-R₃, wherein R₂ is a C₂-C₄ alkylene group, such as ethylene, propylene, or butylene, and R₃ is H or C₁-C₂₂ alkyl group, alkyl-aryl group, or aryl group, and n=1-500. X can be -O- or -NHR₄. When X is -O-, an anhydride can be formed, and when X is -NHR₄, and imide ring. R₄ is H, alkyl, substituted alkyl, aryl, substituted aryl, or an oxyalkylene group (R₂O)ₓ-R₃. A preferred substituted alkyl is hydroxy ethyl and dimethyl amino propyl. A preferred substituted aryl is a residue derived from nonyl phenol. Preferably the molar ratio of styrene (a) to maleic (b) is greater than 1:1. More preferably, the styrene:maleic ratio is ≥ 2:1. Preferably, a and b are numbers such that the copolymer has a number average molecular weight from 1,000 to 20,000.

Specific examples of these types of solubilizing agents capable of controlling the air content in cementitious compositions are given below. Note, the amount of ethylene oxide should be selected so that the products referred to below are water-soluble.
PLURONIC® products (ex BASF) are block copolymers of ethylene oxide (EO) and propylene oxide (PO).

TERGITOL® NP, from Union Carbide Company, is a polymer of ethylene oxide and nonylphenol (ethoxylated nonylphenol).

JEFFFOX® products, from Huntsman Chemical Company, are mono alkyl polyoxyalkylenes. Preferred is a 50/50 ethylene oxide/propylene oxide random polymer with a mono-butyl terminal group

\[ \text{Bu-O-(PO)}_x(\text{EO})_x-H. \]


Generally, defoamers with an HLB up to 4 have strong defoaming properties. As the HLB value increases, the defoaming capabilities decrease and foaming abilities increase. In the present invention, the solubilizing agents generally have an HLB value ranging from 5 to 22.

Elevated temperature stability for any combination of insoluble defoamer and dispersant for cementitious compositions can be obtained by increasing the level of the
solubilizing agent. For example, depending upon the insoluble defoamer level and the effectiveness of the solubilizing agent, a temperature increase from 25°C to 45°C may possibly need a 10-20% increase in the amount of solubilizing agent to maintain a clear stable solution.

The admixture of the present invention can be used in combination with any other admixture or additive for cement. Other cement admixtures and additives include, but are not limited to, set retarders, set accelerators, air-entraining or air-detraining agents, corrosion inhibitors, any other dispersants for cement, pigments, wetting agents, water-soluble polymers, strength-enhancing agents, rheology-modifying agents, water repellents, and any other admixture or additive that does not adversely affect the properties of the admixture of the present invention.

A cementitious composition having controlled air content can be formed which comprises cement, water, a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent that solubilizes the water-insoluble defoamer. The cementitious composition can also include fine aggregates, coarse aggregates, pozzolans, air (either entrapped or deliberately entrained), clay, and pigments.

The fine aggregates are materials that pass through a Number 4 sieve (ASTM C125 and ASTM C33), such as natural or manufactured sand. The coarse aggregates are materials that are retained on a Number 4 sieve (ASTM C125 and ASTM C33), such as silica, quartz, crushed round marble, glass spheres, granite, limestone, calcite, feldspar, alluvial sands, or any other durable aggregate, and mixtures thereof.

A method of controlling air in a cementitious composition is also provided according to the present invention which comprises mixing cement, water, a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent that solubilizes the water-insoluble defoamer. Other admixtures and additives are added to the cement mixture at appropriate times prior or subsequent to the addition of the inventive admixture.
The amount of water added to the cementitious composition is calculated based on a desired water to cement (W/C) ratio. The water to cement ratio typically ranges from 0.2 to 0.7 with the water and cement being measured by weight.

5 SPECIFIC EMBODIMENTS OF THE INVENTION

Samples of microemulsion solutions and cementitious compositions were prepared using different insoluble defoamers, solubilizing agents, and a dispersant for cementitious compositions. The cementitious compositions additionally contained cement and aggregate. The dispersant for cementitious compositions used in the following examples was a polycarboxylate dispersant, which was a polymer with polymeric carboxylate backbone with polyether side chains.

The following tests were used: Slump (ASTM C143), and Air content (ASTM C231). Aggregates met the specifications of ASTM C33. The term W/C refers to the water to cement ratio in a cementitious mixture. The term S/A refers to the sand to aggregate ratio by volume.

In the following examples, insoluble defoamer A is a proprietary acetylenic glycol based defoamer sold as DYNOL™ 604 from Air Products and Chemicals. Insoluble defoamer B is a 40% ethylene oxide adduct to 2,4,7,9-tetramethyl-5 decyn-4,7-diol, which is sold as SURFYNOL® 440 from Air Products and Chemicals. Solubilizing agent C is an 85% ethylene oxide adduct to 2,4,7,9-tetramethyl-5 decyn-4,7-diol, which is sold as SURFYNOL® 485 from Air Products and Chemicals. Solubilizing agent D is a 65% ethylene oxide adduct to 2,4,7,9-tetramethyl-5 decyn-4,7-diol, which is sold as SURFYNOL® 465 from Air Products and Chemicals.

Solution Examples S-1 to S-5

Compositions comprising water, a polycarboxylate dispersant, insoluble defoamer A, and solubilizing agents C and D are shown below in Table 1. The amounts of the material are shown as percent by weight of the solution. The solutions were prepared initially by combining water, dispersant, and insoluble defoamer and then
stirring with a magnetic stir bar in a glass beaker. Because of the hydrophobicity of the insoluble defoamer, the resulting solutions were turbid and opaque. The solubilizing agents were then added slowly, with stirring, until the resulting solution was clear. Solutions S-3 and S-5 show a combination of solubilizing agents that differ in ethylene oxide content.

Solution Examples S-6 to S-9

Compositions comprising water, a polycarboxylate dispersant, insoluble defoamer B, and solubilizing agents C and D are shown below in Table 1. The amounts of the material are shown as percent by weight of the solution. The solutions were prepared the same as previously described.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Defoamer (%)</th>
<th>Solubilizing Agent (%)</th>
<th>Cement Dispersant (%)</th>
<th>Water (%)</th>
<th>Stability @ 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>20</td>
</tr>
<tr>
<td>S-1</td>
<td>0.200</td>
<td></td>
<td>1.360</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-2</td>
<td>0.200</td>
<td></td>
<td>3.320</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>S-3</td>
<td>0.200</td>
<td></td>
<td>1.000</td>
<td>0.424</td>
<td>20</td>
</tr>
<tr>
<td>S-4</td>
<td>0.400</td>
<td></td>
<td>1.600</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>S-5</td>
<td>0.400</td>
<td></td>
<td>0.866</td>
<td>0.984</td>
<td>20</td>
</tr>
<tr>
<td>S-6</td>
<td></td>
<td>0.215</td>
<td>2.866</td>
<td></td>
<td>21.5</td>
</tr>
<tr>
<td>S-7</td>
<td></td>
<td>0.215</td>
<td>0.516</td>
<td></td>
<td>21.5</td>
</tr>
<tr>
<td>S-8</td>
<td></td>
<td>0.645</td>
<td>1.511</td>
<td></td>
<td>21.5</td>
</tr>
<tr>
<td>S-9</td>
<td></td>
<td>0.860</td>
<td>2.098</td>
<td></td>
<td>21.5</td>
</tr>
</tbody>
</table>

Solution Examples S-10 to S-19

Compositions comprising various levels of insoluble defoamer A, solubilizing agent C, and polycarboxylate dispersant were prepared as above. The results are listed in Table 2, and the amounts of the material are shown as percent weight of the solution. The resulting solutions were then stored at 43°C for a minimum of five weeks where they remained as clear, stable solutions.
## TABLE 2

<table>
<thead>
<tr>
<th>Solution</th>
<th>Defoamer (%)</th>
<th>Solubilizing Agent (%)</th>
<th>Cement Dispersant (%)</th>
<th>Water (%)</th>
<th>Stability @ 25°C</th>
<th>Stability @ 43°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-10</td>
<td>0.480</td>
<td>2.160</td>
<td>24</td>
<td>73.360</td>
<td>Clear</td>
<td>Clear</td>
</tr>
<tr>
<td>S-11</td>
<td>0.560</td>
<td>2.800</td>
<td>28</td>
<td>68.640</td>
<td>Clear</td>
<td>Clear</td>
</tr>
<tr>
<td>S-12</td>
<td>0.600</td>
<td>3.000</td>
<td>30</td>
<td>66.400</td>
<td>Clear</td>
<td>Clear</td>
</tr>
<tr>
<td>S-13</td>
<td>0.840</td>
<td>3.696</td>
<td>28</td>
<td>67.464</td>
<td>Clear</td>
<td>Clear</td>
</tr>
<tr>
<td>S-14</td>
<td>0.960</td>
<td>7.200</td>
<td>24</td>
<td>67.840</td>
<td>Clear</td>
<td>Clear</td>
</tr>
<tr>
<td>S-15</td>
<td>1.120</td>
<td>5.320</td>
<td>28</td>
<td>65.560</td>
<td>Clear</td>
<td>Clear</td>
</tr>
<tr>
<td>S-16</td>
<td>1.280</td>
<td>5.760</td>
<td>32</td>
<td>60.960</td>
<td>Clear</td>
<td>Clear</td>
</tr>
<tr>
<td>S-17</td>
<td>1.400</td>
<td>5.600</td>
<td>28</td>
<td>65.000</td>
<td>Clear</td>
<td>Clear</td>
</tr>
<tr>
<td>S-18</td>
<td>1.200</td>
<td>3.600</td>
<td>20</td>
<td>75.200</td>
<td>Clear</td>
<td>Clear</td>
</tr>
<tr>
<td>S-19</td>
<td>1.920</td>
<td>8.640</td>
<td>24</td>
<td>65.440</td>
<td>Clear</td>
<td>Clear</td>
</tr>
</tbody>
</table>

Concrete Performance Examples

Solutions S-1 to S-9, S-14, and S-17 were prepared in sufficient quantity to evaluate their performance in concrete. Additional samples of solutions S-15 and S-18, designated as S-15a and S-18a, were prepared using a 5.26% and 11.11% increase in the solubilizing agent C, respectively. The amounts of the materials shown in Tables 3 to 6 are based on percent by weight of cement.

The concrete mixture proportions for the examples shown in Tables 3 and 4 were based on a 600 lb./yd³ mixture using Type I portland cement, a sand to aggregate (S/A) ratio of 0.44-0.45 using limestone coarse aggregate and sand, and sufficient amount of water to obtain the desired slump of approximately 6 to 8 inches.

The concrete mixture proportions for the examples shown in Table 5 were based on a 356 kg/m³ mixture using Type I portland cement, a sand to aggregate (S/A) ratio of 0.42 using limestone coarse aggregate and sand, and sufficient amount of water to obtain the desired slump of approximately 6 to 8 inches (15.25-20.3 cm).

The concrete mixture proportions for the examples shown in Table 6 were based on a 390 or 307 kg/m³ mixture using Type I portland cement, a sand to aggregate (S/A) ratio of 0.415-0.42 using limestone coarse aggregate and sand, and sufficient amount of water to obtain the desired slump of approximately 6 to 8 inches (15.25-20.3 cm).
Table 3 summarizes the performance data for various polycarboxylate dispersant and insoluble defoamer microemulsion compositions in non-air-entrained concrete. A reference sample with the polycarboxylate cement dispersant only was prepared. Control samples with the polycarboxylate dispersant with insoluble defoamer without the solubilizing agent were prepared at levels that correspond to those contained in the solution examples. The solutions were dosed in order to provide a level of cement dispersant equivalent to 0.14 to 0.20 percent by cement weight. Admixture examples 1, 2, and 3 were formulated to bracket the level of solubilizing agent C provided by solution S-1. Admixture examples 4, 5, and 6 were formulated to bracket the level of solubilizing agent D provided by solution S-2. All of the values shown are expressed as percent active material by cement weight in the concrete mixture. Slump and air content determinations were made after 5 minutes of mixing.

<table>
<thead>
<tr>
<th>Admixture</th>
<th>Cement Dispersant (%)</th>
<th>Defoamer (%)</th>
<th>Solubilizing Agent (%)</th>
<th>Slump (cm)</th>
<th>Air (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td>0.14</td>
<td></td>
<td></td>
<td>19.05</td>
<td>4.3</td>
</tr>
<tr>
<td>Control 1</td>
<td>0.14</td>
<td>0.0014</td>
<td></td>
<td>19.05</td>
<td>2.1</td>
</tr>
<tr>
<td>1</td>
<td>0.14</td>
<td>0.0014</td>
<td>0.01260</td>
<td>18.4</td>
<td>2.8</td>
</tr>
<tr>
<td>S-1</td>
<td>0.14</td>
<td>0.0014</td>
<td>0.00952</td>
<td>19.05</td>
<td>2.9</td>
</tr>
<tr>
<td>2</td>
<td>0.14</td>
<td>0.0014</td>
<td>0.00840</td>
<td>18.4</td>
<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>0.14</td>
<td>0.0014</td>
<td>0.00420</td>
<td>19.05</td>
<td>2.4</td>
</tr>
<tr>
<td>4</td>
<td>0.14</td>
<td>0.0014</td>
<td>0.02800</td>
<td>19.7</td>
<td>2.7</td>
</tr>
<tr>
<td>S-2</td>
<td>0.14</td>
<td>0.0014</td>
<td>0.02324</td>
<td>19.05</td>
<td>2.7</td>
</tr>
<tr>
<td>5</td>
<td>0.14</td>
<td>0.0014</td>
<td>0.02100</td>
<td>16.5</td>
<td>2.7</td>
</tr>
<tr>
<td>6</td>
<td>0.14</td>
<td>0.0014</td>
<td>0.01400</td>
<td>19.05</td>
<td>2.7</td>
</tr>
<tr>
<td>S-3</td>
<td>0.14</td>
<td>0.0014</td>
<td>0.00700</td>
<td>19.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Control 2</td>
<td>0.14</td>
<td>0.0028</td>
<td></td>
<td>15.2</td>
<td>2.0</td>
</tr>
<tr>
<td>S-4</td>
<td>0.14</td>
<td>0.0028</td>
<td>0.01120</td>
<td>17.8</td>
<td>2.3</td>
</tr>
<tr>
<td>S-5</td>
<td>0.14</td>
<td>0.0028</td>
<td>0.00606</td>
<td>15.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Control 3</td>
<td>0.14</td>
<td>0.0014</td>
<td></td>
<td>21.6</td>
<td>2.3</td>
</tr>
<tr>
<td>Control 4</td>
<td>0.14</td>
<td>0.0056</td>
<td></td>
<td>20.3</td>
<td>2.7</td>
</tr>
<tr>
<td>S-6</td>
<td>0.14</td>
<td>0.0014</td>
<td>0.01866</td>
<td>20.3</td>
<td>3.8</td>
</tr>
<tr>
<td>S-7</td>
<td>0.14</td>
<td>0.0014</td>
<td>0.00336</td>
<td>11.4</td>
<td>2.6</td>
</tr>
<tr>
<td>S-8</td>
<td>0.14</td>
<td>0.0042</td>
<td>0.00984</td>
<td>21.0</td>
<td>3.0</td>
</tr>
<tr>
<td>S-9</td>
<td>0.14</td>
<td>0.0056</td>
<td>0.01366</td>
<td>20.3</td>
<td>2.9</td>
</tr>
<tr>
<td>S-6</td>
<td>0.20</td>
<td>0.0020</td>
<td>0.02666</td>
<td>19.7</td>
<td>4.7</td>
</tr>
<tr>
<td>S-7</td>
<td>0.20</td>
<td>0.0020</td>
<td>0.00480</td>
<td>19.05</td>
<td>3.1</td>
</tr>
<tr>
<td>S-9</td>
<td>0.20</td>
<td>0.0080</td>
<td>0.01952</td>
<td>17.8</td>
<td>3.4</td>
</tr>
</tbody>
</table>
Except for solution S-6, which contained a low level of insoluble defoamer B and a high level of solubilizing agent D, all of the solutions and additional admixture examples demonstrated defoaming properties. Air contents were found to be lower than the dispersant-only reference and similar to the dispersant + defoamer controls. In solutions S-1 and S-2, where the solubilizer amount was bracketed by admixtures 1, 2, 3 and 4, 5, 6, respectively, air contents were the same. This indicated that the defoaming potential is governed primarily by the insoluble defoamer level and that the level of solubilizing agent did not significantly affect the air response.

Tables 4, 5 and 6 summarize performance data for a polycarboxylate dispersant, insoluble defoamer, and solubilizing agent microemulsion compositions in air-entrained concrete. The air-entraining agent, a commercially available, proprietary product, trademark MICRO-AIR®, manufactured by Master Builders Inc., was used at the dosages listed in the tables. Concrete mixture proportions were similar to those in the previous examples with the batch volume increase from the entrained air adjusted for by removing sand and coarse aggregate and maintaining the S/A ratio.

<table>
<thead>
<tr>
<th>Admixture</th>
<th>Cement Dispersant (%)</th>
<th>Defoamer A (%)</th>
<th>Solubilizing Agent C (%)</th>
<th>AEA (%)</th>
<th>Slump/Air (cm)/(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5 min. 10 min. 15 min.</td>
</tr>
<tr>
<td>Control 1</td>
<td>0.14</td>
<td>0.0014</td>
<td></td>
<td>0.00415</td>
<td>20.3/7.1 10.15/4.8 6.35/3.5</td>
</tr>
<tr>
<td>S-1</td>
<td>0.14</td>
<td>0.0014</td>
<td>0.00952</td>
<td>0.00415</td>
<td>21.6/11.2 16.5/8.5 8.9/5.5</td>
</tr>
<tr>
<td>Control 2</td>
<td>0.14</td>
<td>0.0028</td>
<td></td>
<td>0.00415</td>
<td>20.3/5.3 14.0/4.0 8.9/3.1</td>
</tr>
<tr>
<td>S-4</td>
<td>0.14</td>
<td>0.0028</td>
<td>0.01120</td>
<td>0.00415</td>
<td>21.6/8.1 14.0/5.3 7.6/3.8</td>
</tr>
</tbody>
</table>

In Table 4, all mixture proportions and dosages were fixed in order to compare the air response over time of solutions S-1 and S-4 to controls containing only insoluble defoamer. The results show that the air response pattern over time was similar for both microemulsion solutions and their respective controls. While the initial air content for solution S-1 was somewhat high, increasing the amount of insoluble defoamer, as in S-4, resulted in lower initial air.
TABLE 5

<table>
<thead>
<tr>
<th>Solution</th>
<th>Cement Dispersant (%)</th>
<th>Defoamer A (%)</th>
<th>Solubilizing Agent C (%)</th>
<th>AEA (%)</th>
<th>Slump (cm)</th>
<th>Air (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 4</td>
<td>0.14</td>
<td>0.0056</td>
<td></td>
<td>0.00415</td>
<td>19.7</td>
<td>4.5</td>
</tr>
<tr>
<td>Control 5</td>
<td>0.14</td>
<td>0.0070</td>
<td></td>
<td>0.00415</td>
<td>19.05</td>
<td>4.0</td>
</tr>
<tr>
<td>Control 6</td>
<td>0.14</td>
<td>0.0084</td>
<td></td>
<td>0.00415</td>
<td>19.05</td>
<td>3.7</td>
</tr>
<tr>
<td>S-15a</td>
<td>0.14</td>
<td>0.0056</td>
<td>0.028</td>
<td>0.00415</td>
<td>19.05</td>
<td>5.9</td>
</tr>
<tr>
<td>S-17</td>
<td>0.14</td>
<td>0.0070</td>
<td>0.028</td>
<td>0.00415</td>
<td>17.8</td>
<td>4.7</td>
</tr>
<tr>
<td>S-18a</td>
<td>0.14</td>
<td>0.0084</td>
<td>0.028</td>
<td>0.00415</td>
<td>20.3</td>
<td>5.1</td>
</tr>
<tr>
<td>7</td>
<td>0.14</td>
<td>0.0056</td>
<td>0.035</td>
<td>0.00415</td>
<td>19.7</td>
<td>5.8</td>
</tr>
<tr>
<td>8</td>
<td>0.14</td>
<td>0.0070</td>
<td>0.035</td>
<td>0.00415</td>
<td>17.8</td>
<td>4.6</td>
</tr>
<tr>
<td>9</td>
<td>0.14</td>
<td>0.0084</td>
<td>0.035</td>
<td>0.00415</td>
<td>19.7</td>
<td>5.0</td>
</tr>
<tr>
<td>S-14</td>
<td>0.14</td>
<td>0.0056</td>
<td>0.042</td>
<td>0.00415</td>
<td>19.05</td>
<td>6.2</td>
</tr>
<tr>
<td>10</td>
<td>0.14</td>
<td>0.0070</td>
<td>0.042</td>
<td>0.00415</td>
<td>19.05</td>
<td>5.7</td>
</tr>
<tr>
<td>11</td>
<td>0.14</td>
<td>0.0084</td>
<td>0.042</td>
<td>0.00415</td>
<td>19.7</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Table 5 compared three levels of defoamer, each with three levels of solubilizing agent C and a fixed dosage of air-entraining agent. These results demonstrate that at a sufficient insoluble defoamer level, air contents are controlled to desirable levels and that the level of solubilizer does not significantly affect the air response.

TABLE 6

<table>
<thead>
<tr>
<th>Admixture</th>
<th>Cement Content</th>
<th>Cement Dispersant (%)</th>
<th>Defoamer A (%)</th>
<th>Solubilizing Agent C (%)</th>
<th>AEA (%)</th>
<th>Slump/Air (5 min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>658</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17.8/6.6</td>
</tr>
<tr>
<td>S-18a</td>
<td>658</td>
<td>0.08</td>
<td>0.0048</td>
<td>0.016</td>
<td>0.00249</td>
<td>21.6/7.6</td>
</tr>
<tr>
<td>S-18a</td>
<td>658</td>
<td>0.14</td>
<td>0.0084</td>
<td>0.028</td>
<td>0.00415</td>
<td>19.05/5.4</td>
</tr>
<tr>
<td>S-18a</td>
<td>658</td>
<td>0.20</td>
<td>0.0120</td>
<td>0.040</td>
<td>0.00746</td>
<td>26.05/5.2</td>
</tr>
<tr>
<td>S-18a</td>
<td>517</td>
<td>0.20</td>
<td>0.0120</td>
<td>0.040</td>
<td>0.00705</td>
<td>16.5/5.1</td>
</tr>
<tr>
<td>S-18a</td>
<td>517</td>
<td>0.14</td>
<td>0.0084</td>
<td>0.028</td>
<td>0.00415</td>
<td>18.4/6.0</td>
</tr>
<tr>
<td>S-18a</td>
<td>517</td>
<td>0.08</td>
<td>0.0048</td>
<td>0.016</td>
<td>0.00249</td>
<td>7.5/6.8</td>
</tr>
</tbody>
</table>

Table 6 summarizes the results in air entrained concrete for solution S-18a used at three different levels of cement dispersant in concrete mixtures having different cement contents. The dosage of air-entraining agent was adjusted for the different
amounts of solution to maintain an air content between 5-8%. The results show similar performance for the different cement content mixtures and that the air contents were controlled by increasing the level of air-entraining agent to correspond with an increase of the solution level.

Therefore, the present invention provides an admixture containing a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent capable of solubilizing the water-insoluble defoamer for controlling the amount of air in a predictable manner in cementitious compositions.

The present invention also provides a cementitious composition comprising cement, water, a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent capable of solubilizing the water-insoluble defoamer for controlling the amount of air in a predictable manner in the cementitious composition.

The present invention also provides a method of making a cementitious composition comprising mixing cement, water, a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent capable of solubilizing the water-insoluble defoamer for controlling the amount of air in a predictable manner in the cementitious composition.

It should be appreciated that the present invention is not limited to the specific embodiments described above, but includes variations, modifications and equivalent embodiments defined by the following claims.
CLAIMS

1. An admixture for cementitious compositions comprising a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent capable of solubilizing the water-insoluble defoamer, characterized in that

(i) the dispersant is a polycarboxylate dispersant;

(ii) the solubilizing agent is present in an amount from 0.25 wt.% to 40 wt.% based on the weight of the polycarboxylate dispersant to form a stable microemulsion having a particle size of 0.01 to 0.05 μm; and

(iii) the solubilizing agent is at least one of alkoxylated R, carboxylated alkoxylated R, sulfated alkoxylated R, sulfonated alkoxylated R, styrene-maleic copolymer, or styrene-maleic copolymer derivatized with alkoxy, sulfonate, hydroxy alkylester or dimethyl amino propyl, wherein R is a hydrocarbon, sorbitan, polypropylene oxide, fatty acid, fatty alcohol, isononanol, styrene-maleic copolymer, or styrene-maleic copolymer derivatized with alkoxy, sulfonate, hydroxy alkylester or dimethyl amino propyl.

2. The admixture of claim 1, wherein the solubilizing agent is at least one of an alkoxylated R, where R is at least one of a hydrocarbon, sorbitan, polypropylene oxide, fatty acid, or fatty alcohol.

3. The admixture of claim 1, wherein the water insoluble defoamer is at least one of a mineral oil, a vegetable oil, a fatty acid, a fatty acid ester, a hydroxyl functional chemical, an amide, a phosphoric ester, a metal soap, a silicone, a polymer containing propylene oxide moieties, a hydrocarbon, and an acetylenic diol.

4. The admixture of claim 1 further comprising an air entrainer.

5. A cementitious composition comprising cement, water, a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent capable of solubilizing the water-insoluble defoamer, characterized in that
(i) the dispersant is a polycarboxylate dispersant;
(ii) the solubilizing agent is present in an amount from 0.25 wt.% to 40 wt.% based on the weight of the polycarboxylate dispersant to form a stable microemulsion having a particle size of 0.01 to 0.05µm; and
(iii) the solubilizing agent is at least one of alkoxylated R, carboxylated alkoxylated R, sulfated alkoxylated R, sulfonated alkoxylated R, styrene-maleic copolymer, or styrene-maleic copolymer derivatized with alkoyxl, sulfonate, hydroxy alkylester or dimethyl amino propyl, wherein R is a hydrocarbon, sorbitan, polypropylene oxide, fatty acid, fatty alcohol, isononanol, styrene-maleic copolymer, or styrene-maleic copolymer derivatized with alkoxyl, sulfonate, hydroxy alkylester or dimethyl amino propyl.

6. A method of making a cementitious composition comprising mixing cement, water, a water-insoluble defoamer, a dispersant for cementitious compositions, and a solubilizing agent capable of solubilizing the water-insoluble defoamer, characterized in that
(i) the dispersant is a polycarboxylate dispersant;
(ii) the solubilizing agent is present in an amount from 0.25 wt.% to 40 wt.% based on the weight of the polycarboxylate dispersant to form a stable microemulsion having a particle size of 0.01 to 0.05 µm; and
(iii) the solubilizing agent is at least one of alkoxylated R, carboxylated alkoxylated R, sulfated alkoxylated R, sulfonated alkoxylated R, styrene-maleic copolymer, or styrene-maleic copolymer derivatized with alkoxyl, sulfonate, hydroxy alkylester or dimethyl amino propyl, wherein R is a hydrocarbon, sorbitan, polypropylene oxide, fatty acid, fatty alcohol, isononanol, styrene-maleic copolymer, or styrene-maleic copolymer derivatized with alkoxyl, sulfonate, hydroxy alkylester or dimethyl amino propyl.