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<p>(21) International Application Number: PCT/US96/18300 (22) International Filing Date: 15 November 1996 (15.11.96) (30) Priority Data: 60/006,900 17 November 1995 (17.11.95) US (71) Applicant (for all designated States except US): W. R. GRACE & CO.-CONN. [US/US]; 1114 Avenue of the Americas, New York, NY 10036 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): JEKNAVORIAN, Ara, A. [US/US]; 4 Percheron Road, Chelmsford, MA 01824 (US). SHEN, Ding, Feng [US/US]; 1 Park Street, Lexington, MA 02173 (US). (74) Agents: LEON, Craig, K. et al.; W. R. Grace & Co.-Conn., 55 Hayden Avenue, Lexington, MA 02173 (US).</p>	<p>(81) Designated States: AL, AM, AT, AU (Petty patent), AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DE (Utility model), DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: MULTIPURPOSE ADMIXTURE FOR HYDRAULIC CEMENT COMPOSITION</p>		
<p>(57) Abstract</p> <p>Exemplary multifunctional hydraulic cement composition admixtures of the invention comprise a set accelerator, preferably a calcium salt, and a fatty acid aminosulfonic acid surfactant. Further exemplary admixtures additionally comprise a water reducing agent, such as a lignosulfonate, and/or an early strength enhancing agent, such as an alkanolamine.</p>		

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10 **MULTIPURPOSE ADMIXTURE FOR HYDRAULIC CEMENT**
 COMPOSITION

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Field of the Invention

 The present invention relates to admixtures for hydraulic cement compositions, and more particularly to a multifunctional admixture that combines set acceleration and air entrainment properties.

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Background of the Invention

 The term "hydraulic cement" refers to a cement which hardens by a chemical interaction or reaction with water. It is publicly known that certain properties of hydraulic cements can be modified by the addition of any number of chemical additives. For example, it is known to add calcium nitrate as a set accelerator.

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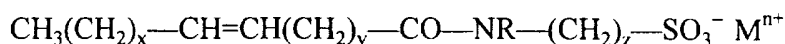
 However, calcium nitrate may be incompatible when combined in the hydratable cement mixture with other kinds of additives, chemicals, and agents. In the present invention, the inventors have discovered a novel combination of chemical additives for simultaneously achieving a number of properties in a hydraulic cement composition.

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Summary of the Invention

The present invention relates to a multifunctional hydraulic cement composition admixture which comprises a set accelerator which is an alkali or alkaline earth metal salt which is a salt of an organic or inorganic acid, and a fatty acid aminosulfonic acid surfactant.

10 In a preferred embodiments, the set accelerator is a calcium salt, such as calcium nitrate, calcium chloride, calcium formate, or calcium nitrite, and a fatty acid aminosulfonic acid having the general formula



wherein

15 “R” is a hydrogen, alkyl group or aryl group;

“x” is 1 to 10;

“y” is 3 - 10;

“z” is 1 to 10;

“M” is an alkali or alkaline earth metal, ammonium, or alkyl ammonium ion;

20 and

“n” is 1 to 3.

In a further preferred admixture formulation, the set accelerator comprises calcium nitrate, and the surfactant comprises sodium N-methyl oleoyl taurate, which is believed to have the formula $\text{CH}_3(\text{CH}_2)_7\text{—CH=CH}(\text{CH}_2)_7\text{—CO—N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{SO}_3^-$
 25 Na^+ .

Another preferred multi-functional hydraulic cement admixture of the invention further comprises, in addition to the set accelerator and surfactant, a water reducing agent, an early strength enhancing agent, and preferably both. The water reducing agent may comprise a lignosulfonate, such as calcium lignosulfonate. The
 30 early strength enhancing agent may comprise an alkanolamine, preferably a triethanolamine.

Accordingly, preferred multi-functional hydraulic cement composition admixtures of the invention can comprise a set accelerator, a water reducing agent, an early strength enhancing agent, and a fatty acid aminosulfonic acid surfactant which is
 35 believed to be operative to act as an air entraining agent. While some of these functions may have been combined simultaneously within one admixture formulation,

5 it is believed that the combination of certain of these functional components, such as the set accelerator with the surfactant agents, not to mention all four of the functional components just described, has not been disclosed or suggested by the prior art.

The present invention further relates to hydraulic cement mixes, including concrete mixes, comprising multi-functional admixtures described above and
10 hereinafter.

Detailed Description of Exemplary Embodiments

The term "cement composition" as used herein refers to pastes, mortars and concrete compositions comprising a hydraulic cement binder. The above terms are terms of art. Pastes are mixtures composed of a hydraulic cement binder, for example,
15 Portland cement, either alone or in combination with other components such as fly ash, silica fume or blast furnace slag, and water; mortars are pastes additionally including fine aggregate, and concretes are mortars additionally including coarse aggregate. The cement compositions of this invention are formed by mixing certain amounts of required materials, e.g., a hydraulic cement, water, and fine or coarse
20 aggregate, as may be applicable for the particular cement composition being formed.

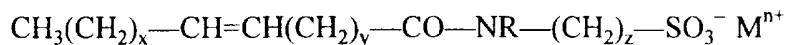
The term "concrete," where used herein, includes and refers to a mixture of such hydraulic cements and inert aggregates. Typical aggregates include conventional "coarse" aggregates such as gravel, granite, limestone, quartz sieve, etc., as well as those materials conventionally referred to as "fine" aggregates such as sand and fly
25 ash. Conventional hydraulic cement concretes, e.g., Portland cement concretes, employ major amounts of such aggregates, i.e. over 50% and usually up to about 75% by volume, in the set product.

The present invention pertains to a hydraulic cement composition admixture comprising a set accelerator component, preferably calcium nitrate, and a fatty acid
30 aminosulfonic acid surfactant component, preferably sodium N-methyl oleoyl taurate. Other preferred admixtures additionally comprise a water reducing agent, such as an alkanolamine and more preferably a triethanolamine; an early strength enhancing component, such as a lignosulfonate and preferably a calcium lignosulfonate; and, still more preferably, the admixture additionally comprises both the triethanolamine and

5 calcium lignosulfonate. The admixture components can be blended into a stable solution using conventional mixing equipment.

The set-accelerating component may be any compound which, when added to a cement composition, reduces the amount of time required for the cement composition to harden. For example, an alkali or alkaline earth metal salt which is a salt of an organic or inorganic acid may be employed. Although the following list is not meant to be limiting, examples of these compounds are alkali or alkaline earth metal nitrate, nitrite, and formate; alkali or alkaline earth metal salts of Group VII halogen and pseudohalogen acids, such as alkali or alkaline earth metal chloride, bromide, iodide, cyanide, cyanate, azide, and thiocyanate; alkali or alkaline earth metal thiosulfate and perchlorate; and alkali or alkaline earth metal aluminates, silicates, and hydroxides, e.g., sodium hydroxide. Calcium salts are particularly advantageous, especially calcium nitrate, calcium chloride, calcium formate, and calcium nitrite. Calcium nitrate is preferred.

The fatty acid aminosulfonic acid, which is believed to operate as an air entraining agent in a hydraulic cement composition, may be an alkali or alkali earth metal salt of an N-alkyl-N-tall oil aminosulfonic acid, having the general formula



wherein

“R” is a hydrogen, alkyl group or aryl group;

25 “x” is 1 to 10;

“y” is 3 - 10;

“z” is 1 to 10;

“M” is an alkali or alkaline earth metal, ammonium, or alkyl ammonium ion;

and

30 “n” is 1 to 3.

A preferred fatty acid aminosulfonic acid surfactant comprises sodium N-methyl-N-oleoyl taurate, which is available from Rhone-Poulenc, Cranbury, New Jersey, under the tradename Igepon T-33.

The water reducing agent may be an alkali or alkaline earth metal salt of lignosulfonic acid, polycarboxylic acid, naphthalene sulfonic acid condensate, melamine sulfonic acid condensate, hydroxylated carboxylic acids, and carbohydrates

5 such as corn syrup. Preferably, the water reducing agent is a lignosulfonate, such as calcium lignosulfonate.

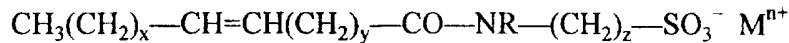
Early strength enhancing agents are known, as is the term "early strength," by which is meant compressive strength at 1 - 3 days (see e.g., ASTM C-39). Early strength enhancing agents include alkanolamines. An alkanolamine is a generic term
10 for a group of compounds in which trivalent nitrogen is attached directly to a carbon atom of an alkyl alcohol, and examples are monoethanolamine, diethanolamine, and triethanolamine. Alkanolamines also include methyldiethanolamine and triisopropanolamine.

Preferred multi-functional admixtures of the invention are preferably used in
15 an amount of 0.05-1.0% s/s based on cement in the concrete, where "% s/s" designates percent admixture solids on cement solids. A preferred admixture may comprise calcium nitrate in the range of 90-99.5% s/s and sodium N-methyl oleoyl taurate in the range of 0.5-10.0% s/s. Another preferred admixture comprises calcium nitrate (50-90% s/s); calcium lignosulfonate (5.0-40.0% s/s); triethanolamine or
20 triisopropanolamine (0.1-5.0% s/s); and sodium N-methyl oleoyl taurate (0.01-5.0% s/s).

5 We claim:

1. A multifunctional, hydraulic cement composition admixture comprising: a set accelerator which is an alkali or alkaline earth metal salt which is a salt of an organic or inorganic acid, and a fatty acid aminosulfonic acid surfactant.

2. The admixture of claim 1 wherein the set accelerator comprises
10 calcium nitrate, calcium chloride, calcium formate, or calcium nitrite; and the fatty acid aminosulfonic acid has the general formula



wherein

“R” is a hydrogen, alkyl group or aryl group;

15 “x” is 1 to 10;

“y” is 3 - 10;

“z” is 1 to 10;

“M” is an alkali or alkaline earth metal, ammonium, or alkyl ammonium ion;

and

20 “n” is 1 to 3.

3. The admixture of claim 2 wherein said fatty acid amino sulfonic acid comprises sodium N-methyl oleoyl taurate.

4. The admixture of claim 2 further comprising a water reducing agent comprising an alkali or alkaline earth metal salt of lignosulfonic acid, polycarboxylic
25 acid, naphthalene sulfonic acid condensate, melamine sulfonic acid condensate, hydroxylated carboxylic acids, or a carbohydrate.

5. The admixture of claim 4 wherein said water reducing agent comprises calcium lignosulfonate.

6. The admixture of claim 2 further comprising an early strength
30 enhancing agent.

7. The admixture of claim 6 wherein said early strength enhancing agent comprises an alkanolamine.

8. The admixture of claim 7 wherein said alkanolamine comprises triethanolamine or triisopropanolamine.

9. The admixture of claim 1 wherein said set accelerator comprises
35 calcium nitrate, said fatty acid aminosulfonic acid surfactant comprises sodium N-

5 methyl oleoyl taurate, and said admixture further comprises calcium lignosulfonate
and triethanolamine.

10. A hydraulic cement composition comprising portland cement, a
calcium salt set accelerator, and a fatty acid aminosulfonic acid surfactant.

11. The cement composition of claim 10 further comprising at least one
10 aggregate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/18300

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) : CO4B 22/00; 24/08, 24/12, 24/18 US CL : 106/696, 725, 727, 819, 823 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. : 106/696, 725, 727, 819, 823 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		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,432,212 A (HONDA et al.) 11 June 1995, col.4, line 17.	1-11
Y	US 5,322,562 A (ELLENBERGER et al.) 21 June 1994, col.1, line 60-61.	1-11
Y	US 5,316,572 A (OKAMURA et al.) 31 May 1994, col.4, line 43 and col.5, lines 1-5).	1-11
Y	US 5,352,290 A (TAKESHITA et al.) 4 October 1994, cols. 17-19, claims 1-13 and col.5, lines 53-55..	1-11
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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