IN THE UNITED STATED DISTRICT COURT
FOR THE EASTERN DISTRICT OF TEXAS
MARSHALL DIVISION

MIRACON TECHNOLOGIES, LLC	§	
	§	
Plaintiff,	§	
	§	Civil Action No. __________________
vs.	§	
	§	
CRH, PLC,	§	JURY TRIAL DEMANDED
OLDCASTLE, INC.,	§	
OLDCASTLE MATERIALS, INC.,	§	
STAKER & PARSON COMPANIES d/b/a	§	
JACK B. PARSON COMPANIES,	§	
LONNIE JAMES GRAY	§	
DOUGLAS BEDINGFIELD	§	
and W. R. GRACE & CO. - CONN.	§	
	§	
Defendants.		

PLAINTIFF'S ORIGINAL COMPLAINT AND REQUEST FOR INJUNCTION

Plaintiff Miracon Technologies, LLC ("Miracon"), files this Original Complaint for patent infringement, injunctive relief, breach of contract, misappropriation of trade secrets, tortious interference with existing contracts, tortious interference with prospective relations, unjust enrichment, fraud, and conspiracy against Defendants, CRH, Plc., Oldcastle, Inc., Oldcastle Materials, Inc., Staker & Parson Companies d/b/a Jack B. Parson Companies, Lonnie James Gray, Douglas Bedingfield, and W.R. Grace & Co. – Conn. (collectively, "Defendants"). Miracon also seeks declaratory judgment with respect to all United States Patents issued to the sole inventor Lonnie James Gray (the "Gray Patents") (1) enjoining Defendants from the unauthorized practice of Miracon's United States Patent No. 6,153,005 ("the '005 Patent"), (2) finding that the Gray Patents are each improvements upon the '005 Patent, (3) finding that, as a matter of law, the Gray Patents cannot be practiced without practicing the '005 Patent, and (4) enjoining Defendants from practicing the Gray Patents.

Miracon alleges as follows:

THE PARTIES

1. Miracon is the exclusive licensee of the patent-in-suit. Miracon is a Texas limited liability company organized and existing under the laws of the State of Texas, having a principal place of business at 401 S. Sherman Street, Suite 101, Richardson, Texas 75081.

2. Upon information and belief, Defendant CRH, Plc. ("CRH") is an Irish company having its principal place of business at Belgard Castle, Clondalkin, Dublin 22, Ireland. CRH may be served pursuant to the Hague Convention to which the government of Ireland is a signatory country and which governs service of process on corporations organized and existing in signatory countries.

3. Upon information and belief, Defendant Oldcastle, Inc. ("Oldcastle") is a subsidiary of CRH conducting business in the United States. It is registered as a Delaware corporation having a principal place of business at 900 Ashwood Pkwy., Suite 600, Atlanta, GA 30338. Oldcastle does business in the State of Texas and may be served with process by serving its registered agent, Corporation Service Company d/b/a CSC - Lawyers Incorporating Service Company, 211 E. 7th Street, Suite 620, Austin, TX 78701.

4. Upon information and belief, Defendant Oldcastle Materials, Inc. ("Oldcastle Materials") is a subsidiary of Oldcastle. It is registered as a Delaware corporation having a principal place of business at 900 Ashwood Pkwy., Suite 600, Atlanta, GA 30338. Oldcastle does business in the State of Texas and may be served with process by serving its registered agent, Corporation Service Company d/b/a CSC - Lawyers Incorporating Service Company, 211 E. 7th Street, Suite 620, Austin, TX 78701.

5. Upon information and belief, Defendant Staker & Parson Companies, doing business as Jack B. Parson Companies ("Staker & Parson"), is a subsidiary of CRH and an affiliate of Oldcastle. Staker & Parson is the assignee of the Gray Patents, including but not limited to the United States Patent Nos. 7,621,995, 7,670,426, 8,167,997, and 8,871,021. It is registered as a Utah corporation having a principal place of business at 2350 South 1900 West, Ogden, UT

84401. Upon information and belief, Staker & Parson may be served with process by serving its registered agent, Corporation Service Company, 10 E South Temple, Suite 850, Salt Lake City, UT 84133.

6. Upon information and belief, Defendant Lonnie James Gray ("Gray") is an employee of Staker & Parson. Gray may be served with process in person at his place of employment at 1730 North Beck Street, Salt Lake City, UT 84116. In the alternative, Gray may also be served with process in person at his place of residence at 101 West American Avenue, Murray, UT 84107.

7. Upon information and belief, Defendant Douglas Bedingfield ("Bedingfield") is an employee of Staker & Parson. Bedingfield may be served with process in person at his place of employment at 2350 South 1900 West, Ogden, UT 84401.

8. Upon information and belief, Defendant W. R. Grace & Co. - Conn. ("W. R. Grace") is registered as a Connecticut corporation having a principal place of business at 5400 Broken Sound Blvd NW, Suite 300, Boca Raton, FL 33487. Upon information and belief, W. R. Grace may be served with process by serving its registered agent, The Prentice-Hall Corporation System, Inc., 211 E. 7th Street, Suite 620, Austin, TX 78701.

JURISDICTION AND VENUE

9. This is an action for patent infringement in violation of the Patent Act of the United States, 35 U.S.C. §1 *et seq.*

10. The Court has original and exclusive subject matter jurisdiction over the patent infringement claims for relief under 28 U.S.C. §§ 1331 and 1338(a).

11. In the alternative, this Court has jurisdiction pursuant to 28 U.S.C. §1332 because of the existing diversity of citizenship between the parties and because the matter in controversy exceeds the sum of seventy-five thousand dollars ($75,000), exclusive of interest and costs. The Court's jurisdiction is also proper under 28 U.S.C. §§ 2201 and 2202.

12. Personal jurisdiction exists generally over the Defendants because the Defendants' contacts with the Eastern District of Texas are significant and pervasive. The Eastern District of Texas is a large and important market for the sale of Defendants' products. Defendants have sales representatives, dealers, and distributors located in the Eastern District of Texas that market, promote, and sell Defendants' products. Defendants have conducted business continuously and systematically in the State of Texas and in this judicial district for many years and continue to conduct that business actively today, which render them essentially at home in the form and can support general jurisdiction.

13. Venue is proper in this Court under 28 U.S.C. §§ 1391 as well as 28 U.S.C. §1400(b).

14. Furthermore, Defendant Staker & Parson has consented to venue in the Eastern District of Texas pursuant to the License Agreement between Miracon and Staker & Parson dated January 15, 2004 and the License and Supply Agreement between Miracon and Staker & Parson effective July 30, 2004.

BACKGROUND

A. Miracon's Air Entrainment Technology

15. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

16. Miracon is a small Texas employer with big potential based on the novel technology it has developed over the years. Miracon was founded in 1999 by Charles and Martha Welker, a husband and wife team who have devoted their time, sweat, and financial resources to developing a unique state-of-the-art air entrainment system that unequivocally enhances the quality of concrete.

17. Miracon's proprietary technology is comprised of machine, formula, and software. As a result of these inventions, the concrete manufactured using Miracon's technology is more stable, with tested potential for new markets and ground-breaking applications.

18. Concrete is typically composed of water, hydraulic cement, supplementary cementitious materials, and aggregates. To modify the properties of fresh or hardened concrete, a variety of chemical admixtures may be added to concrete mixtures, included air entraining admixtures. Air entraining admixtures provide important benefits of entrained air in both freshly mixed and hardened concrete and can improve the durability of concrete exposed to cycles of freezing and thawing and deicer chemicals.

19. The conventional methods of making concrete have proven to be unpredictable and not controllable. The commercially available compositions are not sufficiently stable in cementitious media and the results are often not consistent.

20. The technology developed by Miracon is unique because, unlike its competitors, it offers a product that solves the many problems related to entrainment of air, while being accessible and very cost effective.

21. Miracon's innovative product inhibits the factors that contribute to making the entrainment of air a very difficult process with unpredictable end product. Among other advantages, the technology pioneered by Miracon reduces the effects of water damage, ice damage, thermal conductivity and permeability and it improves the slump, the water tightness and the workability of fresh concrete while eliminating or reducing bleeding.

22. Miracon was the first company to offer a product providing concrete compositions of tailorable and predictable densities, strengths, and other properties that do not have accelerated, unusual, or undesirable characteristics associated with the concrete compositions of the prior art.

23. On April 16, 1999, a detailed patent application, Application Serial No. 09/293,613, was filed with the United States Patent and Trademark Office ("PTO") describing Miracon's product and methodology.

24. On November 28, 2000, after full and fair examination, the PTO issued United States Patent No. 6,153,005 titled "Foamed Concrete Composition and Process" ("the '005 Patent"), a copy of which is attached as **Exhibit A**.

25. The '005 Patent discusses fluorochemical foam stabilizers used to yield foams that are exceptionally stable in cementitious media. Such stabilized foams are useful as novel ultra-lightweight foam aggregates in concrete compositions of tailorable density or strength. The '005 Patent also describes methods of making concrete compositions including these foam aggregates.

26. The '005 Patent is valid and enforceable.

B. <u>The Relationship Between Miracon and Defendants</u>

27. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

28. After significant technological advances, Miracon made a commitment to use its proprietary and confidential information to develop and commercialize the world's first mechanically produced preformed air entrainment system, for production of concrete.

29. In 2003, Miracon, still a young company looking to launch its technology in the ready-mix category, participated in a world concrete show where it was approached by two representatives of Staker & Parson, Gray and Rod Higley ("Higley").

30. Defendant Staker & Parson is a subsidiary of CRH and together with its affiliate, Oldcastle, claims to be North America's largest manufacturer of building products and the largest supplier of ready-mixed concrete, as well as construction and paving services in the United States.

31. On or about January 15, 2004, the parties entered into a Letter of Intent Between Staker and Parson Companies and Miracon Technology, Inc. (the "Letter of Intent"). Among other things, the purpose of the Letter of Intent was for the parties to enter into a proprietary relationship within the geography that was covered by Staker & Parson. Generally, the Letter of Intent set forth certain limitations regarding Miracon's actions for the ready mix market in specific geographies, testing information, technical support, and hardware provisions. Certain cooperation efforts and purchasing commitments were required of Staker & Parson.

32. Also on or about January 15, 2004, Miracon and Staker & Parson executed the Miracon Technologies, Inc. License Agreement (the "License Agreement"). Pursuant to the same, Staker & Parson became a non-exclusive Licensee of the right to use Miracon's technology.

33. On or about July 30, 2004, Miracon and Staker & Parson entered into a non-exclusive License and Supply Agreement (the "Supply Agreement").

34. The License Agreement and the Supply Agreement limit Defendant Staker & Parson's ability to use Miracon's confidential information. Moreover, the License Agreement and Supply Agreement make clear that Miracon retains all proprietary and intellectual property rights including all patent rights. Staker & Parson also agreed to various restrictions relating to reverse engineering, decompiling, disassembling, or copying Miracon's technology.

35. Defendant Staker & Parson, corporately and as to all individuals employed by Staker & Parson, further agreed to safeguarding all confidential information from unauthorized use or disclosure to third parties.

36. Due to the breaches of the License Agreement and Supply Agreement, Miracon has been irreparably injured and is entitled to seek injunctive relief, in addition to all other legal and equitable remedies.

37. On or about July 30, 2004, a Distribution Agreement between Miracon and Staker & Parson Companies (the "Distribution Agreement") was also entered into by the two parties.

38. Pursuant to the Distribution Agreement, Miracon agreed to certain limitations about sales to other ready-mixed concrete companies, and Staker & Parson agreed to engage in actions that would increase the use of Miracon product for all high-air and lightweight concrete mixes throughout its network of locations and affiliates.

39. Pursuant to licensing agreements, Staker & Parson also agreed to certain limitations directed to Miracon chemicals, machines and software.

40. Upon information and belief, the last shipment of the chemical ordered by Staker & Parson was shipped on or about April 2007 to Four Corners Materials ("4 Corners") in Farmington, New Mexico, one of Oldcastle's affiliates under Staker & Parson management.

41. Miracon has not heard from Staker & Parson, its parent, or its affiliates since.

C. Defendants' Infringing Conduct/Facts Concerning Fraud and Conspiracy Charges

42. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

43. A large scale launch of a new air entrainment product for the production of concrete requires numerous laboratory and on site demonstrations, testing and implementation of quality control programs.

44. Miracon's formal collaboration with Staker & Parson, its parent CRH and its affiliates, Oldcastle and Oldcastle Materials started with on-site testing at Staker & Parson's main laboratory and testing facility in Salt Lake City, Utah in mid 2003, and it continued with on-site work at various laboratories and plants through early 2007. Throughout this time, Miracon's president, Mr. Charles Welker ("Welker"), worked with executives of these

companies as well as with numerous employees and team leads. Welker's main contact was with the Defendant Gray.

45. Upon information and belief, in the beginning of his work relationship with Welker in 2003, Gray was employed by Staker & Parson where he was a member of the technical services team.

46. Upon information and belief, prior to his employment with Staker & Parson, Gray had limited experience in the field of ready-mixed concrete. Before his collaboration with Welker, Gray had little to no experience with air entrainment products.

47. During 2003 and the early months of 2004, Gray was solely an observer and a facilitator of Mr. Welker's demonstrations to Staker & Parson. Gray's function was to prepare the concrete plants and the research centers prior to testing. After the execution of the License Agreement and Supply Agreement, Gray was assigned to work very closely with Welker.

48. On or about April 2004, Gray became intensively involved in all testing and demonstrations concerning the Miracon technology at various Staker & Parson research facilities and concrete plants in Utah, including California Avenue, Point South, Spanish Fork, and Park City. Gray worked side-by-side with Welker in order to understand the product and the methodology pioneered by Miracon.

49. At the end of his education process, which was marked on or about April 2005, Gray became very familiar with the Miracon product and the critical steps of the methodology used by Miracon.

50. During 2005 and 2006, Welker had various communications with another representative of Staker & Parson, Douglas Bedingfield ("Bedingfield"). Bedingfield was employed by Staker & Parson where he kept the title of Quality Control Manager.

51. Despite great reviews and impressive performance of the Miracon technology, Bedingfield showed reluctance in recommending and promoting the Miracon product.

52. Upon information and belief, Bedingfield sabotaged several of Miracon's testing either by not providing the complete details of the field and laboratory batches or by other similar methods.

53. Upon information and belief, there were numerous instances where Bedingfield would cite Miracon at fault for what was later proved to be issues with the materials provided by Staker & Parson. Such accusations would delay and derail Miracon's testing as well as result in additional work for Welker and Gray who would have to reveal the real issues with the failed testing.

54. Specifically, in or about 2006, several tests were designed and conducted of the Miracon product. Bedingfield's faulty design of the testing led to poor results and to Bedingfield's desired conclusion that the Miracon product is too expensive and therefore could not be utilized.

55. Upon information and belief, Bedingfield was motivated in his actions by his reported close affiliation with Craig Nelson ("Nelson"), representative for W. R. Grace, who had been selling to Staker & Parson various admixture products used with the conventional methods of producing concrete.

56. Upon information and belief, and during the timeframe of 2004 through 2006, Nelson offered various kickbacks to Bedingfield, such as trips and golf clubs, in return for his business and loyalty to the W. R. Grace products.

57. On two separate occasions in 2004, Bedingfield requested Welker to compensate Nelson if Miracon wanted to enter the concrete market. Such requests were made immediately after testing performed at the Staker & Parson Research Center in Salt Lake City, Utah.

58. On at least one occasion, Gray was a witness to Bedingfield's pressure that Miracon join in offering kickbacks to Nelson.

59. Bedingfield's poor testing reports addressing Miracon's product intensified during 2005. Specifically, during the spring and summer months of 2005, Bedingfield refused to recommend Miracon and stated that the product was allegedly too expensive to survive the market.

60. Notably, the tests made on the Miracon product not designed by Bedingfield, such as those performed in 2003 and throughout 2004, showed great performance results of the Miracon product.

61. Finally, on or about the Spring of 2005, after having gained the intricate knowledge of Miracon's products and technology while working with Welker, Gray and the other Defendants, upon information and belief, were able to copy Miracon's product and put it through commercial production of the foamed admixture, selling the product to Miracon's competition notwithstanding Miracon patent rights and in total violation of the License Agreement and the Supply Agreement.

62. Thus, Staker & Parson successfully eliminated Miracon from its competition pool. This opened a world of opportunities, including selling and/or licensing Miracon technology to other users of ready-mix compositions in total violation of Miracon patent and licensing rights.

63. On or about September 2005, unbeknownst to Miracon, Gray began filing multiple patent applications based on Miracon's patented technology listing himself as the only inventor.

64. Miracon learned of the Gray Patents in or about October 2014, while performing searches in advance of its filing of a non-provisional patent application.

65. Upon information and belief, Staker & Parson, Oldcastle, Oldcastle Materials, and CRH utilized Miracon's trade secrets, confidential information and inventions in their efforts to appropriate Miracon's technology, develop a patent portfolio, and segregate Miracon from the major players in the construction industry.

66. Defendants Staker & Parson, Oldcastle, Oldcastle Materials, and CRH have benefited substantially from their access, through Gray, to and use of Miracon's confidential and proprietary technology, because they did not have to "re-invent the wheel." They stole Miracon's know-how, confidential information and invention and are using such information to develop competing products.

67. Defendants Staker & Parson, Oldcastle, Oldcastle Materials, and CRH misappropriated confidential and proprietary information belonging to Miracon. The same Defendants have benefited, and will benefit, from this misappropriation. They did not have to spend the millions of dollars and years of research and development that they otherwise would have had to spend. Unless stopped, defendants will continue to use such information and continue to obtain significant financial benefit at the detriment of Miracon.

68. Through their actions, Defendants Staker & Parson, Oldcastle, Oldcastle Materials, and CRH gained an unfair competitive advantage in the industry and can develop improvements without paying for the technology pioneered by and misappropriated from Miracon.

D. <u>The Gray's Patent Applications</u>

69. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

70. Upon information and belief, on September 9, 2005, with knowledge of the '005 Patent, Gray filed with the PTO the provisional patent application Serial No. 60/715,458 ("the '458 application") entitled "Concrete Mixtures Having Aqueous Foam Admixtures."

71. The '458 application disclosed and claimed the subject matter related to Miracon's air entrainment system for cementing or concreting, including Miracon's fluorochemical surfactant. Such information had been already disclosed in the '005 Patent and

was demonstrated by Welker through the business relationship between Miracon and the Defendants.

72. On December 19, 2005, the ‘458 application was converted into the non-provisional U.S. patent applications: Serial No. 11/305,959 (“the ‘959 application”) entitled “Concrete Mixtures Incorporating High Carbon Pozzolans and Foam Admixtures”, Serial No. 11/305,960 (“the ‘960 application”) entitled “Concrete Mixtures Having High Flowability,” and Serial No. 11/311,490 (“the ‘490 application”) entitled “Concrete Mixtures Having Aqueous Foam Admixtures.”

73. On or about December 12, 2005, Gray assigned the ‘959, the ‘960, and the ‘490 applications to Staker & Parson.

74. On February 5, 2010, Gray filed with the PTO the non-provisional U.S. patent application Serial No. 12/701,398 (“the ‘398 application”) entitled “Concrete Mixtures Having Stabilized Foam Admixture.” The ‘398 application is a continuation-in-part of the ‘490 application and it claims priority from the ‘458 application.

75. On or about February 5, 2010, Gray assigned the ‘398 application to Staker & Parson.

76. On March 8, 2011, Gray filed with the PTO the provisional U.S. patent application Serial No. 61/450,614 (“the ‘614 application”) entitled “Concrete Mixtures Including Carbon Encapsulating Admixture.”

77. On March 8, 2012, Gray filed with the PTO the non-provisional U.S. patent application Serial No. 13/415,824 (“the ‘824 application”) entitled “Concrete Mixtures Including Carbon Encapsulating Admixture.” The ‘824 application claims priority from the ‘614 application.

78. On or about March 8, 2012, Gray assigned the ‘824 application to Staker & Parson.

79. The PTO Examiner, Paul Marcantoni ("Marcantoni"), examined all applications filed by Gray. The '959 application was rejected by examiner Marcantoni for being unpatentable over the '005 Patent under 35 U.S.C. § 103(a).

80. On or about August 27, 2009, the '959 application was abandoned after Gray's failure to file a reply to Marcantoni's rejection.

81. Next, examiner Marcantoni rejected the '960 application under 35 U.S.C. § 103(a) as being unpatentable over the '005 Patent. On May 27, 2009 Marcantoni conducted a telephonic interview with Staker & Parson's counsel, Mr. Andrew S. Hansen ("Hansen"), during which he was advised that Gray's application differed from the '005 Patent because of a particular order of mixing ingredients classified by Hansen as critical in achieving the aims of the claimed invention.

82. Despite the fact that no single claim in the '960 application is a method claim, Marcantoni, without further research and trusting the candor of Staker & Parson's counsel, allowed the issuance of United States Patent No. 7,621,995 ("the '995 patent"). A true and correct copy of the '995 patent is attached hereto as **Exhibit B**.

83. Similarly, the '490 application was rejected by examiner Marcantoni under 35 U.S.C. § 102(b) as anticipated by or, in the alternative, under 35 U.S.C. § 103(a) as obvious over the '005 Patent. Following the May 27, 2009 interview with Hansen, Marcantoni allowed the issuance of United States Patent No. 7,670,426 ("the '426 patent") dated March 2, 2010. A true and correct copy of the '426 patent is attached hereto as **Exhibit C**.

84. Continuing the review of Gray's applications, Marcantoni listed the '005 Patent as prior art in the prosecution of the '398 application. Nevertheless, he allowed the issuance of the United States Patent No. 8,167,997 ("the '997 patent") dated May 1, 2012 without further examination. A true and correct copy of the '997 patent is filed under the seal as **Exhibit D**.

85. Finally, upon very limited examination, Marcantoni allowed the ‘824 application. The ‘005 Patent was not disclosed within this application. The United States Patent No. 8,871,021 (“the ‘021 patent”) was issued on October 8, 2014, a true and correct copy of which is attached hereto as **Exhibit E**.

86. As set forth in the foregoing allegations and in Exhibits B-E, the Gray Patents are all based on Miracon’s ‘005 Patent.

87. Thus, all the Gray Patents are invalid as unpatentable over ‘005 Patent. Even if Gray’s invention would be considered as novel, the Gray Patents are obvious improvements upon the ‘005 Patent and, therefore, the Gray Patents cannot be practiced without infringing the ‘005 Patent.

88. Upon information and belief, Defendants, and each one of them independently, is practicing and/or advertising they are practicing the Gray Patents by at least making, using, selling, and offering for sale air entraining products, cellular air products, and air technology to be used as a lightweight composite in precast and ready-mix concrete based on Miracon’s technology. Therefore, each Defendant is practicing the ‘005 Patent literally and/or under the doctrine of equivalents.

89. Defendants are not authorized to practice the ‘005 Patent.

COUNT I
INFRINGEMENT OF UNITED STATES PATENT NO. 6,153,005
(CRH, Oldcastle, Oldcastle Materials, Staker & Parson, W. R. Grace)

90. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

91. Miracon is the exclusive licensee and has standing to enforce of the ‘005 Patent.

92. In violation of 35 U.S.C. § 271, CRH, Oldcastle, Oldcastle Materials, Staker & Parson, W. R. Grace (“Infringing Defendants”), have infringed and, if not enjoined, will continue to infringe the ‘005 Patent by (1) manufacturing, using, marketing, selling, offering for sale,

and/or importing, without authority, products and services that are covered by one or more claims of the ‘005 Patent, literally and/or under the doctrine of equivalents, in violation of 35 U.S.C. § 271(a); and/or (2) inducing infringement of one or more claims of the ‘005 Patent, in violation of 35 U.S.C. § 271(b). In particular, Infringing Defendants infringe one or more claims of the ‘005 Patent directly and indirectly, literally and/or under the doctrine of equivalents, and by inducement by (1) manufacture, use, marketing of, sale, and/or offer for sale of air entrainment products based on Miracon technology; and (2) using method and process claimed in the ‘005 Patent.

93. Infringing Defendants directly infringe one or more claims of the ‘005 Patent at least by making, using, selling, and offering for sell air entraining products, cellular air products, air technology to be used as a lightweight composite in precast and ready-mix concrete based on Miracon’s technology.

94. Specifically, Staker & Parson and Oldcastle Materials market and sell what is believed to be the infringing products sold in the United States under the trade name Carbon Knight and ProFlo based on Miracon’s technology. These products are sold to customers and potential customers that include, for example, companies in the construction industry in the United States, in addition to individual customers in the United States.

95. Staker & Parson and its affiliates market and sell their air entraining products (MICRO-AE) and ready-mix concrete based on Miracon’s technology to customers and potential customers that include, for example, companies in the construction industry in the United States, in addition to individual customers in the United States.

96. Infringing Defendants indirectly infringe one or more claims of the ‘005 Patent at least because they have had knowledge of the ‘005 Patent and have induced others to infringe the ‘005 Patent.

97. Infringing Defendants had knowledge of the ‘005 Patent since at least the beginning of their collaboration with Miracon in 2004.

98. Infringing Defendants have and continue to indirectly infringe one or more claims of the ‘005 Patent by inducing others (e.g., customers and end-users) to directly infringe the ‘005 Patent in this District and elsewhere in the United States in violation of the 35 U.S.C. § 271(b).

99. Through its website, sales personnel, and advertising, Staker & Parson, its affiliates and Gray market and promote the use of its air entraining products and ready-mix concrete based on Miracon’s technology, which infringe the ‘005 Patent when they are used as Stalker & Parson intends by its customers and end-users. Staker & Parson and its affiliates further instructs its customers and end-users how to use such products in a manner that infringes the ‘005 Patent claims.

100. Infringing Defendants have been contributorily infringing the ‘005 Patent in violation of the 35 U.S.C. § 271 through, among other things providing air-entraining products for performing the method claims of the ‘005 Patent; instructing and encouraging users of these products to perform the method claims of the ‘005 Patent, encouraging its business partners to make, use, sell, import, and offer to sell the infringing products or components thereof.

101. Infringing Defendants do not have a license or permission to use the claimed subject matter in the ‘005 Patent.

102. Miracon has been injured and has been caused significant financial damage as a direct and proximate result of the Infringing Defendants’ infringement of the ‘005 Patent.

103. Infringing Defendants will continue to infringe the ‘005 Patent, and thus cause irreparable injury and damage to Miracon unless enjoined by this Court.

104. Miracon is entitled to recover from Infringing Defendants the damages sustained by Miracon as a result of Defendants’ wrongful acts in an amount subject to proof at trial.

COUNT II
INFRINGEMENT OF UNITED STATES PATENT NO. 6,153,005 BY PRACTICE OF THE GRAY PATENTS
(CRH, Oldcastle, Oldcastle Materials, Staker & Parson, W. R. Grace)

105. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

106. Miracon is the exclusive licensee and has standing to enforce of the ‘005 Patent.

107. The ‘005 Patent was duly and legally issued by the USPTO and it is valid and enforceable.

108. Each of the Gray Patents are based on Miracon’s pioneer ‘005 Patent. To the extent any and all of the claims of the Gray Patents are inventive and patentable, such invention is an obvious improvement upon the ‘005 Patent.

109. Because the Gray Patents are mere improvement patents based on Miracon’s 005 Patent, as a matter of law, Defendants cannot practice the Gray Patents without practicing the ‘005 Patent. Thus, Defendants cannot manufacture, use, market of, sell, and/or offer for sale of air entrainment products that practice the claims of any of the Gray Patents without also manufacturing, using, marketing, selling, and/or offering for sale of air entrainment products that practice at least one of the claims of the ‘005 Patent.

110. Further, Infringing Defendants cannot use any method or process claimed in Gray Patents without also using at least one method or process claimed in the ‘005 Patent.

111. Infringing Defendants are not authorized to practice the ‘005 Patent.

112. Infringing Defendants directly infringe one or more claims of the ‘005 Patent at least by making, using, selling, and offering for sell air entraining products, cellular air products, air technology to be used as a lightweight composite in precast and ready-mix concrete that practice the Gray Patents; and using method and process claimed in the Gray Patents.

113. Infringing Defendants indirectly infringe one or more claims of the ‘005 Patent at least because they have knowledge of the ‘005 Patent and have induced others to infringe the ‘005 Patent by practicing the Gray Patents.

114. Infringing Defendants contributorily infringe one or more claims of the ‘005 Patent at least by providing air-entraining products for performing the method claims of the ‘005 Patent and by instructing and encouraging users of these products to perform the method claims of the ‘005 Patent, encouraging its business partners to make, use, sell, import, and offer to sell the infringing products or components thereof.

115. Miracon has been injured and has been caused significant financial damage as a direct and proximate result of the Defendants’ infringement of the ‘005 Patent.

116. Infringing Defendants have caused and will continue to cause irreparable injury and damage to Miracon as a result of its direct, indirect, and /or contributory infringement of the ‘005 Patent by practicing the Gray Patents. Infringing Defendants will suffer further irreparable injury, for which there is no adequate remedy at law, unless and until Defendants are enjoined from infringing the ‘005 Patent and from practicing the Gray Patents.

117. Miracon is entitled to injunctive relief under 35 U.S.C. §283.

118. Miracon is entitled to recover from Infringing Defendants the damages sustained by Miracon as a result of Infringing Defendants’ wrongful acts in an amount subject to proof at trial under 35 U.S.C. §284.

119. This is an exceptional case warranting an award of attorney’s fees to Miracon under 35 U.S.C. §285.

EXCEPTIONAL CASE

120. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

121. Infringing Defendants have willfully and deliberately infringed, induced others to infringe, and/or contributed to the infringement of the '005 Patent with full knowledge and wanton disregard of Miracon's rights thereunder, rendering this an "exceptional" case within the meaning of 35 U.S.C. § 285.

122. Miracon has incurred attorneys' fees, costs, and expenses in the prosecution of this action. Pursuant to 35 U.S.C. § 285, Miracon is entitled to recover its reasonable and necessary fees and expenses.

COUNT III
BREACH OF CONTRACT
THE LICENSE AGREEMENT
(Staker & Parson, Oldcastle, Oldcastle Materials)

123. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

124. The License Agreement constitutes a contract between Miracon, Staker & Parson and Staker & Parson's affiliates.

125. Because Staker & Parson and its affiliates make, use, import, sell, and/or offer for sale products that embody one or more claims patented within the '005 Patent, the termination provisions of the License Agreement are invoked.

126. Staker & Parson and its affiliates are liable to Miracon for material breaches of the License Agreement, including, but not limited to, misappropriating Miracon's proprietary and patented processes, by reverse engineering, disassembling, breaking down by chemical analysis, and copying Miracon's Products and by failing to keep secret Miracon's confidential information and failing to obligate their employees to treat as secret such confidential information.

127. The foregoing breaches of contract constitute material breaches that have caused irreparable injury and substantial damages to Miracon. Miracon is entitled to a judgment against

Staker & Parson, Oldcastle, and Oldcastle Materials for injunctive relief, damages, costs, and attorney fees caused by Staker & Parson's breach of contract.

128. All conditions precedent have been satisfied by Miracon.

COUNT IV
BREACH OF CONTRACT
THE SUPPLY AGREEMENT
(Staker & Parson, Oldcastle, Oldcastle Materials)

129. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

130. The Supply Agreement constitutes a contract between Miracon, Staker & Parson and Staker & Parson's affiliates.

131. Because Staker & Parson and its affiliates make, use, import, sell, and/or offer for sale products that embody one or more claims patented within the '005 Patent, the termination provisions of the Supply Agreement are invoked.

132. Staker & Parson and its affiliates are liable to Miracon for material breaches of the Supply Agreement, including but not limited to failing to keep secret Miracon's confidential information and failing to obligate their employees to treat as secret such confidential information and by misappropriating Miracon's proprietary and intellectual property including all patent rights in and to all designs, engineering details, formulae and other similar data and confidential information relating to the Products as described in Section 1 as well as by reverse engineering, disassembling, breaking down, and copying Miracon's Products or permitting any of the foregoing to occur.

133. The foregoing breaches of contract constitute material breaches that have caused irreparable injury and substantial damages to Miracon. Miracon is entitled to a judgment against Staker & Parson, Oldcastle, and Oldcastle Materials for injunctive relief, damages, costs, and attorney fees caused by Staker & Parson's breach of contract.

134. All conditions precedent have been satisfied by Miracon.

ATTORNEYS' FEES UNDER TEXAS CIVIL PRACTICE & REMEDIES CODE 38

135. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

136. Section 38.001 of the Texas Civil Practice & Remedies Code provides that "a person may recover reasonable attorney's fees from an individual or corporation, in addition to the amount of a valid claim and costs, if the claim is for … (8) an oral or written contract."

137. It is necessary for Miracon to be represented by attorneys to pursue the remedies sought in this petition.

138. Defendants are liable for Miracon's attorneys' fees in the prosecution of this action.

COUNT V
MISAPPROPRIATION OF TRADE SECRETS
(Staker & Parson, Oldcastle, Oldcastle Materials, CRH, Gray, Bedingfield)

139. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

140. Miracon's product and technology, including all patent rights in the formulae, process, designs, engineering details, schematics, drawings, specifications, and know-how, constitute trade secrets as defined by the Texas Uniform Trade Secrets Act. TEX. CIV. PRAC. & REM. CODE §134A.002(6).

141. Miracon's product and technology derive independent economic value from not being generally known to the public or to Miracon's competitors in that competitors do not know how to replicate the Miracon's unique product and methodology. Additionally, the technology is of great value to Miracon because Miracon expended significant time and resources in researching and developing its revolutionary technology, giving Miracon a competitive edge and lending to its profits. Any competitor who improperly acquired information about how to produce, develop, and use Miracon's product and technology would gain an unfair competitive

advantage in that they would not be required to expend the significant time and resources necessary to develop this trade secret information.

142. The technology developed by Miracon is not readily ascertainable by proper means by others in the construction industry, but rather it is the product of Miracon's independent research and development.

143. Staker & Parson, Oldcastle, Oldcastle Materials, and CRH misappropriated and disclosed Miracon's trade secrets that they acquired under circumstances giving rise to a duty to maintain their secrecy and limit their use.

144. Miracon took reasonable efforts to maintain the secrecy of the above described trade secrets by executing the License Agreement and the Supply Agreement with Staker & Parson. Pursuant to these agreements Staker & Parson was not granted any rights in the trade secrets owned by Miracon. In fact, Staker & Parson was restricted from reverse engineering, disassembling, breaking down or copying Miracon's products and methodology or permit any of the foregoing to occur.

145. Pursuant to the same agreements, Staker & Parson was under the obligation to limit the dissemination of Miracon's proprietary and intellectual property to select employees who have agreed to be bound by the terms of the agreements.

146. Gray misappropriated Miracon's trade secrets by wrongfully copying Miracon's information, despite his contractual obligations and legal duty to maintain the secrecy of and limit the use of such information. Gray's conduct was wrongful because at the time he reverse engineered Miracon's product and used Miracon's trade secrets, Gray knew that he was legally and contractually obligated to refrain from using this information.

147. Gray further misappropriated Miracon's trade secrets by wrongfully disclosing and claiming Miracon's trade secrets as his own inventive ideas in various patent applications,

despite his contractual obligations and legal duty to maintain the secrecy of and limit the use of such information.

148. Bedingfield misappropriated Miracon's trade secrets through his collaboration with Nelson and W. R. Grace.

149. Staker & Parson, Oldcastle, Oldcastle Materials, CRH, Gray, and Bedingfield jointly and severally, misappropriated Miracon's trade secrets by using Miracon's trade secrets they acquired from Gray to directly compete with Miracon and benefit from selling the Miracon technology. Staker & Parson, Oldcastle, Oldcastle Materials, CRH, Gray, and Bedingfield's conduct was wrongful because they knew or had reason to know at the time they used the trade secrets that Staker & Parson as well as its employees were legally and contractually obligated to maintain the secrecy of and limit the use of Miracon's trade secrets.

150. In light of Staker & Parson, Oldcastle, Oldcastle Materials, CRH, Gray, and Bedingfield's continued use of Miracon's trade secrets, Miracon has no adequate remedy at law to prevent them from continuing to misappropriate the trade secrets. Therefore, Miracon is entitled to injunctive relief, enjoining the above mentioned defendants from using, disclosing, or disseminating any trade secrets belonging to Miracon.

151. As a result of the misappropriation of Miracon's trade secrets, Miracon lost customers orders, its relationships with other customers were adversely affected, and Miracon's reputation and goodwill as the exclusive developer of the product and technology was damaged. Thus, Miracon is entitled to actual damages caused by the use and continued use of its trade secrets by Staker & Parson, Oldcastle, Oldcastle Materials, CRH, Gray, and Bedingfield.

152. As a proximate result of Staker & Parson, Oldcastle, Oldcastle Materials, CRH, Gray, and Bedingfield's misappropriation of Miracon's trade secrets, Staker & Parson, Oldcastle, Oldcastle Materials, CRH, Gray, and Bedingfield have been unjustly enriched in an amount subject to proof at the time of trial.

153. Additionally, Miracon is entitled to royalties on any profits received by Staker & Parson, Oldcastle, Oldcastle Materials, CRH, Gray, and Bedingfield from their misuse of Miracon's trade secrets.

154. Staker & Parson, Oldcastle, Oldcastle Materials, CRH, Gray, and Bedingfield misappropriated Miracon's trade secrets willfully and maliciously within the meaning of the Texas Uniform Trade Secrets Act in that they deliberately used this information with the intent to injure Miracon's business and enhance their own business relationships. Staker & Parson, Oldcastle, Oldcastle Materials, CRH, Gray, and Bedingfield acted with malice, and deliberately caused and intended to cause great economic harm to Miracon with full knowledge of the wrongfulness of their conduct. Defendants' conduct as alleged above was carried on by Staker & Parson, Oldcastle, Oldcastle Materials, CRH, Gray, and Bedingfield with a willful and conscious disregard of Miracon's rights. Therefore, Miracon should be awarded exemplary damages sufficient to punish Staker & Parson, Oldcastle, Oldcastle Materials, CRH, Gray, and Bedingfield for engaging in this conduct and to deter similar conduct on their part in the future. TEX. CIV. PRAC. & REM. CODE §134A.004(b).

155. Due to Staker & Parson, Oldcastle, Oldcastle Materials, CRH, Gray, and Bedingfield's willful and malicious misappropriation of Miracon's trade secrets, Miracon is entitled to recover its reasonable attorneys' fees and costs pursuant to the Texas Uniform Trade Secrets Act. TEX. CIV. PRAC. & REM. CODE §134A.005.

COUNT VI
TORTIOUS INTERFERENCE WITH EXISTING CONTRACTS
(Gray)

156. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

157. Upon information and belief, Gray was aware of the contractual and legal obligations of Defendants Staker & Parson, Oldcastle, and Oldcastle Materials.

158. Gray intentionally and wrongfully lent substantial assistance to Staker & Parson and its affiliates in breaching their contracts with Miracon.

159. Defendants Gray, Staker & Parson, Oldcastle, and Oldcastle Materials, as co-conspirators, pursued a common plan and design to intentionally and maliciously interfere with the secrecy of Miracon's proprietary intellectual property and its operations. Gray actively and intentionally assisted Staker & Parson and its affiliates in the breach of contracts by misappropriating Miracon's confidential information and filing a myriad of patent applications based on the knowledge obtained through collaboration with Welker.

160. Miracon has suffered and is continuing to suffer damages and/or loses as a result of same.

COUNT VII
TORTIOUS INTERFERENCE WITH EXISTING CONTRACTS
(Bedingfield)

161. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

162. Miracon has fully performed all of its obligations under the License Agreement and the Supply Agreement with Staker & Parson.

163. Defendant Bedingfield, not a party to these Agreements, willfully and intentionally interfered with such Agreements between Miracon and Staker & Parson, having knowledge of their existence and obligations.

164. Bedingfield intentionally interfered with these Agreements by sabotaging Miracon's testing, drafting poor testing reports of Miracon's performance, and providing negative reviews concerning Miracon's product and technology.

165. Furthermore, Bedingfield willfully and intentionally interfered with these Agreements by utilizing and misappropriating Miracon's trade secrets and other confidential and

proprietary information for the purpose of continuing its collaboration with Nelson and W.R. Grace and to secure the construction market independently from Miracon.

166. This tortious interference was a proximate cause of the injury to Miracon.

167. Miracon has suffered and is continuing to suffer damages and/or losses as a result of same.

COUNT VIII
TORTIOUS INTERFERENCE WITH EXISTING CONTRACTS
(W. R. Grace)

168. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

169. Miracon has fully performed all of its obligations under its Agreements with Staker & Parson.

170. Defendant W. R. Grace, not a party to these Agreements, willfully and intentionally interfered with such Agreements between Miracon and Staker & Parson, having knowledge of their existence and obligations.

171. W. R. Grace intentionally interfered with these Agreements through its representative's unlawful relationship with Bedingfield and by misappropriating Miracon's confidential information.

172. This tortious interference was a proximate cause of the injury to Miracon.

173. Miracon has suffered and is continuing to suffer damages and/or losses as a result of same.

COUNT IX
UNJUST ENRICHMENT
(Gray)

174. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

175. Gray has been unjustly enriched by, among other things, his misappropriation of invention, trade secrets and confidential information properly belonging to Miracon. Such invention, trade secrets and confidential information has been of significant benefit to Gray and the circumstances are such that it would be unjust for Gray to retain the benefit conferred upon him by continuing to use and enjoin Miracon's invention, trade secrets and confidential information.

COUNT X
UNJUST ENRICHMENT
(W. R. Grace)

176. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

177. W. R. Grace has been unjustly enriched by, among other things, its misappropriation of invention, trade secrets and confidential information properly belonging to Miracon. Such invention, trade secrets and confidential information has been of significant benefit to W. R. Grace and the circumstances are such that it would be unjust for W. R. Grace to retain the benefit conferred upon it by continuing to use and enjoin Miracon's invention, trade secrets and confidential information.

COUNT XI
DECLARATORY JUDGMENT OF INVALIDITY OF THE GRAY PATENTS

178. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

179. A case or controversy exists between Staker & Parson and Miracon concerning the invalidity of the Gray Patents which require a declaration of rights by this Court.

180. The Gray Patents are invalid for failure to meet the requirements of patentability under 35 U.S.C. § 102 and § 103.

181. Furthermore, the Gray Patents are invalid for lack of disclosure of proper inventorship information.

182. Finally, the Gray Patents are invalid because of the fraud on the PTO as described below.

183. Miracon is entitled to a declaratory judgment that the Gray Patents are invalid.

COUNT XII
DECLARATORY JUDGMENT OF UNENFORCEABILITY OF THE GRAY PATENTS

184. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

185. A case or controversy exists between Staker & Parson and Miracon concerning the unenforceability of the Gray Patents, which require a declaration of rights by this Court.

186. The Gray Patents are unenforceable due to inequitable conduct. During the prosecution of the applications for these patents, individuals owing a duty of candor to the PTO, including the inventor of the patents, his predecessors in title, and the attorney prosecuting the patents, mischaracterized the ‘005 Patent. Staker & Parson and its representative, Hansen, owed a duty of candor to the Examiner Marcantoni. Upon information and belief, the statements made by Hansen during the May 27, 2009 interview with Marcantoni advising the PTO of the difference from prior art was false. Furthermore, Hansen’s statement was erroneously applied to the ‘960 application discussing a product instead of the alleged method claim.

187. Staker & Parson’s failure to disclose the real and intimate connection with the ‘005 Patent and Miracon and Hansen’s false statements to the Examiner were to intentionally mislead and deceive the PTO. As such, the ‘995 patent is unenforceable due to inequitable conduct.

188. Upon information and belief, Examiner Marcantoni applied to all other Gray's patent applications the same or similar reasoning as guided by Hansen on May 27, 2009, thus allowing them for issuance.

189. Miracon is entitled to a declaratory judgment that the Gray Patents are unenforceable.

COUNT XIII
DECLARATORY RELIEF THAT PRACTICING THE GRAY PATENTS INFRINGES THE UNITED STATES PATENT NO. 6,153,005
(CRH, Oldcastle, Oldcastle Materials, Staker & Parson, W. R. Grace)

190. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

191. Each of the Gray Patents are based on the pioneer '005 Patent. To the extent any and all of the claims of the Gray Patents are inventive and patentable, such invention is an obvious improvement upon the '005 Patent.

192. Because the Gray Patents are mere improvement patents based on the '005 Patent, as a matter of law, no individual or entity can practice the Gray Patents without practicing the '005 Patent. Thus, an entity cannot manufacture, use, market, sell, and/or offer for to sell of air entrainment products that practice the claims of any of the Gray Patents without also manufacturing, using, marketing, selling, and/or offering for sale of air entrainment products that practice at least one of the claims of the '005 Patent. Further, an entity cannot use any method or process claimed in Gray Patents without also using at least one method or process claimed in the '005 Patent.

193. Infringing Defendants have caused and will continue to cause irreparable injury and damage to Miracon as a result of its direct, indirect, and /or contributory infringement of the '005 Patent by practicing the Gray Patents. Miracon will suffer further irreparable injury, for

which there is no adequate remedy at law, unless and until Defendants are enjoined from infringing the ‘005 Patent and from practicing the Gray Patents.

194. Miracon has been damaged as a result of Infringing Defendants’ direct, indirect, and /or contributory infringement of the ‘005 Patent.

195. Miracon is entitled to a preliminary and permanent injunction enjoining Defendants from infringing the Gray Patents and a finding that an entity or individual that practices the Gray Patents practices the ‘005 Patent.

196. Infringing Defendants have caused and will continue to cause irreparable injury and damage to Miracon as a result of its direct, indirect, and /or contributory infringement of the ‘005 Patent by practicing the Gray Patents.

197. Miracon will suffer further irreparable injury, for which there is no adequate remedy at law, unless and until Infringing Defendants are enjoined from infringing the ‘005 Patent and from practicing the Gray Patents.

198. Miracon is entitled to injunctive relief under 35 U.S.C. §283.

199. Miracon seeks Declaratory Relief that an entity or individual that practices the Gray Patents practices the ‘005 Patent.

COUNT XIV

FRAUD

(Staker & Parson, Oldcastle, Oldcastle Materials, CRH)

200. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

201. Defendants Staker & Parson and its affiliates have committed fraud against Miracon by engaging in conduct that reasonably caused Miracon to enter into the License and Supply Agreements and to divulge proprietary and intellectual property information capable of revolutionizing the construction industry.

202. Stake & Parson and its affiliates have committed fraud on Miracon by making false representation of facts, or making a false promise that Miracon's intellectual property would be kept secret and not misused by defendants.

203. Specifically, prior to January 2004 Staker & Parson and its affiliates promised Miracon, during numerous conversations between the parties' executives at Salt Lake City, Utah, that all testing information would remain mutually confidential.

204. Stake & Parson and its affiliates made the representation or promise to induce Miracon to enter into the License and Supply Agreements.

205. Specifically, starting in January 2004, Staker & Parson and its affiliates promised to Welker, on numerous occasions, that Miracon would be able to enter the ready-mix market. On or about July 30, 2004, during communications with Welker, Staker & Parson promised Miracon that Staker & Parson and its affiliates would utilize Miracon in all of their concrete that had an 8% or higher air composition as well as in all of their lightweight concrete. In addition, Staker & Parson requested that Miracon not make any further effort to develop the ready mix market within the geography covered by Staker & Parson and its affiliates.

206. Furthermore, throughout 2004 and 2005, Welker was requested routinely in meetings and written correspondence with executives of Staker & Parson that Miracon provide technical support during the parties' collaboration.

207. Stake & Parson and its affiliates made the representation or promise with the intention that Miracon rely on such representation or promise.

208. Miracon was ignorant of the falsity of the representation or promise and had a reasonable right to rely and actually did rely on the representation.

209. Miracon has been injured by its reasonable reliance on that representation or promise.

210. Miracon reasonably relied on the conduct of Staker & Parson and its affiliates and its principals made significant disclosures in relation to Miracon's proprietary information and intellectual property. In addition, Miracon made significant financial investments during its collaboration with Staker & Parson.

211. Miracon would not have disclosed its proprietary information and intellectual property had it known that Staker & Parson and its affiliates would steal and assert ownership of it and try to gain financial benefits by segregating Miracon within the construction community.

212. Miracon has been greatly damaged as a result of Staker & Parson and its affiliates' fraudulent conduct.

COUNT XV
FRAUD
(Gray)

213. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

214. Gray has committed fraud against Miracon by engaging in conduct that reasonably caused Miracon to enter into the License and Supply Agreements and to divulge proprietary and intellectual property information capable of revolutionizing the construction industry.

215. Gray has committed fraud on Miracon by making false representation of facts, or making a false promise that Miracon's intellectual property would be kept secret and not misused by Gray.

216. Upon information and belief, during conversations with Welker throughout 2003, 2004, and 2005 at various Staker & Parson locations and operation sites, Gray stated that his role was that of a facilitator and that he would keep Miracon's information secret.

217. Gray made the representation or promise to induce Miracon and its principals to disclose its trade secrets.

218. Gray made the representation or promise with the intention that Miracon rely on such representation or promise.

219. Miracon was ignorant of the falsity of the representation or promise and had a reasonable right to rely and actually did rely on the representation.

220. Miracon has been injured by its reasonable reliance on that representation or promise.

221. Miracon reasonably relied on Gray's conduct and its principals made significant disclosures in relation to Miracon's proprietary information and intellectual property.

222. Miracon would not have disclosed its proprietary information and intellectual property had it known that Gray would seek to steal and assert ownership of it and try to gain financial benefits at Miracon's expense.

223. Miracon has been greatly damaged as a result of Gray's fraudulent conduct.

COUNT XVI
CONSPIRACY
(All Defendants)

224. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

225. Defendants conspired to misappropriate Miracon's trade secrets and to cause the breaches of contract and fraud set forth herein.

226. Defendants had a meeting of the minds and embarked upon an agreed course of action to misappropriate Miracon's trade secrets and to induce the breaches of contract and fraud described above.

227. Specifically, Gray, Bedingfield, Staker & Parson and its affiliates, together with W.R. Grace conspired to steal Miracon's ground-breaking technology and segregate Miracon, thus eliminating Miracon as a competitor in their market.

228. Upon information and belief, Staker & Parson's employees, Bedingfield and Gray, were not their only associates who collaborated with Nelson and other representatives of W. R. Grace in order to misappropriate Miracon's trade secrets and further secure their market independently from Miracon.

229. Upon information and belief, most such actions were taken by Staker & Parson, its affiliates and W. R. Grace between the 2004-2006 time frame, at different locations in Utah such as Salt Lake City, Park City, Spanish Fork, Murray, Ogden, Lehi, St. George, at locations in Idaho such as Nampa and Eagle and at locations in New Mexico such as Farmington and Albuquerque.

230. Defendants' conduct is unlawful as set forth herein and was accompanied by complete disregard of Miracon's rights.

231. Miracon has been damaged as a result of Defendants' illegal and unlawful conspiracy and is entitled to compensatory and exemplary damages as a result thereof.

COUNT XVII
TORTIOUS INTERFERENCE WITH PROSPECTIVE RELATIONS
(Staker & Parson, Oldcastle, Oldcastle Materials, and CRH)

232. Miracon restates and re-alleges each of the allegations set forth above and incorporates them herein.

233. At all relevant times, Staker & Parson and its affiliates knew of Miracon's prospective business relations with various clients and customers throughout the United States based upon Miracon's ability to provide their customers with unique technology and high quality service.

234. There was a reasonable probability that Miracon would have entered into further business dealings with these customers.

235. Defendants knowingly, willfully, and intentionally interfered with and disrupted Miracon's prospective business relations by among other things, engaging in misappropriation of trade secrets, fraud, and conspiracy.

236. Upon information and belief, during their collaboration with Miracon, Staker & Parson and its affiliates did not intend to honor the License and Supply Agreements with Miracon or to develop, promote, and maximize the use of the Miracon product, but to steal Miracon's technology.

237. Upon information and belief Staker & Parson and its affiliates intentionally interfered with Miracon's prospective business relations with various clients and customers in order to gain the know-how of Miracon's revolutionary technology and then to steal Miracon's clientele.

238. Upon information and belief, beginning with December 2006, Staker & Parson had approached various Miracon's prospective business partners discouraging them to enter into business relations with Miracon.

239. Defendants have engaged in these wrongful acts for the sole purpose of injuring Miracon so that Miracon will be eliminated from all areas served by Staker & Parson and its affiliates.

240. Staker & Parson and its affiliates knew that in taking the actions described above they would interfere with the business interests of Miracon.

241. Miracon was damaged as a proximate result of the conduct described above.

242. Staker & Parson and its affiliates in doing the acts herein alleged acted with oppression, fraud or malice, entitling Miracon to an award of exemplary damages.

DEMAND FOR TRIAL BY JURY

Miracon, specifically requests a trial by jury on all issues so triable, pursuant to Rule 38 of the Federal Rules of Civil Procedure.

PRAYER FOR RELIEF

WHEREFORE, Plaintiff Miracon respectfully request that judgment be entered in its favor and against Defendants and that the Court grant the following relief to Plaintiff:

1. Judgment that Defendants have infringed the ‘005 Patent;
2. That the Court award actual damages to Miracon for Defendants’ infringing activities, which may include lost profits and/or a reasonable royalty;
3. Judgment that each of the Gray Patents is an obvious improvement patent based upon the ‘005 Patent;
4. Judgment that any entity that practices one or more claims of any of the Gray Patents, without Miracon’s authority to practice the ‘005 Patent, infringes directly, indirectly, or contributorily at least one of the claims of the ’005 Patent;
5. Judgment that this case is exceptional;
6. That this Court award Miracon increased damages in an amount not less than three times the amount of damages found by the jury or assessed by this Court, for Defendants willful infringement pursuant to 35 U.S.C. § 285;
7. That the Court enter a preliminary and thereafter a permanent injunction against Defendants, their officers, directors, agents, servants, affiliates, employees, subsidiaries, divisions, branches, parents, attorneys, representatives, and all others acting in concert or privity with them, from direct infringement of the ‘005 Patent;
8. That the Court enter a preliminary and thereafter a permanent injunction against Defendants, their officers, directors, agents, servants, affiliates, employees, subsidiaries, divisions, branches, parents, attorneys, representatives, and all others acting in concert or privity with them, from directly infringing the ‘005 Patent, by manufacturing, using, marketing, selling, offering for sale, and/or importing, without Miracon’s authority to practice the ‘005 Patent,

products and services that are covered by one or more claims of any of the Gray Patents, literally and/or under the doctrine of equivalents;

9. That the Court enter a preliminary and thereafter a permanent injunction against Defendants, their officers, directors, agents, servants, affiliates, employees, subsidiaries, divisions, branches, parents, attorneys, representatives, and all others acting in concert or privity with them, from active inducements of infringement and/or contributory infringements of the '005 Patent by inducing and/or contributing to third parties' manufacturing, using, marketing, selling, offering for sale, and/or importing, without Miracon's authority to practice the '005 Patent, products and services that are covered by one or more claims of any of the Gray Patents, literally and/or under the doctrines of equivalents;

10. That the Court enter a preliminary and thereafter a permanent injunction against Defendants' active inducements of infringement and/or contributory infringements of the '005 Patent by others;

11. That this Court enter an order directing Defendants to deliver to Miracon, and serve upon Miracon's counsel, within thirty (30) days after entry of the order of injunction, a report setting forth the manner and form in which Defendants have complied with the injunction;

12. Judgment that Staker & Parson and its affiliates breached the License Agreement;

13. Judgment that Staker & Parson and its affiliates breached the Supply Agreement;

14. That the Court award damages to Miracon to which it is entitled, including, but not limited to, the full amount of actual damages caused by Defendants' breach of the License Agreement;

15. That the Court award damages to Miracon to which it is entitled, including, but not limited to, the full amount of actual damages caused by Defendants' breach of the Supply Agreement;

16. Judgment that if the License Agreement has terminated, one or more claims of the ‘005 Patent has been infringed, either literally or under the doctrine of equivalents, by the Defendants;

17. Judgment that if the Supply Agreement has terminated, one or more claims of the ‘005 Patent has been infringed, either literally or under the doctrine of equivalents, by the Defendants;

18. Judgment that Gray willfully and intentionally interfered with the existing contracts between Miracon and Staker & Parson and award Miracon its damages suffered;

19. Judgment that Bedingfield willfully and intentionally interfered with the existing contracts between Miracon and Staker & Parson and award Miracon its damages suffered;

20. Judgment that W. R. Grace intentionally interfered with the existing contracts between Miracon and Staker & Parson and award Miracon its damages suffered;

21. Judgment that Defendants misappropriated Miracon’s trade secrets and award Miracon its damages suffered;

22. Judgment that Gray was unjustly enriched at Miracon’s expense and award Miracon the amount of Gray’s enrichment;

23. Judgment that W. R. Grace was unjustly enriched at Miracon’s expense and award Miracon the amount of W. R. Grace’s enrichment;

24. Judgment that the claims of the United States Patent No. 7,621,995, No. 7,670,426, No. 8,167,997 and No. 8,871,021 are invalid;

25. Judgment that the claims of the United States Patent No. 7,621,995, No. 7,670,426, No. 8,167,997 and No. 8,871,021 are unenforceable;

26. Judgment that Defendants committed fraud and award Miracon its damages suffered;

27. Judgment that Defendants committed conspiracy and award Miracon its damages suffered;

28. That this Court award pre-judgment and post-judgment interest;

29. That this Court award Miracon’s costs and attorney fees incurred in this action; and

30. That this Court award such further and other relief and the Court may deem meet and proper in the premises.

Date: January 9, 2015

Respectfully submitted,

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US006153005A

United States Patent [19]

Welker et al.

[11] **Patent Number: 6,153,005**

[45] **Date of Patent: Nov. 28, 2000**

[54] **FOAMED CONCRETE COMPOSITION AND PROCESS**

[75] Inventors: **Charles D. Welker**, 5940 Royal Palms, Plano, Tex. 75093; **Martha A. Welker**, Plano, Tex.; **Mark F. Welker**, Hudson, Ohio; **Mark A. Justman**, Hoffman Estates, Ill.; **Randy S. Hendricksen**, Arlington, Tex.

[73] Assignee: **Charles D. Welker**, Plano, Tex.

[21] Appl. No.: **09/293,613**

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[58] **Field of Search** 106/677, 678, 106/708, 714, 724, 725, 727, 802, 808, 809, 823, 790, 795

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,963,507	6/1976	Kuramoto et al.	521/83
4,019,919	4/1977	DeSalvo	524/8
4,373,955	2/1983	Bouchard et al.	106/646
5,595,595	1/1997	Glenn	106/672

FOREIGN PATENT DOCUMENTS

2806327	8/1979	Germany	106/677
58-135836	8/1983	Japan .	
7-17752	1/1995	Japan .	

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[57] **ABSTRACT**

The present invention describes fluorochemical foam stabilizers used in combination with surfactants to yield foams that are exceptionally stable in cementitious media. The stabilized foams that incorporate these fluorochemical agents are useful as novel ultra-lightweight foam aggregates in concrete compositions of tailorable density, strength, and other properties. Methods of making concrete compositions that include such foam aggregates are also described.

24 Claims, No Drawings

FOAMED CONCRETE COMPOSITION AND PROCESS

FIELD OF THE INVENTION

The present invention relates to concrete compositions that include foams stabilized with fluorochemical agents as a component. Upon dilution with water and subsequent aeration, suitable surfactant containing formulations or compositions that include the fluorochemical foam stabilizers described herein produce foams that demonstrate exceptional stability and strength in cementitious media. The introduction of such stabilized foams, hereinafter referred to as "foam aggregates", as new and unique ultra-lightweight components in concrete compositions yields high performance materials of tailorable density, strength, and other properties. Concrete compositions incorporating these novel foam aggregates provide a wide variety of cost effective materials with tailored physical properties that are alternatives to common structural and non-structural materials such as wood, steel and normal-weight concrete. Methods of making such concrete compositions are also disclosed.

BACKGROUND OF THE INVENTION

Concrete is a composite material that is composed of water, cement, and aggregate. Common aggregates include sand, gravel, or crushed stone. Concrete is a well-known structural component with typical compressive strengths of approximately 2500 psi. More detailed discussions regarding concrete and its properties can be found in Concrete, by S. Mindess and J. F. Young (Prentice Hall, Inc, Englewood Cliffs, N.J. 1981), in Design and Control of Concrete Mixtures, 13th Ed., by H. Kosmatka and W. C. Panarese (Portland Cement Association, Skokie, Ill., 1988), and in the ACI Manual of Concrete Practice (American Concrete Institute, 1987). There are numerous applications where a lower density concrete may be suitable, useful, or desirable, especially when combined with other attributes such as better processing, higher strength to weight ratio, improved insulation properties, and or enhanced acoustic properties.

Useful concrete compositions of reduced density are produced by the introduction of solid aggregates of lower density, by incorporating significant amounts of air or other gas, or by a combination of these methods such as including expanded polystyrene or other polymer foam. Structural lightweight concrete compositions (85–115 lb/ft^3) are most commonly prepared using lightweight aggregates (35–70 lb/ft^3, as compared to 75–110 lb/ft^3 for normal weight aggregates) such as kiln expanded clays, shales, and slates; sintering grade expanded shales and slates; pelletized or extruded fly-ash; and expanded slags. The use of these lightweight aggregates is limited by their lower limit of density, their availability, phase separation or non-uniformity upon curing, as well the high cost associated with material, fuel, labor, processing, and transportation.

Other types of lightweight aggregates are available. For example, Desalvo, U.S. Pat. No. 4,019,919, used irregular roughened polyethylene particles for some or all of the aggregate, but particles of this nature tend to separate from the mix as well as rise to the surface, leading to non-uniform compositions. Applications of this technology are also limited by polyethylene's density and cost.

Glenn, U.S. Pat. No. 5,595,595, used aquagels as lightweight aggregates. The use of aqueous gels of polysaccharides requires considerable processing that may include heating, cooling, precipitation into immiscible non-aqueous liquids, chemical treatment, filtration, centrifuging, extruding, vibration molding, or forming. Refrigerated storage is required if the aquagels are not used immediately.

Given the inherently low density of gasses and their relative abundance or ease of generation, their incorporation can have significant advantages for lowering the density of concrete. There are two fundamentally different approaches to incorporating air or other low density gasses. One approach generates gas in situ by chemical reaction and the other approach generates small pockets of air or gas either by whipping the concrete or by including preformed bubbles or foam into the wet mix before curing.

The in situ generation of gas typically involves the production of hydrogen gas from the base catalyzed reaction of a finely divided reactive metal species such as aluminum. AEROCRETE®, from Aircrete Corp., and DUROX®, from U.S. Durox Corp. are examples. This approach requires uniform premixing, the fine control of many processing parameters, and significant capital investment for dedicated special equipment. Other drawbacks to this approach may include the use of autoclaves to cure the concrete under pressurized hydrothermal conditions, the need for molds or other types of undesirable processing steps, and limited vertical uniformity (usually less than two feet). Large shapes or complicated designs are usually precluded from this approach.

Although whipping air into concrete is capable of entrapping bubbles and reducing density, this method is not always practical. Foams are often generated separately using surfactants and other foaming agents in combination with water and air before being introduced to a premixed paste of cement, water, and aggregate. Cellulose based foaming agents are described by Kuramoto et al. in U.S. Pat. No. 3,963,507. A commercially available cellulose based foaming concentrate, "CELLUCON", is also available from Romaroda Chemicals Pty., Ltd., Victoria Australia. Bouchard et al. in U.S. Pat. No. 4,373,955 described a hydrolyzed protein based foaming agent and a hydrolyzed protein based foaming concentrate, MEARL™, is available from The Mearl Corporation, Roselle Park, N.J.

Previously, economical and convenient surfactant based foams for use in concrete have not maintained their structures for 90 minute mixing cycles as well as prolonged cure cycles. Despite many advantages, concrete compositions including foam aggregates have often been limited to insulating, non-structural, or non-load-bearing bearing applications, since most commercially available foaming agents are not sufficiently stable in cementitious media and the results are often not consistent. In the previous art, the size and distribution of foam cells have been difficult to control and the cells have had a limited period of usefulness or lifetime. The foam cells have tended to agglomerate, coalesce, and recombine to give larger cells and a wide range of sizes. Long mixing times, such as required for transportation from a concrete production facility to a construction site, have been precluded due to bubbles collapsing and air escaping from the mix. Even when additives have been used to stabilize these foams, such as described by Johansson et al. in U.S. Pat. No. 5,160,540, it is not always practical to add the foam to the cementitious mix at the concrete station since the foam's stability and useful lifetime may prevent transportation. Nakano et al. in U.S. Pat. No. 4,683,003 alter the cure speed to match the foam's useful lifetime using accelerators, retarders, and autoclaving. This method is not trivial and it is impractical for many targeted applications.

A colloidal solution, or sol-gel, stabilizer is described by Gelbman et al. in U.S. Pat. No. 4,900,359. This method may extend the useful lifetime of the foamed concrete, but requires a minimum of 5 percent sol-gel in the foam. The cost of raw materials and the difficult preparation and mixing are prohibitive for many applications using this approach.

OBJECTS OF THE INVENTION

It is therefore an object of the present invention to provide easily accessible and economically manufactured concrete compositions of tailorable and predictable densities, strengths, and other characteristics that can be used to produce structural and non-structural products having excellent and highly desirable performance attributes such as strength, insulation, fireproofing, and or durability.

It is a further object of this invention to provide concrete compositions of tailorable and predictable densities, strengths, and other properties that do not have accelerated, unusual, erratic, undesirable, or otherwise unacceptable setting or curing characteristics associated with many of the tailorable concrete compositions of the prior art.

It is yet another object of this invention to provide concrete compositions of tailorable and predictable densities, strengths, and other properties that have and maintain a discreet, uniform, and symmetric structure without loss of cell integrity and that do not demonstrate undesirable shrinkage or other diminished properties of the product due to agglomeration, coalescence, recombination, or collapse of bubbles prior to setting or hardening of the concrete.

An even further object of this invention is to easily provide a uniform, stable, lightweight aggregate material from the cured cellular concrete by heretofore known crushing methods for further use in a wide variety of concrete compositions such as structural and non-structural concretes, steel fireproofing, insulating materials, and lightweight concrete blocks.

SUMMARY OF THE INVENTION

The present invention relates to fluorochemical foam stabilizers used in combination with surfactants to yield aqueous based foams that are exceptionally stable in cementitious media. The stabilized foams that incorporate these fluorochemical agents are useful as novel ultra-lightweight foam aggregates in concrete compositions of tailorable density, strength, and other properties. Methods of making concrete compositions that include such foam aggregates are also described.

DETAILED DESCRIPTION

The present invention relates to fluorochemical agents that are useful in surfactant containing formulations or compositions to improve the stability and resilience of foams containing such agents when in contact with cementitious compositions. The bubbles of these derived foam aggregates retain their discreet structures throughout various processing steps such as transportation, pumping, molding, and curing. The high stability and resilience of the resultant foams enable their use as novel stable ultra-lightweight aggregates in combinations with other concrete components including but not limited to water, cement, hydraulic hydrated lime, ground granulated iron blast furnace slags, sand, silica, stone, other, natural and byproduct pozzolanic materials, as well as chemical admixtures such as water-reducers and superplasticizers. The fluorochemical foam stabilizers enable exceptionally stable foam aggregates that are useful components in economical, lightweight to near normal-weight, high performance concrete compositions having a wide variety of applications. These materials constitute a significant advancement in structural and non-structural materials when compared to conventional normal-weight concrete compositions (130–160 lb/ft^3), conventional lightweight concrete compositions (15–130 lb/ft^3), steel, or wood.

When compared to conventional normal-weight concrete, the freshly mixed (plastic) concrete compositions incorporating these novel foam aggregates in wet cementitious compositions can demonstrate several advantages such as improved plasticity, ductility, workability, flowability, resistance to freeze-thaw, and ease of transport; reduced water demand, bleeding, and segregation; and easily tailored properties such as density, viscosity, and thixotropy.

When compared to conventional normal-weight concrete, the hardened concretes derived from compositions incorporating these novel foam aggregates can demonstrate significant improvements in workability, ease of machining, watertightness, and deicer scaling; increased resistance to sulfate, alkali-silica reactivity, and freeze-thaw; and easily tailored properties such as density, compressive strength relative to density, thermal resistance, and acoustic characteristics.

The fluorochemical foam stabilizers of the present invention are generally identified and characterized as fluorinated surfactants. The fluorochemical foam stabilizers are water soluble and must be stable to the various chemical species contained in concrete, such as Ca^{+2} cations. The fluorochemical foam stabilizers of the invention are characterized by chemical moieties represented by the general formula, $F—E_a—(S)_b—[M_1]_x—[M_2]_y—H$ (Formula I), and mixtures thereof. It is understood that Formula I is not intended to depict the actual sequence of the oligomer or macromer units since the units can be randomly distributed throughout. It is also assumed that the monomers from which M_1 and M_2 units are derived are known per se.

R_f is a straight chain, branched chain, or cyclic perfluoroalkyl of 1–20 carbon atoms, or said perfluoroalkyl substituted by perfluoroalkoxy of 2–20 carbon atoms, or an oligomer or polymer of greater than 10 carbon atoms such as oligo(hexafluoropropylene oxide) and it is understood that R_f often represents a mixture of perfluoroalkyl moieties.

E is a direct bond or independently a branched chain, straight chain, or cyclic alkylene connecting group of 2 to 20 carbon atoms, or said connecting group interrupted by one or more groups selected from, but not limited to, —NR—, —O—, —S—, —SO_2—, —COO—, —OOC—, —CONR—, —NRCO—, —SO_2NR—, —NRSO_2—, —SiR_2—; or is terminated at the R_f end with —CONR— or —SO_2NR— where R_f is attached to carbon or sulfur atom. R is independently hydrogen, alkyl of 1–10 carbon atoms, or hydroxyalkyl of 2 to 10 carbon atoms; and a and b are independently 0 or 1.

M_1 and M_2 are water soluble groups or mixtures thereof. Examples may include but are not limited to —W—(—$C_mH_{2m}NH)_p$ or —W—(—$C_mH_{2m}N—)_q$ where W represents —CO— or —SO_2—, m is 2–20, p and q are 0 to 500, and p+q are equal to or larger than 1. Preferably, M_1 represents a non-ionic hydrophilic monomer unit and M_2 represents an anionic hydrophilic monomer unit, and x and y represent the number of monomer units present in the co-oligomers and are both greater than 0; the sum of x and y being between 5 and 200, and y/(x+y) being between 0.01 and 0.98.

Many non-ionic hydrophilic monomers of the type M_1 are known per se and many are commercially available. Especially valuable non-ionic hydrophilic monomers of the type

M_1 are acrylamide, methacrylamide, diacetone acrylamide, and 2-hydroxyethyl methacrylate. Other examples of such monomers include derivatives of acrylic, methacrylic, maleic, fumaric, and itaconic acids, such as hydroxyalkyl esters of acrylic acids; amides such as N-vinyl-pyrrolidone, N-(hydroxyalkyl)-acrylamides, or N-(hydroxyalkyl)-methacrylamides; and vinyl esters with 1–20 carbons in the ester group such as vinyl acetate, butyrate, laurate, or stearate. The above listed non-ionic hydrophilic monomers of the type M_1 can be used alone or in combination with each other as well as in combination with suitable anionic hydrophilic monomers of the type M_2. Some non-ionic hydrophilic monomers of the type M_1 may require a co-monomer for polymerization, such as di(hydroxyalkyl) maleates with ethoxylated hydroxyalkyl maleates.

Many anionic hydrophilic monomers of the type M_2 which do co-oligomerize with non-ionic hydrophilic monomers of the type M_1 are known per se and many are commercially available. Especially valuable anionic hydrophilic monomers of the type M_2 are acrylic and methacrylic acids and salts thereof. Other examples of such monomers include maleic, fumaric, and itaconic acids and salts thereof; acrylamidopropane sulfonic acid and salts thereof; and mono-olefinic sulfonic and phosphonic acids and salts thereof.

The preferred foaming concentrates of the present invention are comprised of aqueous solutions of fatty alcohols preferably selected from the group consisting of straight and branched chain fatty alcohols of 8 to 16 carbon atoms and mixtures thereof, a polysaccharide gum preferably selected from the group consisting of Rhamsan gums, Xanthan gums, Guar gums and Locust Bean gums, and a non-fluorinated anionic surfactant preferably selected from the group consisting of C-8 to C-18 anionic surfactants and most preferably, C-10 to C-18 alpha olefin sulfonates, as well as mixtures of such surfactants. The concentrate may also contain a solvent, preferably selected from the group consisting of glycol ethers and C-2 to C-8 aliphatic diols.

Table 1 below sets forth the foaming concentrate compositions of the present invention. In Table 1, column 1 specifies the useful ranges for each component, column 2 specifies preferred ranges for each of the components and column 3 describes the highly preferred ranges for each of the components. In Table 1, all compositions are in parts by weight. The fluorochemical surfactant is normally supplied as a solution in an alcohol such as tert-butyl alcohol.

TABLE 1

	1	2	3
Solvent	0–50%	0–20%	1–10%
Fatty Alcohol	0.1–10%	0.1–1.0%	0.2–1.0%
Polysaccharide Gum	0.1–10%	0.1–5.0%	0.5–4.0%
Anionic Surfactant	0.1–50%	0.1–20%	0.5–8.0%
Fluorochemical	0.1–15%	0.1–5.0%	0.5–3.0%
Water	Balance	Balance	Balance

Specifically preferred as the solvent, if used, is propylene glycol t-butyl ether. The preferred fatty alcohol comprises a mixture of equal parts n-dodecanol, n-tetra decanol and n-hexadecanol. Preferred as the anionic surfactant are mixtures of sodium alkenyl sulfonate, sodium tetradecene sulfonate, and sodium hexadecene sulfonate in a ratio of about 4:1:1.

Other ingredients can be employed in the composition of the surfactant formulation to effect specific environmental or shelf-life concerns. Examples of such ingredients are freezing point depressants, such as ethylene glycol, and preservatives, such as that available under the trade name DOWICIDE (Dow).

Other embodiments of the present invention relate to additional foams or foaming concentrates intended for use as components in concrete wherein said foam formulations or compositions contain fluorinated foam stabilizers. For example, fluorochemical agents that are foam stabilizers in concrete can be added to other known foaming surfactant concentrates such as the cellulose based "CELLUCON" (Romaroda Chemicals Pty.) or the hydrolyzed protein based MEARL™ (The Mearl Corporation).

While the stabilized foams of this invention are useful in producing concrete compositions that also contain common aggregates such as sand, gravel, or crushed stone, they also have utility in their own right as "foam aggregates" to provide unique ultra-lightweight aggregate when no sand or other common aggregate is used. The stabilized foam can be the only aggregate for very low density concrete. In such cases, the resultant material is most typically useful as a lightweight insulation material; it is not typically useful as a structural material for most applications since it possesses minimal structural strength. Consequently, Table 2 below that describes useful (column 1), preferred (column 2) and highly preferred (column 3) ranges of composition for the foamed concrete materials of the present invention, does not require the inclusion of sand or course aggregate. In Table 2, all compositions except for the optional water reducing chemical admixtures and set accelerating admixtures are expressed in percent by volume. The amounts of water reducing chemical admixtures and set accelerating admixtures are expressed in ounces per 100 pounds of cementitious and pozzolanic material added.

TABLE 2

	1	2	3
Portland Cement	1–50%	6–50%	10–25%
Washed Sand	0–75%	0–60%	0–40%
Coarse Aggregate	0–60%	0–50%	0–40%
Water	4–50%	5–50%	10–25%
Cementitious and Pozzolanic Material	0–50%	0–20%	0–5.0%
Air as Provided as Foam	1–90%	1–85%	1–75%
Water Reducers	0–20 oz	0–6.0 oz	0–4.5 oz
Accelerators	0–20 oz	0–12 oz	0–8.0 oz

The cementitious and pozzolanic materials of this composition are those well known in the concrete art, namely, such materials as fly ash (both types C and F), ground blast furnace slag, diatomaceous earth, hydrated lime, natural cement, etc. Water reducing chemicals are also well known in the art. Non-limiting examples of such materials are, lignosulfonates, sulfonated melamine formaldehyde and naphthalene formaldehyde condensates, hydroxylated carboxylic acids, and carbohydrates. Set accelerating mixtures include such materials as calcium chloride, triethanol amine, sodium thiocyanate, calcium formate, calcium nitrate, and calcium nitrite.

In the compositions described in Table 2, the concentrate of Table 1 comprises from about 1 to about 10 percent by weight of the "air provided as foam". Preferably, this concentration ranges from 1 to 5 percent. More preferably, this concentration ranges from about 1.5 to about 3 percent. Water and air comprise the balance of the "air provided as foam".

The fluorinated foam stabilizers of the present invention are also useful as stabilizers for surfactant based foaming compositions of a more general type, namely, as stabilizers for any surfactant based foam material wherein it is desired to produce a bubble having exceptional stability in cementitious media. For example, hydrolyzed protein or cellulose based foaming compositions, such as the foams derived from the Mearl and Cellucon products discussed above in the prior art, will similarly benefit from the addition of the fluorochemical foam stabilizers of the present invention, as will other similar surfactant based foaming materials. The addition of fluorochemical foam stabilizers to all such materials so as to enhance foam stability in cementitious media is contemplated as within the scope of the instant invention.

Foam production can be performed by drawing water and concentrate from separate sources, in the ratios described above, and injecting them using high pressure air or other suitable gas, preferably at about 125 psi, into a chamber where the mixture is subjected to shearing forces and thereby producing stabilized bubbles or foam. Any number of foam production devices may be used for producing the stabilized foam of the present invention, and the invention is not limited to any specific such device. Such devices are well known in the art and familiar to the skilled artisan. Whatever mechanism used, it must be adequate to produce a stream of bubbles suitable for introduction into an appropriate concrete mixture.

The following examples demonstrate the use of the present invention to prepare novel and unique foam aggregates as critical components for high performance cellular concrete materials having densities that vary from 20–140 lb/ft^3. The density of any given cured concrete material is, of course, determined by the volume of the novel foam aggregate that is incorporated as well as the choice and proportions of other components such as cement, sand, other aggregate, water, and any other additives or admixtures introduced to the mix. The representative examples that follow produce approximately 4 ft^3 of a cured cellular concrete material in a 7 ft^3 paddle-type mortar mixer; however, any standard concrete mixer such as a tilting or non-tilting rotary-drum mixer, or open-top revolving blade mixer operating at conventional speeds can be substituted.

Concentrate I

COMPONENT	CAS NUMBER/TRADE NAME	w/w %
Sodium alkenyl sulfonates (mixture)	68439-57-6, 11066-21-0, 11067-19-9	7.0
1-t-Butoxy-2-propanol	57018-52-7	5.0
Rhamsan gum	96949-21-2	2.0
Perfluoroethylthia acrylic telomer	Lodyne ™ K90'90 (Ciba-Geigy Corp.)	1.4
n-Alkanols (mixture)	112-53-8, 112-72-1, 36653-82-4	1.0
2-Methyl-2-propanol	75-65-0	0.2
Water	7732-18-5	balance

EXAMPLE 1

A 7.0 ft^3 paddle-type mortar mixer is charged with 35.0 lb of water, 227.5 lb of washed sand, 110 lb of Type I/II Portland cement (Texas Industries, Inc.), and 2.5 oz of Daracem™ ML 330 (a water reducer-superplasticizer available from W. R. Grace). Subsequent mixing at 32 r.p.m. for 5–10 minutes produces a uniform cementitious slurry.

A stable and resilient aqueous foam aggregate is produced separately by diluting Concentrate I to 2.5 w/w % water (39 parts water to one part Concentrate I, respectively) and then

aerating it through a foam generating chamber where the mixture is subjected to shearing forces to produce the stabilized foam aggregate. While continuing to mix the cementitious slurry, 1.0 ft^3 of the foam aggregate is added to the slurry over approximately one minute. The resultant cellular concrete slurry should be mixed 5 minutes to uniformly disperse the foam aggregate, but can be mixed in excess of 90 minutes without any loss of foam aggregate volume. The cellular concrete slurry is very flowable and readily pours into and completely fills standard cylindrical molds such as those used for ASTM method C-39.

Cylindrical concrete samples (3"×6" and 6"×12") were made from a cellular concrete slurry prepared as above and then cured and tested as specified in ASTM method C-39. The cylinders demonstrated compressive strengths of 2100–2210 psi after 7 days and 2840–3080 psi after 28 days. All of the samples had a density of 107 lb/ft^3.

EXAMPLE 2

Using a method similar to Example 1,85.5 lb of Type I/II Portland cement, 28.5 lb of ASTM C 618 Class C fly ash, 34.6 lb of water, 207.0 lb of washed sand, 3.4 oz of Daracem™ ML 330, and 9.0 oz of PolarSet™ (an accelerating admixture available from W. R. Grace) are mixed at 32 r.p.m. for 5–10 minutes to yield a uniform cementitious slurry.

As in Example 1, a stable and resilient aqueous foam aggregate is produced separately by diluting Concentrate I to 2.5 w/w % with water (39 parts water to one part Concentrate I, respectively) and then aerating it. While continuing to mix the cementitious slurry, 1.6 ft^3 of the foam aggregate is added to the slurry over approximately one minute. The resultant cellular concrete slurry should be mixed 5 minutes to uniformly disperse the foam aggregate, but can be mixed in excess of 90 minutes without any loss of foam aggregate volume. The cellular concrete slurry is very flowable and readily pours into and completely fills standard cylindrical molds such as those used for ASTM method C-39.

Cylindrical concrete samples (3"×6" and 6"×12") were made from a cellular concrete slurry prepared as above and then cured and tested as specified in ASTM method C-39. The cylinders demonstrated compressive strengths of 1140 psi after 7 days and 1510 psi after 28 days. All of the samples had a density of 92 lb/ft^3.

As the invention has been described, it will be apparent to those skilled in the art that the same may be varied in many ways without departing from the spirit and scope thereof. Any and all such modifications are intended to be included within the scope of the appended claims.

What is claimed is:

1. A concrete mix comprising from about 1 to about 50 percent by volume of cement, from about 0 to about 75 percent by volume of washed sand, from about 0 to about 60 percent by volume of coarse aggregate, from about 4 to about 50 percent by volume water, from about 0 to about 50 percent by volume of a member selected from the group consisting of cementitious and pozzolanic materials, from about 0 to about 20 oz of water reducer per 100 pounds of cementitious and pozzolanic material, from about 0 to about 20 oz of accelerator per 100 pounds of cementitious and pozzolanic material, and from about 1 to about 90 percent by volume of air as bubbles comprising from about 0.01 to about 1.0 percent by weight of a foam stabilizing fluorinated surfactant of the formula

$$R_f—E_a—(S)_b—[M_1]_x—[M_2]_y—H$$

wherein R_f is a perfluorinated alkyl selected from the group consisting of straight chain, branched chain, and cyclic perfluoroalkylenes of 1 to about 20 carbon atoms, perfluoroalkyls substituted with perfluoroalkoxy of 2 to about 20 carbon atoms, perfluoroalkyl oligomers and polymers of greater than 10 carbon atoms, and mixtures thereof, E is selected from the group consisting of direct bonds, alkylenes containing from 2 to about 20 carbon atoms and selected from the group consisting of branched chain, straight chain, and cyclic alkylenes, alkylenes interrupted by one or more members selected from the group consisting of, —NR—, —O—, —S—, —SO$_2$—, —COO—, —OOC—, —CONR—, —NRCO—, —SO$_2$NR—, —NRSO$_2$—, —SiR$_2$—, alkylenes terminated with a member selected from the group consisting of —CONR— and —SO$_2$NR— in which case R_f is attached to the carbon or sulfur atom, and wherein R is selected from the group consisting of hydrogen, alkyl of from 1 to about 10 carbon atoms and hydroxyalkyl having 2 to about 10 carbon atoms, a and b are independently 0 or 1, M_1 is a nonionic hydrophilic monomer or mixture of nonionic hydrophilic monomers, and M_2 is an anionic hydrophilic monomer or mixture of anionic hydrophilic monomers, wherein x and y are both greater than zero, the sum of x+y is between about 5 and 200, and y/x+y is between about 0.01 and 0.98.

2. The concrete mix of claim **1** wherein M_1 is selected from the group consisting of acrylamide, methacrylamide, diacetone acrylamide, 2-hydroxyethyl methacrylate, derivatives of acrylic, methacrylic, maleic, fumaric and itaconic acids, amides, and vinyl esters containing from 1 to about 20 carbon atoms in the ester group.

3. The concrete mix of claim **1** wherein M_2 is selected from the group consisting of acrylic and methacrylic acids and salts thereof, maleic, fumaric and itaconic acids and salts thereof, acrylamidopropane sulfonic acid and salts thereof, and mono-olefinic sulfonic and phosphonic acids and salts thereof.

4. The concrete mix of claim **3** wherein M_1 is selected from the group consisting of acrylamide, methacrylamide, diacetone acrylamide, 2-hydroxyethyl methacrylate, derivatives of acrylic, methacrylic, maleic, fumaric and itaconic acids, amides, and vinyl esters containing from 1 to about 20 carbon atoms in the ester group.

5. The concrete mix of claim **1** wherein said foam stabilizing fluorinated surfactant is provided in said mix as a surfactant concentrate comprising an aqueous solution of a fatty acid alcohol or mixtures of fatty acid alcohols, a polysaccharide gum, a non-fluorinated anionic surfactant or mixtures of non-fluorinated anionic surfactants, and said foam stabilizing fluorinated surfactant.

6. The concrete mix of claim **5** wherein said surfactant concentrate further includes a solvent.

7. The concrete mix of claim **6** wherein said solvent is propylene glycol t-butyl ether.

8. The concrete mix of claim **5** wherein said fatty acid alcohol is selected from the group consisting of straight and branched chain fatty acid alcohols of about 8 to about 16 carbon atoms, said polysaccharide gum is selected from the group consisting of Rhamsan gums, Xanthan gums, Guar gums, and Locust Bean gums, and said non-fluorinated anionic surfactant is selected from the group consisting of non-fluorinated anionic surfactants comprising from about 8 to about 18 carbon atoms.

9. A method for producing a stabilized foam concrete mix comprising: adding to a concrete mix comprising from about 1 to about 50 percent by volume of cement, from about 0 to about 75 percent by volume of washed sand, from about 0 to about 60 percent by volume of coarse aggregate, from about 4 to about 50 percent by volume water, from about 0 to about 50 percent by volume of a member selected from the group consisting of cementitious and pozzolanic materials, from about 0 to about 20 oz of water reducer per 100 pounds of cementitious and pozzolanic material, and from about 0 to about 20 oz of accelerator per 100 pounds of cementitious and pozzolanic material, a foam aggregate comprising from about 1 to about 90 percent by volume of air as bubbles and comprising from about 0.01 to about 1.0 percent by weight of a foam stabilizing fluorinated surfactant of the formula

$$R_f—E_a—(S)_b—[M_1]_x—[M_2]_y—H$$

wherein R is a perfluorinated alkyl selected from the group consisting of straight chain, branched chain, and cyclic perfluoroalkylenes of 1 to about 20 carbon atoms, perfluoroalkyls substituted with perfluoroalkoxy of 2 to about 20 carbon atoms, perfluoroalkyl oligomers and polymers of greater than 10 carbon atoms, and mixtures thereof, E is selected from the group consisting of direct bonds, alkylenes containing from 2 to about 20 carbon atoms and selected from the group consisting of branched chain, straight chain, and cyclic alkylenes, alkylenes interrupted by one or more members selected from the group consisting of, —NR—, —O—, —S—, —SO$_2$—, —COO—, —OOC—, —CONR—, —NRCO—, —SO$_2$NR—, —NRSO$_2$—, —SiR$_2$—, alkylenes terminated with a member selected from the group consisting of —CONR— and —SO$_2$NR— in which case R_f is attached to the carbon or sulfur atom, and wherein R is selected from the group consisting of hydrogen, alkyl of from 1 to about 10 carbon atoms and hydroxyalkyl having 2 to about 10 carbon atoms, a and b are independently 0 or 1, M_1 is a nonionic hydrophilic monomer or mixture of nonionic hydrophilic monomers, and M_2 is an anionic hydrophilic monomer or mixture of anionic hydrophilic monomers, wherein x and y are both greater than zero, the sum of x+y is between about 5 and 200, and y/x+y is between about 0.01 and 0.98.

10. The method of claim **9** wherein M_1 is selected from the group consisting of acrylamide, methacrylamide, diacetone acrylamide, 2-hydroxyethyl methacrylate, derivatives of acrylic, methacrylic, maleic, fumaric and itaconic acids, amides, and vinyl esters containing from 1 to about 20 carbon atoms in the ester group.

11. The method of claim **9** wherein M_2 is selected from the group consisting of acrylic and methacrylic acids and salts thereof, maleic, fumaric and itaconic acids and salts thereof, acrylamidopropane sulfonic acid and salts thereof, and mono-olefinic sulfonic and phosphonic acids and salts thereof.

12. The method of claim **11** wherein M_1 is selected from the group consisting of acrylamide, methacrylamide, diacetone acrylamide, 2-hydroxyethyl methacrylate, derivatives of acrylic, methacrylic, maleic, fumaric and itaconic acids, amides, and vinyl esters containing from 1 to about 20 carbon atoms in the ester group.

13. The method of claim **9** wherein said foam stabilizing fluorinated surfactant is provided in said mix as a surfactant concentrate comprising an aqueous solution of a fatty acid alcohol or mixtures of fatty acid alcohols, a polysaccharide gum, a non-fluorinated anionic surfactant or mixtures of non-fluorinated anionic surfactants, and said foam stabilizing fluorinated surfactant.

14. The method of claim **13** wherein said surfactant concentrate further includes a solvent.

15. The method of claim **14** wherein said solvent is propylene glycol t-butyl ether.

16. The method of claim **13** wherein said fatty acid alcohol is selected from the group consisting of straight and branched chain fatty acid alcohols of about 8 to about 16 carbon atoms, said polysaccharide gum is selected from the group consisting of Rhamsan gums, Xanthan gums, Guar gums, and Locust Bean gums, and said non-fluorinated anionic surfactant is selected from the group consisting of non-fluorinated anionic surfactants comprising from about 8 to about 18 carbon atoms.

17. A concrete mix for the formation of a foamed concrete product comprising cement, water in an amount adequate to hydrate said cement, coarse aggregate, and a stabilized foam aggregate comprising from about 1 to about 90 percent by volume of air as bubbles comprising from about 0.01 to about 1.0 percent by weight of a foam stabilizing fluorinated surfactant of the formula

$$R_f—E_a—(S)_b—[M_1]_x—[M_2]_y—H$$

wherein R_f is a perfluorinated alkyl selected from the group consisting of straight chain, branched chain, and cyclic perfluoroalkylenes of 1 to about 20 carbon atoms, perfluoroalkyls substituted with perfluoroalkoxy of 2 to about 20 carbon atoms, perfluoroalkyl oligomers and polymers of greater than 10 carbon atoms, and mixtures thereof, E is selected from the group consisting of direct bonds, alkylenes containing from 2 to about 20 carbon atoms and selected from the group consisting of branched chain, straight chain, and cyclic alkylenes, alkylenes interrupted by one or more members selected from the group consisting of, —NR—, —O—, —S—, —SO_2—, —COO—, —OOC—, —CONR—, —NRCO—, —SO_2NR—, —NRSO_2—, —SiR_2—, alkylenes terminated with a member selected from the group consisting of —CONR— and —SO_2NR— in which case R_f is attached to the carbon or sulfur atom, and wherein R is selected from the group consisting of hydrogen, alkyl of from 1 to about 10 carbon atoms and hydroxyalkyl having 2 to about 10 carbon atoms, a and b are independently 0 or 1, M_1 is a nonionic hydrophilic monomer or mixture of nonionic hydrophilic monomers, and M_2 is an anionic hydrophilic monomer or mixture of anionic hydrophilic monomers, wherein x and y are both greater than zero, the sum of x+y is between about 5 and 200, and y/x+y is between about 0.01 and 0.98.

18. The concrete mix of claim **17** wherein M_1 is selected from the group consisting of acrylamide, methacrylamide, diacetone acrylamide, 2-hydroxyethyl methacrylate, derivatives of acrylic, methacrylic, maleic, fumaric and itaconic acids, amides, and vinyl esters containing from 1 to about 20 carbon atoms in the ester group.

19. The concrete mix of claim **17** wherein M_2 is selected from the group consisting of acrylic and methacrylic acids and salts thereof, maleic, fumaric and itaconic acids and salts thereof, acrylamidopropane sulfonic acid and salts thereof, and mono-olefinic sulfonic and phosphonic acids and salts thereof.

20. The concrete mix of claim **19** wherein M_1 is selected from the group consisting of acrylamide, methacrylamide, diacetone acrylamide, 2-hydroxyethyl methacrylate, derivatives of acrylic, methacrylic, maleic, fumaric and itaconic acids, amides, and vinyl esters containing from 1 to about 20 carbon atoms in the ester group.

21. The concrete mix of claim **17** wherein said foam stabilizing fluorinated surfactant is provided in said mix as a surfactant concentrate comprising an aqueous solution of a fatty acid alcohol or mixtures of fatty acid alcohols, a polysaccharide gum, a non-fluorinated anionic surfactant or mixtures of non-fluorinated anionic surfactants, and said foam stabilizing fluorinated surfactant.

22. The concrete mix of claim **21** wherein said surfactant concentrate further includes a solvent.

23. The concrete mix of claim **22** wherein said solvent is propylene glycol t-butyl ether.

24. The concrete mix of claim **21** wherein said fatty acid alcohol is selected from the group consisting of straight and branched chain fatty acid alcohols of about 8 to about 16 carbon atoms, said polysaccharide gum is selected from the group consisting of Rhamsan gums, Xanthan gums, Guar gums, and Locust Bean gums, and said non-fluorinated anionic surfactant is selected from the group consisting of non-fluorinated anionic surfactants comprising from about 8 to about 18 carbon atoms.

* * * * *

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(54) **CONCRETE MIXTURES HAVING HIGH FLOWABILITY**

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See application file for complete search history.

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(57) **ABSTRACT**

A viscosity modifying agent is added to a concrete mixture to give the concrete desirable rheological properties. The viscosity modifying agent is incorporated into a foam admixture before it is mixed into the concrete. Because the viscosity modifying agent is a component of the foam admixture, the viscosity modifying agent is dispersed in the aqueous film that forms the foam bubbles. The viscosity modifier in the foam bubbles gives the foam beneficial rheological properties. The viscosity modifier performs more efficiently when included in the foam bubbles as compared to being mixed directly into the concrete. The foam bubbles containing the viscosity modifier can be stabilized using a fluorochemical stabilizer, which is included in the foam admixture. The foam bubbles can be further stabilized with respect to cement mixtures by including a hydration stabilizing in the cement mixture.

31 Claims, No Drawings

CONCRETE MIXTURES HAVING HIGH FLOWABILITY

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Patent Application Ser. No. 60/715,458, filed Sep. 9, 2005, entitled "Concrete Mixtures Having Aqueous Foam Admixtures," the disclosure of which is incorporated herein in its entirety.

BACKGROUND OF THE INVENTION

1. The Field of the Invention

The present invention relates to flowable concrete mixtures and cured concrete obtained therefrom. More particularly, the present invention relates to concrete mixtures that have an aqueous based foam admixture that includes a viscosity modifier.

2. Related Technology

Concrete mixtures are composite materials that are usually composed of water, cement, and aggregate. Common aggregates include sand, gravel, or crushed stone. Concrete is a well-known structural component with typical compressive strengths of about 2500 psi, when cured.

Admixtures are often added to concrete to give the concrete mixture and or the cured concrete desired properties. For example, admixtures can be used to lower the concrete's density, improve the concrete's workability, improve the concrete's strength to weight ratio, give the concrete insulating properties, and/or enhance the acoustic properties of the concrete, among others. These beneficial properties are often accomplished by adding several different admixtures.

Viscosity modifying agents (VMA), also known as viscosity modifiers, Theological modifiers, and rheology modifying agents, can be added to the concrete mixture to facilitate uniform flow of the particles and reduces bleed, or free water formation. Viscosity modifiers are often water-soluble polymers and function by increasing the apparent viscosity of the mix water.

Viscosity modifiers are particularly useful for concrete mixtures that are highly flowable. Water and water reducers are added to concrete mixtures to make the mixture flowable. However, there is a limit to the amount of water and water reducers that can be added to the concrete mixture before the components (e.g. aggregate) begin to separate. Viscosity modifiers are flowable but viscous. The viscosity modifiers help to suspend aggregates and other components in the mixture, thereby holding the mixture together.

Despite the beneficial properties of viscosity modifiers, viscosity modifiers are not widely used in concrete because the amount of viscosity modifier that must be added to see beneficial results is often cost prohibitive. Currently, the use of viscosity modifiers is mostly limited to high performance concrete mixes such as so called self-compacting concrete (SCC mixtures).

The flowability and consistency of SCC mixtures is such that the mixture will consolidate or compact without the need to vibrate the concrete after it has been placed. Consolidating the concrete to remove air bubbles is important to maintain the integrity and strength of the cured concrete. Since SCC mixtures self compact, these mixtures require less manpower and avoid human error associated with manually vibrating the placed concrete. Unfortunately, the cost of making SCC mixtures often outweighs the benefits of SCC mixtures. The viscosity modifier is a significant cost in making SCC concrete. The cost of the viscosity modifier is in large part a consequence of the amount of viscosity modifier that has to be added to obtain the desired results. For example, SCC mixtures often include 15-20 oz of viscosity modifier per 100 lbs cement to achieve the desired rheological effect.

BRIEF SUMMARY OF THE INVENTION

The present invention relates to flowable concrete mixtures comprising a viscosity modifying agent. The viscosity modifying agent is incorporated into a foam admixture, which is mixed into the concrete. Because the viscosity modifying agent is a component of the foam admixture, the viscosity modifying agent is dispersed in the aqueous film that forms the foam bubbles. The viscosity modifier in the foam bubbles creates cohesion between the liquid phase of the concrete and the solid phase of the concrete. The concrete mixture can be made highly flowable using water and/or water reducers without causing segregation.

By incorporating the viscosity modifier into the foam admixture, the amount of viscosity modifier needed to provide the desired cohesion and dispersion of the solid and liquid phases of the concrete is surprisingly much less than the amount needed to achieve the same properties if the viscosity modifier is mixed directly into the concrete mixture. It is currently believed that less viscosity modifier is needed to achieve desired results because the viscosity modifier is in a thin film, which increase the interface between the viscosity modifier and the components of the concrete mixtures (e.g. aggregate). Consequently, providing the viscosity modifier in the thin film of the foam bubbles allows the viscosity modifier to be used more efficiently in the concrete mixture.

In one embodiment, the foam admixtures of the present invention are incorporated into a concrete mixture having a high flow spread as measured using a 12 inch slump cone. In a preferred embodiment, the concrete mixture has a flow spread greater than about 12 inches, more preferably greater than about 24 inches and more preferably greater than 30 inches. The viscosity modifier in the foam helps disperse the aggregate and cement throughout the spread. In a preferred embodiment, the spread is substantially homogenous with respect to the aggregate and cement.

In a preferred embodiment, a fluorochemical surfactant is added to the foam admixture to stabilize the foam bubbles. This stabilization prevents the foam bubbles from bursting, which ensures the efficient use of the viscosity modifier in foam bubbles. Fluorochemical surfactants compounds have been used in firefighting foams to generate foams suitable for spraying on burning chemicals. The aqueous nature of these foams and the stability of the foam bubbles make these foams particularly useful in the concrete mixtures of the present invention. The use of at least one such foam in a concrete mixture is described in U.S. Pat. No. 6,153,005 to Welker et al., which is incorporated herein by reference.

In addition to the fluorochemical surfactant, the foam bubbles can be stabilized with respect to the hydraulic cement. Over a period of time, the hydraulic cement in the concrete can destroy the foam bubbles and thus the beneficial effect of the viscosity modifier. The inventor of the present invention has found that a hydration stabilizer can be added to the concrete mixture to inhibit the hydration of the hydraulic cement thereby inhibiting deleterious interactions between the cement and the aqueous foam that can destroy the foam bubbles. The stabilizing effect of the hydration stabilizer allows the foam to be successfully combined with concrete mixtures and/or allows the foam to last longer in the concrete mixture.

The hydration stabilizer used in the present invention includes a hydration retarder that can slow or stop hydration of the siliceous and/or aluminous component of hydraulic cements. Preferred hydration stabilizers are those that can bind calcium, such as derivatives of phosphonic acid and carboxylic acids having hydroxyl or amino groups. Because of the retarding effect that the hydration retarder can have on setting, the hydration stabilizer may also include an accelerator.

The stabilizing effect of the hydration stabilizer is distinct and in-addition to the stabilizing effect of the fluorochemical surfactant. The fluorochemical surfactant is a component of the foam bubble and provides stability within the bubble. In contrast, the hydration stabilizer is a component of the concrete mixture to prevent deleterious interactions between the cement and the aqueous foam. Stabilizing the foam using the hydration stabilizer can be particularly beneficial for concrete mixtures used in applications that require relatively long initial set times (e.g. ready mix applications).

The resulting concrete compositions have many improved properties, including decreased permeability, decreased shrinkage, decreased absorption and bleeding, improved acoustic properties, lower densities, and increased initial flowability. The concrete mixtures also have reduced water migration, which improves the hydration of cement and can improve the reaction between free lime and pozzolans. The concrete mixtures also have improved aesthetics due to a reduction in rock pockets.

These and other features of the present invention will become more fully apparent from the following description and appended claims.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

I. Introduction

The present invention relates to cement mixtures having a viscosity modifying agent to give the concrete desirable Theological properties. The viscosity modifying agent is incorporated into a foam admixture before it is mixed into the concrete. Because the viscosity modifying agent is a component of the foam admixture, the viscosity modifying agent is dispersed in the aqueous film that forms the foam bubbles. The viscosity modifier performs more efficiently when included in the foam bubbles as compared to being mixed directly into the concrete.

For purposes of the present invention, “flow spread” is a measurement of the flow of a concrete mixture on a horizontal surface as determined using a 12 inch slump cone in a manner known in the art, (e.g. according to the ASTM C 143 standard, which is incorporated herein by reference). The measurement does not include the distance traveled by water that has segregated from the cement paste.

For purposes of the present invention, the “initial set time” occurs when the concrete reaches a compressive strength of 500 psi.

For purposes of the present invention, the term “air” includes all gases including mixtures of gases and pure gasses, whether obtained from the atmosphere or generated by chemical reaction.

II. Concrete Mixtures

The concrete mixtures of the present invention can have very different compositions depending on the desired use for the concrete. However, in general, the concrete mixtures of the present invention include at least hydraulic cement, water (either from the foam or added separately), an aggregate, and

an aqueous foam admixture that includes a viscosity modifier. In a preferred embodiment, the concrete mixtures also include a fluorochemical stabilizer in the foam admixture to stabilize the foam bubbles and/or a hydration stabilizer in the concrete mixture to stabilize the foam bubbles with respect to the hydraulic cement. Other admixtures can also be included in the concrete mixtures to give the mix desired properties.

A. Hydraulic Cement and Water

The cement included in the concrete mixtures of the present invention is a hydraulic material such as Portland cement, modified Portland cement, or masonry cement. For purposes of this invention, Portland cement includes all cementitious compositions which have a high content of tricalcium silicate, including Portland cement, cements that are chemically similar or analogous to Portland cement, and cements that fall within ASTM specification C-150-00. Other cementitious materials include ground granulated blast-furnace slag, hydraulic hydrated lime, white cement, slag cement, calcium aluminate cement, silicate cement, phosphate cement, high-alumina cement, magnesium oxychloride cement, and combinations of these and other similar materials.

Water is added to the concrete mixture in sufficient amounts to hydrate the cement. Additional water can also be added to give the concrete added slump or flowability. The amount of additional water will depend on the desired flowability and on the amounts and types of admixtures included in the concrete composition, particularly the amount of water reducers, which are discussed below. Typically, it is desirable to add as little of additional water as possible since excess water in the concrete mixture is known to weaken the cured concrete. In general, suitable amounts of water for hydrating the cement ranges from about 1% to about 50%, more preferably about 5-50%, and most preferably about 10% to about 25% of the concrete mixture by weight.

B. Foam Admixtures

The foams used in the concrete mixtures of the present invention include water, air, and at least one foaming agent (e.g. surfactant), and a viscosity modifier. The foam admixtures comprise a plurality of cellular bubbles that trap air in the concrete and provide the uncured concrete with desired properties such as flowability and/or workability and provide the cured concrete with properties such as increased strength and/or resistance to cracking during freeze thaw cycles.

The foams of the present invention can be made from a foaming concentrate. A detailed description of how to make the aqueous foam admixture using a foaming concentrate, air, and water is described below in connection with the methods of the present invention and the examples.

The composition of the foaming concentrate is in large part responsible for the properties of the foam admixture. The following is a description of suitable foaming concentrate compositions. In addition to the viscosity modifier, the foaming concentrates typically include a foaming agent, solvents, and other surfactants, and/or additives that allow the foaming concentrate to form foam bubbles that can be added to concrete.

1. Foaming Concentrates

(a) Foaming Agents and Solvents

The foaming concentrates include at least one foaming agent suitable for forming an aqueous based foam. Typical foaming agents include ionic, cationic, anionic surfactants, natural and synthetic resins, fatty acids, proteinaceous material, sulfonated hydrocarbons, and the like. In an exemplary embodiment, the foaming concentrate comprises a combination of foaming agents and/or solvents. In an exemplary embodiment, the foaming agent can comprise a non-fluorinated anionic surfactant preferably selected from the group consisting of C_8 to C_{18} anionic surfactants and most preferably, C_{10} to C_{18} alpha olefin sulfonates, as well as mixtures of these surfactants.

Suitable solvents include glycol ethers and fatty alcohols preferably selected from the group consisting of straight and branched chain fatty alcohols of about 8 to about 16 carbon atoms and mixtures thereof. Specifically preferred as the solvent, if used, is propylene glycol t-butyl ether. The preferred fatty alcohol comprises a mixture of equal parts n-dodecanol, n-tetra decanol and n-hexadecanol. Preferred as the anionic surfactant are mixtures of sodium alkenyl sulfonate, sodium tetradecene sulfonate, and sodium hexadecene sulfonate in a ratio of about 4:1:1.

Other ingredients can be employed in the composition of the surfactant formulation to effect specific environmental or shelf-life concerns. Examples of such ingredients are freezing point depressants, such as ethylene glycol, and preservatives, such as that available under the trade name DOWICIDE (Dow Chemical Company).

There are many other known foaming concentrates that can be used with the present invention. Suitable foaming surfactant concentrates include cellulose based concentrates (e.g. "CELLUCON" (Romaroda Chemicals)) and hydrolyzed protein based concentrates (e.g. MEARL (The Mearl Corporation)).

The foam concentrates include surfactants and additives that lead to foams with sufficient mechanical stability to withstand the mixing involved in making concrete compositions. The foregoing concentrates, if needed, can be structurally strengthened (i.e. stabilized) using a fluorochemical surfactant as described below, or other similar stabilizing additive.

(b) Viscosity Modifiers

Viscosity modifying agents, also known as rheological modifiers or rheology modifying agents, can be included in the foaming concentrates of the present invention to give the foam admixture improved rheological properties. The viscosity modifiers are usually water-soluble polymers and function by increasing the apparent viscosity of the mix water. This enhanced viscosity facilitates uniform flow of the aggregates and reduces bleed, or free water formation, on the fresh paste surface.

Suitable viscosity modifiers that can be used in the present invention include, for example, cellulose ethers (e.g., hydroxyethyl cellulose (HEC), hydroxyproplmethyl cellulose (HPMC), sodium carboxymethyl cellulose (CMC), carboxymethylhydroxyethyl cellulose (CMHEC), and the like); synthetic polymers (e.g., polyacrylates, polyvinyl alcohol (PVA), polyethylene glycol (PEG), and the like); exopolysaccharides (also known as biopolymers, e.g., welan gum, xanthan, rhamsan, gellan, dextran, pullulan, curdlan, and the like); marine gums (e.g., algin, agar, carrageenan, and the like); plant exudates (e.g., locust bean, gum arabic, gum Karaya, tragacanth, Ghatti, and the like); seed gums (e.g., Guar, locust bean, okra, psyllium, mesquite, and the like); starch-based gums (e.g., ethers, esters, and related derivatized compounds). See, for example, Shandra, Satish and Ohama, Yoshihiko, "Polymers In Concrete", published by CRC press, Boca Ration, Ann Harbor, London, Tokyo (1994).

Viscosity modifying agents are typically used with water reducers in highly flowable mixtures to hold the mixture together. Viscosity modifiers can disperse and/or suspend components of the concrete thereby assisting in holding the concrete mixture together. This property of viscosity modifiers makes them useful for making self compacting concrete, which requires high flowability. The viscosity modifier allows water reducers to be added to the concrete mixture without causing the concrete to segregate.

One or more of the same or a different viscosity modifier can be directly mixed into the concrete mixture (i.e. apart from the viscosity modifier in the foam). The amount of viscosity modifier directly mixed into the concrete mixture is typically much less when a viscosity modifier is included in the foam admixture. In a preferred embodiment, the amount of viscosity modifier added in addition to the viscosity modifier in the foam is less than 12 oz/(100 lbs cement), more preferably less than 9 oz, even more preferably less than about 5 oz, and most preferably substantially no viscosity modifier is added apart from the foam admixture.

In addition to benefiting the concrete composition, the viscosity modifiers in the foam can be useful because they form a membrane on the surface of solvents that protects the rest of the foam from collapsing. The thixotropic character of some viscosity modifiers can also aid in pumpability of the concrete mixture.

(c) Foam Stabilizing Surfactants

In an exemplary embodiment the foam concentrate includes a fluorochemical foam stabilizing surfactant. Fluorochemical foam stabilizing surfactants are well known in the art of fire fighting foams (e.g. U.S. Pat. Nos. 4,472,286; 4,717,744; and 4,859,349; which are incorporated herein by reference). Particularly useful fluorochemical surfactants are those described in U.S. Pat. Nos. 4,460,480 and 5,218,021 to Kleine et al., and Clark et al., respectively, which are incorporated herein by reference, and which discloses an oligomer surfactant that includes (i) a fluorinated hydrocarbon monomer, (ii) a hydrophilic nonionic monomer, and (iii) a hydrophilic anionic monomer.

Examples of suitable fluorinated hydrocarbon monomer include (i) straight chain, branched chain, or cyclic perfluoroalkyls of 1 to about 20 carbon atoms, (ii) perfluoroalkyls substituted with perfluoroalkoxy groups of 2 to about 20 carbon atoms, (iii) a perfluoroalkyl oligomers or polymers of greater than 10 carbon atoms, or (iv) monomers of the like and/or combination thereof.

Many non-ionic hydrophilic monomers suitable for use in the present invention are known and commercially available. Particularly useful non-ionic hydrophilic monomers include acrylamide, methacrylamide, diacetone acrylamide, and 2-hydroxyethyl methacrylate. Other examples of such monomers include derivatives of acrylic, methacrylic, maleic, fumaric, and itaconic acids, such as hydroxyalkyl esters of acrylic acids; amides such as N-vinyl-pyrrolidone, N-(hydroxyalkyl)-acrylamides, or N-(hydroxyalkyl)-methacrylamides; and vinyl esters with 1-20 carbons in the ester group such as vinyl acetate, butyrate, laurate, or stearate. The above listed non-ionic hydrophilic monomers can be used alone or in combination with each other as well as in combination with suitable anionic hydrophilic monomers described below. Some non-ionic hydrophilic monomers may require a co-monomer for polymerization, such as di(hydroxyalkyl) maleates with ethoxylated hydroxyalkyl maleates.

Many anionic hydrophilic monomers that co-oligomerize with non-ionic hydrophilic monomers are known and are commercially available. Particularly useful anionic hydrophilic monomers include acrylic and methacrylic acids and salts thereof. Other examples of such monomers include maleic, fumaric, and itaconic acids and salts thereof; acrylamidopropane sulfonic acid and salts thereof; and mono-olefinic sulfonic and phosphonic acids and salts thereof.

Oligomers made using the foregoing fluorinated hydrocarbon monomers and hydrophilic monomers are particularly advantageous when used with foams in the concrete mixtures of the present invention. These oligomers are particularly useful for dispersing and/or suspending the cement and/or aggregates in the concrete mixture. By dispersing and/or suspending these and other components of the concrete mixture, the resulting cured concrete has improved strength and resistance to cracking.

In an exemplary embodiment, the fluorochemical foam stabilizers of the present invention can be characterized by chemical moieties represented by the general formula, $R_f\text{-}E_a\text{-}(S)_b\text{-}[M_1]_x\text{-}[M_2]_y\text{-H}$ (Formula I), and mixtures thereof, wherein:

R_f is (i) a straight chain, branched chain, or cyclic perfluoroalkyl of 1 to about 20 carbon atoms, (ii) a perfluoroalkyl substituted with a perfluoroalkoxy of 2 to about 20 carbon atoms, (iii) a perfluoroalkyl oligomer or polymer of greater than 10 carbon atoms (e.g. hexafluoropropylene oxide), or (iv) a mixture of perfluoroalkyl moieties;

E_a is (i) a direct bond, (ii) a branched, straight chain, or cyclic alkylene of 2 to about 20 carbon atoms, (iii) the alkylene of (ii) interrupted by one or more groups selected from the group consisting of —NR—, —C—, —S—, —SO_2—, —COO—, —OOC—, —CONR—, —NRCO—, —SO_2NR—, —$NRSO_2$—, —SiR_2—; or (iii) the alkylene of (ii) terminated at the R_f end with —CONR— or —SO_2NR—;

R is independently hydrogen, an alkyl of 1-10 carbon atoms, or a hydroxyalkyl of 2 to 10 carbon atoms; and

a and b are independently 0 or 1; -$[M_1]$- represents a nonionic hydrophilic monomer unit; -$[M_2]$- represents an anionic hydrophilic monomer unit; and x and y represent the number of monomer units present in the co-oligomers and are both greater than 0; the sum of x and y being between 5 and 200, and y/(x+y) being between 0.01 and 0.98.

Formula (I) does not necessarily depict the actual sequence of the oligomer or macromer units since the units can be randomly distributed throughout. It is also assumed that the monomers for M_1 and M_2 are known as described above.

(d) Exemplary Foaming Concentrates

Table 1 below sets forth exemplary foaming concentrates according to the present invention. In Table 1, column 1 specifies the useful ranges for each component, column 2 specifies preferred ranges for each of the components and column 3 describes the highly preferred ranges for each of the components. In Table 1, all compositions are in parts by weight. The fluorochemical surfactant is normally supplied as a solution in an alcohol such as tert-butyl alcohol.

TABLE 1

	1	2	3
Solvent	0-50%	0-20%	1-10%
Fatty Alcohol	0.1-10%	0.1-1.0%	0.2-1.0%
Viscosity Modifier	0.1-10%	0.1-5.0%	0.5-4.0%
Anionic Surfactant	0.1-50%	0.1-20%	0.5-8.0%
Fluorochemical	0.1-15%	0.1-5.0%	0.5-3.0%
Water	Balance	Balance	Balance

A particularly useful foaming concentrate that includes a fluorochemical surfactant is sold by Miracon Technologies, Inc. under the trademark Miracon®.

C. Hydration Stabilization

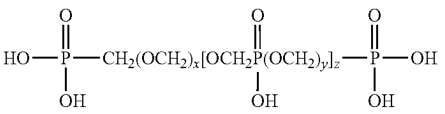
The hydration stabilizer (also known as an extended set retarder) of the present invention is used to inhibit the hydration of the hydraulic cement. The hydration stabilizer slows the rate of hydrate formation by tying up (i.e. chelating, complexing, or otherwise binding) calcium ions on the surface of cement particles. The hydration stabilizer includes a hydration retarder that forms a protective barrier around cementitious particles. The hydration retarder bonded to the cement particles acts as a dispersant preventing hydrates from flocculating and setting. This barrier prevents the hydraulic cement from obtaining initial set.

Another feature of the hydration stabilizer is that it degrades and/or is inactivated over time such that hydration of the cement eventually occurs. Preferably the release of the hydraulic cement is progressive over time so as to provide a controlled release of the cement and an ascertainable delay in set time.

The hydration stabilizer preferably comprises a calcium chelating compound such as a polyphosphonic acid or a carboxylic acid that contains hydroxyl and/or amino groups. Polyphosphonic acids and similar compounds can be particularly advantageous because of their controlled degradation in the concrete mixture over an extended period of time that allows for a timed setting of the concrete.

Suitable examples of hydration stabilizers include N-nitrilo tris(methylene phosphonic acid); 1,2-ethanediyl bis[nitrilo di(methylene phosphonic acid)]; 1,6-hexanediyl bis[nitrilo di(methylene phosphonic acid)] and the like.

Another class of suitable phosphonic acid hydration stabilizing compounds include polymethoxy polyphosphonic acids represented by the formula II



$$\text{HO}-\underset{\text{OH}}{\overset{\text{O}}{\overset{\|}{\underset{|}{\text{P}}}}}-\text{CH}_2(\text{OCH}_2)_x[\text{OCH}_2\underset{\text{OH}}{\overset{\text{O}}{\overset{\|}{\underset{|}{\text{P}}}}}(\text{OCH}_2)_y]_z-\underset{\text{OH}}{\overset{\text{O}}{\overset{\|}{\underset{|}{\text{P}}}}}-\text{OH}$$

wherein x and y are each an integer of from 1-3, and preferably 1, and z is an integer of 0 or 1. It is understood that when z is 0 the radical within the bracket is non-existent and, therefore $(OCH_2)_y$ is nonexistent. The preferred polymethoxy polyphosphonic acid compounds are represented by the above formula when z=0 and x is 1-3. Other suitable polymethoxy polyphosphoic acid compounds are disclosed in U.S. Pat. No. 5,215,585, which is incorporated herein by reference.

A particularly useful hydration stabilizer is amino tris (methylene phosphonic acid), which is a component of the commercially available hydration stabilizer sold by Master Builders under the trademark Delvo. Illustrative examples of hydration stabilizers, including some of those mentioned above, are set forth in U.S. Pat. Nos. 5,427,617 and 5,203,919, which are incorporated herein by reference. Hydration retarders and accelerators suitable for use as hydration stabilizers are also disclosed in U.S. Pat. No. 6,858,074, which is also incorporated herein by reference.

As mentioned, the hydration stabilizer of the present invention prevents or inhibits setting and then degrades or is released from the cement to provide controlled setting. In some cases, it is necessary that the hydration stabilizer also comprise an accelerator to cause the controlled hydration of the cement. The amount of accelerator that needs to be added depends on several factors, such as the amount of hydration retarder, cement type and reactivity, ambient temperature, concrete mixture proportions, and the presence or absence of certain admixtures in the concrete mixture, such as water reducing polymers.

Accelerators that can be used to activate the hydraulic cement can be selected from conventional cement accelerators such as those classified as ASTM C 494 Type C admixtures. These include alkali metal halides (calcium chloride and the like), alkali metal nitrites (calcium nitrite and the like), alkali metal nitrates (calcium nitrate and the like), alkali metal formates (calcium formate and the like), alkali metal thiocyanates (sodium thiocyanate and the like), triethanolamine and the like. The particular set accelerator to be used will depend on the known nature of the accelerators and side effects of the agent. For example, where metal corrosion is not a problem, calcium chloride might be chosen, while if corrosion is a problem, the nitrite or nitrate salts might be better used. The preferred accelerators are calcium nitrate and the like.

The accelerating agent should be added in amounts which effectively cause the combined cement mixture to set and provide conventional 28 day strength for such compositions (e.g. mortars of about 2000-4000 psi; concrete of about 2,500 to 10,000 psi). The amount, based on cement content, should be from about 0.5 to about 6 weight percent, preferably from about 1 to about 5 percent.

The hydration stabilizer is mixed with the cement mixtures in amounts effective to prevent the hydraulic cement from reacting with the aqueous foam for a desired period of time. The specific effective amount depends on the amount and type of cement and the desired amount of stabilization. Preferably, a sufficient amount of hydration stabilizer is included in the concrete mixture to stabilize substantially all of the cement. Suitable amounts typically require from about 1.5 oz to about 8.0 oz per hundred lbs of cement, more preferably about 3.0 oz to about 6 oz, for a concrete mix having a 28 day cure time. The stabilization can be extended by adding about 4 oz of hydration stabilizer per 100 lbs cement per hour of extension.

Hydration stabilizers are known and used in the concrete industry for waste water reclamation and for reusing concrete mixtures. Currently, hydration stabilizers are added to concrete waste water so that the truck or other mixing machinery does not have to be washed out after use or so that the remaining concrete can be used on another job. The hydration stabilizer prevents setting until the cement can be reused. The inventor of the present invention has found that the properties and concentrations of hydration retarders used in these known hydration stabilizing compositions are surprisingly advantageous for stabilizing foam, admixtures according to the present invention. Commercially available hydration stabilizers, in addition to Delvo mentioned above, include Recover (W.R. Grace), Delayed Set (Fritz-Pak Corp.), Stop-Set and Stop-Set L (Axim Italcementi Group), and Polychem Renu (General Resource Technology).

D. Dispersants and/or Water-Reducers

Water reducers are used in concrete mixtures to lower the water content in the. plastic concrete (i.e. uncured concrete) to increase its strength and to obtain higher slump without adding water. Water-reducers will generally reduce the required water content of a concrete mixture for a given slump and are useful for pumping concrete and in hot weather to offset the increased water demand. These admixtures disperse the cement particles in the concrete and make more efficient use of the hydraulic cement. This dispersion increases strength and/or allows the cement content to be reduced while maintaining the same strength. Water-reducers should meet the requirements for Type A in ASTM C 494 Specification.

Another class of water reducers includes mid-range water reducers. These water reducers have a greater ability to reduce the water content of the concrete and are often used because of their ability to improve the finishability of concrete flatwork. Mid-range water reducers should at least meet the requirements for Type A in ASTM C 494.

High range water-reducers (HRWR), also referred to as superplasticizers, are a special class of water-reducer. HRWRs reduce the water content of a given concrete mixture by about 12% to 30%. HRWRs are used to increase strength and reduce permeability of concrete by reducing the water content in the mixture or greatly increase the slump to produce “flowing” concrete without adding water. HRWRs are often used for high strength and high performance concrete mixture that contain higher contents of cementitious materials and mixtures containing silica fume. In a typical concrete mixture, adding a normal dosage of HRWRs to a concrete mixture with a slump of 3 to 4 inches (75 to 100 mm) will produce a concrete with a slump of about 8 inches (200 mm). Exemplary HRWRs that can be used in the present invention are covered by ASTM Specification C 494 and types F and G, and Types I and 2 in ASTM C 1017. Particularly advantageous dispersants include the HRWRS described in U.S. Pat. No. 6,858,074, which is incorporated herein by reference.

It is believed that water reducing dispersants may have a particularly beneficial effect on the concrete compositions of the present invention by working in conjunction with the hydration stabilizer to stabilize the foam admixtures of the present invention.

E. Aggregates

Aggregates are included in the concrete mixture to add bulk and to give the concrete strength. The aggregate can be a fine aggregate and/or a coarse aggregate. The fine aggregates are materials that pass through a Number 4 sieve (ASTM C125 and ASTM C33), such as silica sand. The coarse aggregate 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.

Whether an aggregate needs to be added can depend on the desired use of the cured concrete and on the type of aqueous foam admixture that is used. Some aqueous foam admixtures of the present invention are sufficiently stabilized to function as a foam aggregate. For example, the air bubbles in aqueous foams that are stabilized with a fluorochemical surfactant can have sufficient strength to act as a foam aggregate. In particular, foams stabilized with fluorochemical surfactants that include hydrophilic nonionic and hydrophilic anionic monomers are particularly suited to act as foam aggregates. It is believed that the anionic and nonionic monomers and/or the viscosity modifiers in the foam bubbles are able to disperse the hydraulic cement around the foam bubbles thereby creating a cement matrix similar to the cement matrix that forms around aggregates.

The concrete mixtures of the present invention also include concrete mixtures that include traditional aggregates (i.e. coarse and fine aggregates) in combination with foam aggregates (e.g. aqueous foams stabilized with surfactants having nonionic and anionic monomers). Concrete mixtures of the present invention that incorporate a combination of foam aggregates with fine aggregates and/or coarse aggregates can be made to have superior compressive and flexural strength and/or can include ratios of aggregate sizes that are not possible with traditional concrete mixtures.

For example, ready mixed concrete used in flat work or foundation walls typically has a ratio of fine aggregates to coarse aggregates of 50:50. This ratio can be usually be modified to ratios from 60:40 to 40:60. Using the aqueous foams stabilized with a fluorochemical surfactant, the concrete mixtures of the present invention can be made using ratios of less than 40% of either fine aggregates or coarse aggregates while still maintaining ASTM standards for flexural and compressive strength. In an exemplary embodiment, the aggregate can comprise less than 40% fine aggregate, less than 30% fine aggregate, less than 20% fine aggregate or even substantially no fine aggregate. Alternatively, the aggregate can comprise less than 40% coarse aggregate, less than 30% coarse aggregate, less than 20% coarse aggregate, or even substantially no coarse aggregate. Even with these low percentages of coarse or fine aggregate, a compressive strength of greater than 2500 psi, more preferably greater than 3000 psi, or most preferably greater than 4000 psi can be achieved.

The use of only one size of aggregate is particularly beneficial in areas where both coarse and fine aggregates are not available or a particular size aggregate is in abundance. Also, the concrete mixtures of the present invention are particularly useful for incorporating certain aggregates sizes such as ⅜ inch gravel (i.e. pea gravel), that cannot be used in some concrete mixtures because it leads to lower quality concrete. With the concrete mixtures of the present invention, pea gravel can be used while still maintaining suitable compressive strength (e.g. 3000-4000 psi).

Thus, using the foam aggregates of the present invention, novel combinations of aggregates can be used to make concrete having suitable strength for ready mixed concrete and other applications.

F. Fly Ash

Fly ash is another admixture that can be included in the concrete mixtures of the present invention. ASTM C618 standard, which is incorporated herein by reference, recognizes two major classes of fly ashes for use in concrete—Class C and Class F. These two classes of fly ashes are derived from different kinds of coals that are a result of differences in the coal formation processes occurring over geological time periods. Class F fly ash is normally produced from burning anthracite or bituminous coal, whereas Class C fly ash is normally produced from lignite or sub-bituminous coal. The ASTM C618 standard differentiates Class F and Class C fly ashes primarily according to their pozzolanic properties. Accordingly, in the ASTM C618 standard, the major specification difference between the Class F fly ash and Class C fly ash is the minimum limit of $SiO_2+Al_2O_3+Fe_2O_3$ in the composition. The minimum limit of $SiO_2+Al_2O_3+Fe_2O_3$ for Class F fly ash is 70% and for Class C fly ash is 50%. Thus, Class F fly ashes are more pozzolanic than the Class C fly ashes. Although not explicitly recognized in the ASTM C618 standard, Class C fly ashes typically contain high calcium oxide content. Presence of high calcium oxide content makes Class C fly ashes possess cementitious properties leading to the formation of calcium silicate and calcium aluminate hydrates when mixed with water. The use of Class C fly ash can be particularly useful to replace a portion of the cement in the concrete. Class C fly ash and Portland cement can be blended in weight ratios of ash to cement of about 0/100 to 150/100, preferably 75/100 to 125/100. In some reactive powder blends the portland cement is about 40 to 80 wt % and fly ash 20 to 60 wt %.

Because fly ash is obtained from coal combustion or found naturally, fly ash can include a certain amount of carbon. The amount of carbon in fly ash is measured according loss of ignition (LOI). Fly ash that has an LOI greater than about 1.5 is typically not suitable for use with concrete mixtures that have air entraining agents because the carbon destroys the air entrainment. The inventor of the present invention has found that the foam admixtures of the present invention that are stabilized with a fluorochemical surfactant are surprisingly resistant to destruction by high carbon fly ash. Thus, in one embodiment of the invention, the concrete mixture includes a fly ash having an LOI greater than about 1.5, more preferably greater than about 2, more preferably greater than 4, and most preferably greater than about 6. It has also been found that high carbon fly ash when used in combination with the fluorochemical stabilized foam admixtures of the present invention, increases the strength of the cured concrete over fly ash that is not high carbon.

G. Other Admixtures

Many other types of admixtures can be added to the concrete compositions of the present invention to give the concrete a desired property. As discussed below, other admixtures suitable for use in the concrete mixtures of the present invention include but are not limited to viscosity modifiers, corrosion inhibitors, pigments, wetting agents, water soluble polymers, strength enhancing agents, rheology modifying agents, water repellents, fibers, permeability reducers, pumping aids, fungicidal admixtures, germicidal admixtures, insecticidal admixtures, finely divided mineral admixtures, alkali reactivity reducer, bonding admixtures, and any other admixtures or additive that do not adversely affect the stabilized foam or hydration stabilizers of the present invention.

Corrosion inhibitors in concrete serve to protect embedded reinforcing steel from corrosion due to its highly alkaline nature. The high alkaline nature of the concrete causes a passive and noncorroding protective oxide film to form on the steel. However, carbonation or the presence of chloride ions from deicers or seawater can destroy or penetrate the film and result in corrosion. Corrosion-inhibiting admixtures chemically arrest this corrosion reaction. The materials most commonly used to inhibit corrosion are calcium nitrite, sodium nitrite, sodium benzoate, certain phosphates or fluorosilicates, fluoroaluminates, amines, organic based water repelling agents, and related chemicals.

Dampproofing admixtures reduce the permeability of concrete that have low cement contents, high water-cement ratios, or a deficiency of fines in the aggregate. These admixtures retard moisture penetration into dry concrete and include certain soaps, stearates, and petroleum products.

Permeability reducers are used to reduce the rate at which water under pressure is transmitted through concrete. Silica fume, fly ash, ground slag, natural pozzolans, water reducers, and latex can be employed to decrease the permeability of the concrete.

Pumping aids are added to concrete mixes to improve pumpability. These admixtures thicken the fluid concrete, i.e., increase its viscosity, to reduce de-watering of the paste while it is under pressure from the pump. Among the materials used as pumping aids in concrete are organic and synthetic polymers, hydroxyethylcellulose (HEC) or HEC blended with dispersants, organic flocculents, organic emulsions of paraffin, coal tar, asphalt, acrylics, bentonite and pyrogenic silicas, natural pozzolans, fly ash and hydrated lime.

Bacteria and fungal growth on or in hardened concrete may be partially controlled through the use of fungicidal, germicidal, and insecticidal admixtures. The most effective materials for these purposes are polyhalogenated phenols, dialdrin emulsions, and copper compounds.

Fibers can be distributed throughout a fresh concrete mixture to strengthen it. Upon hardening, this concrete is referred to as fiber-reinforced concrete. Fibers can be made of zirconium materials, carbon, steel, fiberglass, or synthetic materials, e.g., polypropylene, nylon, polyethylene, polyester, rayon, high-strength aramid, or mixtures thereof.

The shrinkage reducing agent which can be used in the present invention can include but is not limited to alkali metal sulfate, alkaline earth metal sulfates, alkaline earth oxides, preferably sodium sulfate and calcium oxide.

Alkali-reactivity reducers can reduce the alkali-aggregate reaction and limit the disruptive expansion forces in hardened concrete. Pozzolans (fly ash and silica fume), blast-furnace slag, salts of lithium, and barium are especially effective.

Bonding admixtures are usually added to hydraulic cement mixtures to increase the bond strength between old and new concrete and include organic materials such as rubber, polyvinyl chloride, polyvinyl acetate, acrylics, styrene butadiene copolymers, and other powdered polymers.

Natural and synthetic admixtures are used to color concrete for aesthetic and safety reasons. These coloring admixtures are usually composed of pigments and include carbon black, iron oxide, phthalocyanine, umber, chromium oxide, titanium oxide and cobalt blue.

Air entrainers can be included in the concrete mixtures of the present invention, although this is usually not necessary since the foam admixtures provide an air entraining features. Unlike foam, air entrainers are added to the concrete mixture in a liquid form (i.e. without the air entrapped).

III. Methods of Making and Using Concrete Mixtures

The present invention also includes methods for making foam and methods for incorporating those foams into concrete mixtures.

A. Method of Making Foam Admixtures

As discussed above, in an exemplary embodiment, the foam admixtures are manufactured from a foam concentrate. Foam production is performed by drawing water and the foam concentrate, in proper ratios, and injecting them into a chamber using high pressure air. The mixture is subjected to shearing forces that produce air bubbles (i.e. foam) in the chamber.

The ratio of water, foam concentrate, and air are controlled to produce air bubbles of a desired size and shape. In a preferred embodiment, the water and foam concentrate are mixed to form a diluted concentrate comprising between at least about 80% water, more preferably greater than about 90% water and more preferably greater than about 95% water. The amount of air injected into the diluted foam is controlled by the air pressure and volume of air.

In an exemplary embodiment, air bubbles are formed having an approximate size of about 0.3 ml to about 1.0 ml, more preferably from about 0.5 ml to about 0.7 ml. In a preferred embodiment, the bubbles are of uniform size and shape. It is believed that the uniform size and shape is beneficial for providing a uniform dispersion of cement and aggregate.

Any number of foam production devices can be used for producing the foam admixtures of the present invention, and the invention is not limited to any specific such device. Such devices are well known in the art. Whatever mechanism used, it should be adequate to produce a stream of bubbles suitable for introduction into the concrete mixtures of the present invention.

The following formula "Concentrate I," shown in the table below, illustrates a suitable concentrate for manufacturing a foam admixture according to the present invention.

CONCENTRATE I

COMPONENT	CAS NUMBER/TRADE NAME	w/w %
Sodium alkenyl sulfonates mixture)	68439-57-6, 11066-21-0, 11067-19-9	7.0
1-t-Butoxy-2-propanol	57018-52-7	5.0
Rhamsan gum	96949-21-2	2.0
Perfluoroethylthia acrylic telomere	Lodyne ™ K90'90 (Ciba-Geigy Corp.)	1.4
n-Alkanols (mixture)	112-53-8, 112-72-1, 36653-82-4	1.0
2-Methyl-2-propanol	75-65-0	0.2
Water	7732-18-5	balance

Concentrate I can be used to form a stable and resilient aqueous foam admixture by diluting Concentrate I to 2.5 w/w % water (39 parts water to one part Concentrate I) and then aerating it through a foam generating chamber at about 92 psi, thereby subjecting the diluted Concentrate I to shearing forces that produce an aqueous foam admixture.

B. Method of Mixing Concrete

The concrete mixtures of the present invention are manufacture by mixing proper amounts of a hydraulic cement, aggregate, water, and foam admixture. Typically the concrete mixture includes a water reducer to give the concrete desired flowability. Typically the hydraulic cement, hydration stabilizer, water, and foam can be mixed together in any order so long as the water is added before the foam. The hydration stabilizer is preferably added to the cement before the cement is mixed with the foam to minimize the reaction of hydraulic cement and foam.

The viscosity modifier in the foam admixture disperses the aggregate and hydraulic cement thereby holding the concrete mixture together. Water reducers, water, and/or other admixtures can be added to the concrete mixture to give the concrete mixture high flowability, without the cement, aggregate, and water separating. Even with no additional viscosity modifier added to the concrete mixture, the concrete mixtures of the present invention can be highly flowable.

Concrete according to the present invention can be manufactured to have a "flow spread" of greater than 10 inches (using a 12 inch slump cone). More preferably the concrete mixtures have a flow-spread greater than about 12-36 inches. Flow spreads of 12, 24, and 36 inches or more can be achieved using the foam admixtures of the present invention. In a preferred embodiment, the concrete mixtures with the desired flow spreads are substantially homogenous.

To achieve the desired flow spread, the concrete mixtures includes at least water and a fluorochemical stabilized foam admixture. Water reducers are also typically added. The addition of water reducers allows the flowability to be modified without adjusting the amount of water, which is typically selected to optimize strength.

The amount type and size of aggregates can have a significant impact on flowability. Because transportation costs are so high for aggregates, concrete mixtures are typically formulated to work with what is available in a particular area. The amount of foam admixture, water, and water reducers is often adjusted to compensate for changes in flowability that result from a particular mixture of aggregate. Those skilled in the art are familiar with adjusting flowability using water and water reducers.

The fluorochemical stabilized foam can also have a significant impact on flowability. The stabilized foams of the present invention have been found to act as a super plasticizer in addition to acting as a viscosity modifier. Consequently, increasing the amount of foam typically has a significant increase on flowability. Often small increases in foam admixture (e.g. 0.5 ft^3/yd^3) can increase the flow spread by 5-12 inches or more.

In a preferred embodiment, a hydration stabilizer is added to the concrete mixture to preserve the foam bubbles. The hydration stabilizer is preferably added to the cement before the cement is mixed with the foam to minimize the reaction of hydraulic cement and foam. It has also been found that adding the hydration stabilizer to the water before the water is mixed with the cement can also increase stability of the foam when the foam is mixed with the cement. Accelerator can be added to the concrete mixture at the same time that the hydration retarding agent is added, or the accelerator can be added at a later point in time, such as just before the concrete is to be poured.

The amount of foam mixed into the concrete mixture is selected to give the concrete a desired percent of air. In an exemplary embodiment, the foam admixture is included in the concrete mixture in an amount sufficient to provide greater than 5% air in the concrete, more preferably greater than 10% air, and most preferably greater than about 15% air by volume of the concrete mixture.

The limit on the amount of foam that can be added depends on the desired final strength of the concrete and the amount of cement in the mixture. In general, lower percentages of air and higher amounts of cement produce stronger cements. However, the concrete mixtures of the present invention can have very high compressive strengths with percentages of air above 5%, as compared with existing cements. Using the aqueous foams of the present invention, air can be entrained into the concrete mixture in percentages greater than 5%, 10%, and even 20% while maintaining compressive strengths of greater than about 2500 psi, and more preferably greater than about 3000 psi, in 28 days. For example, concrete mixtures according to the present invention having 12% air and 300 lbs/yd^3 of cement can achieve about 3000-4000 psi in 28 days. In another example, concrete mixture according to the present invention having 22% air and 650 lbs/yd^3 cement can achieve a compressive strength of about 6500 psi in 28 days. Even at very high percentages of air, significant compressive strength can be achieved. For example, concrete mixtures of 85% air can achieve 90 psi in 28 days.

Because the cement is stabilized with respect to the foam using the hydration stabilizer, the air entrainment provided by the foam can last at least until the concrete sets.

Table 2 below provides 3 different exemplary ranges of typical amounts of the components needed to make concrete mixtures according to the present invention.

TABLE 2

	1	2	3
Portland Cement	1-50%	6-50%	10-25%
Washed Sand	0-75%	0-60%	0-40%
Coarse Aggregate	0-60%	0-50%	0-40%
Water	4-50%	5-50%	10-25%
Pozzolanic Material	0-50%	0-20%	0-5.0%
Foam Admixture	1-90%	1-85%	1-75%
Water Reducers	0-20 oz	0-6.0 oz	0-4.5 oz
Accelerators	0-20 oz	0-12 oz	0-8.0 oz
Hydration Stabilizer	0.5-20 oz	1.0-12 oz	1.5-6.0 oz

In the compositions described in Table 2, the foam admixture is manufactured as described above (e.g. Concentrate I diluted to 2.5 w/w % water and foamed at 92 psi). The weight of the foam admixture includes the weight of the water that makes up the foam. Water is also included as a separate component, which does not include the water in the aqueous foam admixture.

A sufficient amount of hydration stabilizer is included to stabilize the foam admixture for a desired amount of time. The sufficiency of the hydration stabilizer can depend in part on the type of concrete being made. For ready mixed concrete, where transportation is often needed, the hydration stabilizer can be added in greater amounts such that the stabilization lasts during transportation and until the concrete has set.

The amount of hydration stabilizer used in the concrete mixture is determined by the need to stabilize the cement with respect to the foam. A sufficient amount of hydration stabilizer will inhibit the reaction between the cement and the foam such that a majority or substantially all of the foam initially mixed into the concrete lasts until the concrete achieves initial set. Typically, less than 2% of the foam collapses within the first 2 hours.

Regardless of whether the concrete is designed to set in a short period (e.g. less than 1 hour) or over along period of time, a hydration stabilizer can be included to stabilize the foam admixture. The cement in a concrete mixture is most reactive, and thus most destructive to the foam admixture, when it is first mixed with the water. Consequently, the hydration stabilizer provides its greatest benefit during initial mixing of the cement, foam, and water, although significant benefits can still be realized by including the hydration stabilizer after initial mixing. The use of hydration stabilizer during the initial mixing of the concrete differs from most current practices, which add hydration stabilizer to waste concrete after a job is finished or during a job to preserve the concrete for later use. In the present invention, the hydration stabilizer is added to prevent the reaction of the foam and the cement. Accelerators can be added anytime during or after mixing to control set time, if needed.

Those skilled in the art will recognize that there are many applications in which the combination of hydration stabilizer, hydraulic cement, and foam according to the present invention can be easily incorporated into a concrete composition using the foregoing description. The following examples give specific formulations of aqueous foams and concrete composition that employ the concepts of the present invention.

IV. EXAMPLES

Examples 1-4 illustrate concrete compositions according to the present invention.

Example 1 describes a concrete mixture having a homogenous flow spread of 13.5 inches as measured using a 12 inch slump cone. The cured concrete had a compressive strength of 4334 psi in 28 days and 5254 psi in 56 days.

Example 1

COMPONENTS	AMOUNTS
Ashgrove Cement	440 lbs/yd^3
Water	36.8 gal/yd^3
Hydration Stabilizer (Recover, W. R. Grace)	4.5 oz/100-wt
Fine Aggregate (sand, Point East)	1553 lbs/yd^3
Coarse Aggregate (pea gravel, Point West)	1140 lbs/yd^3
Fly Ash (Navajo)	197 lbs/yd^3
Foam Admixture (Miracon)	1.83 ft^3/yd^3

-continued

COMPONENTS	AMOUNTS
High Range WR (30/30, Master Builders)	10.5 oz/100-wt
Low Range WR (27, W. R. Grace)	2.18 oz/100-wt

Example 2 describes a concrete mixture having a homogenous flow spread of 33 inches as measured using a 12 inch slump cone. The cured concrete had a compressive strength of 4093 psi in 28 days and 4618 psi in 56 days.

Example 2

COMPONENTS	AMOUNTS
Ashgrove I/II Cement	446 lbs/yd^3
Water	28.7 gal/yd^3
Fine Aggregate (sand, Point East)	1256 lbs/yd^3
Coarse Aggregate (#8 pea gravel, Point West)	1400 lbs/yd^3
Fly Ash (Navajo)	196 lbs/yd^3
Hydration Stabilizer (Recover, W. R. Grace)	4.43 oz/100-wt
Foam Admixture (Miracon)	2 ft^3/yd^3
High Range WR (30/30)	10.3 oz/100-wt
Low Range WR (27, W. R. Grace)	1.0 oz/100-wt

Example 3 describes a concrete mixture having a homogenous flow spread of 24 inches as measured using a 12 inch slump cone. The cured concrete had a compressive strength of 4111 psi in 28 days and 5056 psi in 56 days.

Example 3

COMPONENTS	AMOUNTS
Ashgrove I/II Cement	440 lbs/yd^3
Water	28.7 gal/yd^3
Fine Aggregate (sand, Point East)	1246 lbs/yd^3
Coarse Aggregate (#8 pea gravel, Point West)	1400 lbs/yd^3
Fly Ash (Navajo)	196 lbs/yd^3
Hydration Stabilizer (Recover, W. R. Grace)	4.5 oz/100-wt
Foam Admixture (Miracon)	2.1 ft^3/yd^3
High Range WR (30/30, Master Builders)	10.4 oz/100-wt
Low Range WR (27, W. R. Grace)	1.0 oz/100-wt

Example 4 describes a concrete mixture having a homogenous slump of 6 inches as measured using a 12 inch slump cone. The cured concrete had a compressive strength of greater than 3000 psi in 28 days.

Example 4

COMPONENTS	AMOUNTS
Portland Cement	308 lbs/yd^3
Water	30 gal/yd^3
Hydration Stabilizer (Recover, W. R. Grace)	5.5 oz/100-wt
Fine Aggregate	1630 lbs/yd^3
Coarse Aggregate	1235 lbs/yd^3
Foam Admixture (Miracon)	2.8 ft^3/yd^3
Mid Range WR (997, Master Builders)	5 oz/100-wt
Low Range WR (27, W. R. Grace)	0.5 oz/100-wt

The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

What is claimed is:

1. A flowable concrete mixture, comprising:

(i) a hydraulic cement;

(ii) an aggregate

(iii) water;

(iv) a foam admixture comprising a viscosity modifier, water, a surfactant, and a plurality of air bubbles, wherein the concentration of the viscosity modifier is higher in the foam admixture compared to the remainder of the flowable concrete mixture; and

(v) a sufficient amount of water and/or a water reducer to give the concrete mixture a flow spread greater than 10 inches.

2. A concrete mixture as in claim **1**, wherein the concrete mixture includes less than 12 oz/(100 lbs cement) of a viscosity modifier in addition to the viscosity modifier in the foam admixture.

3. A concrete mixture as in claim **1**, wherein the concrete mixture includes less than 5 oz of a viscosity modifier in addition to the viscosity modifier in the foam admixture.

4. A concrete mixture as in claim **1**, wherein the concrete mixture includes substantially no viscosity modifier in addition to the viscosity modifier in the foam admixture.

5. A concrete mixture as in claim **1**, wherein the viscosity modifier in the foam comprises one or more of a cellulose ether, a hydroxyproplmethyl cellulose, a sodium carboxymethyl cellulose, a carboxymethylhydroxyethyl cellulose, a polyacrylates, a polyvinyl alcohol, a polyethylene glycol, an exopolysaccharides, a marine gum, a plant exudate, a seed gum, a starch-based gum, or a combination thereof.

6. A concrete mixture as in claim **1**, wherein the flow spread is substantially homogenous.

7. A concrete mixture as in claim **1**, wherein the flowability and consistency make the concrete mixture self-compacting.

8. A concrete mixture as in claim **1**, further comprising a hydration stabilizer that stabilizes the foam in the presence of the hydraulic cement.

9. A concrete mixture as in claim **1**, wherein the hydration stabilizer is included in an amount sufficient to inhibit the reaction between the hydraulic cement and the water in the foam for greater than about 1 hour.

10. A concrete mixture as in claim **1**, wherein the surfactant includes a fluorochemical surfactant, wherein the fluorochemical surfactant comprises an oligomer having one or more hydrophilic nonionic monomers and one or more hydrophilic anionic monomers.

11. A cured concrete made by manufacturing the concrete mixture of claim **1** and allowing the concrete mixture to cure.

12. A concrete mixture as in claim **1** that achieves a compressive strength of greater than 3000 psi in 28 days, when allowed to set.

13. A concrete mixture as in claim **1** that achieves a compressive strength of greater than 4000 psi in 28 days, when allowed to set.

14. A concrete mixture, comprising:

(i) a hydraulic cement;

(ii) water;

(iii) an aggregate;

(iv) a foam comprising a viscosity modifier, water, a fluorochemical surfactant, and a plurality of air bubbles that are stabilized by the fluorochemical surfactant, the fluorochemical surfactant comprising an oligomer having at least one hydrophilic nonionic monomer and at least one hydrophilic anionic monomer, wherein the concentration of the viscosity modifier is higher in the foam admixture compared to the remainder of the flowable concrete mixture; and

(v) a sufficient amount of a water reducing agent to give the concrete a flow spread of at least about 12 inches, wherein the flow spread is substantially homogenous.

15. A concrete mixture as in claim **14**, wherein the flow spread is greater than about 24 inches.

16. A concrete mixture as in claim **14**, wherein the flow spread is greater than about 30 inches.

17. A concrete mixture as in claim **14**, wherein

the foam comprises one or more fatty acid alcohols selected from the group consisting of straight and branched chain fatty acid alcohols of about 8 to about 16 carbon atoms;

the viscosity modifier is an anionic polysaccharide selected from the group consisting of rhamsan gums, xanthan gums, guar gums, and locust bean gums; and

the foam admixture comprises a non-fluorinated anionic surfactant having from about 8 to about 18 carbon atoms.

18. A concrete mixture as in claim **14**, wherein the fluorochemical surfactant has the formula:

$$R_f\text{-}E_a\text{-}(S)_b\text{-}[M_1]_x\text{-}[M_2]_y\text{-}H$$

wherein

R_f is (i) a straight chain, branched chain, or cyclic perfluoroalkyl of 1 to about 20 carbon atoms, (ii) a perfluoroalkyl substituted with a perfluoroalkoxy of 2 to about 20 carbon atoms, (iii) a perfluoroalkyl oligomer or polymer of greater than 10 carbon atoms, or (iv) a combination thereof

E_a is (i) a direct bond; (ii) a branched, straight chain, or cyclic alkylene of 2 to about 20 carbon atoms; (iii) the alkylene of (ii) interrupted by one or more groups selected from the group consisting of —NR—, —O—, —S—, —SO$_2$—, —COO—, —OOC—, —CONR—, —NRCO—, —SO$_2$NR—, —NRSO$_2$—, —SiR$_2$—; or (iv) the alkylene of (ii) terminated at the R_f end with —CONR— or —SO$_2$NR—;

R is independently hydrogen, an alkyl of 1-10 carbon atoms, or a hydroxyalkyl of 2 to 10 carbon atoms;

a and b are independently 0 or 1;

-[M_1]- represents a non-ionic hydrophilic monomer unit;

-[M_2]- represents an anionic hydrophilic monomer unit; and

x and y represent the number of monomer units present in the co-oligomers and are both greater than 0; the sum of x and y being between 5 and 200, and y/(x+y) being between 0.01 and 0.98.

19. A concrete mixture as in claim **18**, wherein:

-[M_1]- is selected from the group consisting of acrylamide, methacrylamide, diacetone acrylamide, 2-hydroxyethyl methacrylate, derivatives of acrylic, methacrylic, maleic, fumaric and itaconic acids, amides, and vinyl esters containing from 1 to about 20 carbon atoms in the ester group, and combinations thereof; and

-[M_2]- is selected from the group consisting of acrylic and methacrylic acids and salts thereof, maleic, fumaric and itaconic acids and salts thereof, acrylamidopropane sulfonic acid and salts thereof, and mono-olefinic sulfonic and phosphonic acids and salts thereof, and combinations thereof.

20. A concrete mixture as in claim **1**, wherein the foam comprises at least about 10% by volume of the concrete mixture.

21. A concrete mixture as in claim **18** that achieves a compressive strength of greater than 3000 psi in 56 days, when allowed to set.

22. A flowable concrete mixture, comprising:

(i) a hydraulic cement;

(ii) an aggregate

(iii) water;

(iv) a hydration stabilizer that inhibits hydration of the hydraulic cement;

(iv) a foam admixture comprising a viscosity modifier, water, and a plurality of air bubbles, wherein the foam admixture is stabilized in the presence of the hydraulic cement by the hydration stabilizer, wherein the concentration of the viscosity modifier is higher in the foam admixture compared to the remainder of the flowable concrete mixture;

(v) wherein the concrete mixture includes less than 12 oz/(100 lbs cement) of a viscosity modifier in addition to the viscosity modifier in the foam admixture.

23. A flowable concrete mixture as in claim **22**, wherein the concrete mixture includes less than about 5 oz of a viscosity modifier in addition to the viscosity modifier in the foam admixture.

24. A flowable concrete mixture as in claim **22**, wherein the viscosity modifier in the foam comprises one or more of a cellulose ether, a hydroxyproplmethyl cellulose, a sodium carboxymethyl cellulose, a carboxymethylhydroxyethyl cellulose, a polyacrylates, a polyvinyl alcohol, a polyethylene glycol, an exopolysaccharides, a marine gum, a plant exudate, a seed gum, a starch-based gum, or a combination thereof.

25. A concrete mixture as in claim **22**, wherein the hydration stabilizer is a calcium binding agent.

26. A concrete mixture as in claim **22**, wherein the hydration stabilizer is selected from the group consisting of N-nitrilo tris(methylene phosphonic acid), 1,2-ethanediyl bis[nitrilo di(methylene phosphonic acid)]; 1,6-hexanediyl bis [nitrilo di(methylene phosphonic acid)], amino tris (methylene phosphonic acid), polymethoxy polyphosphonic acids, and combinations thereof.

27. A concrete mixture as in claim **22**, wherein the hydration stabilizer further comprises an accelerator.

28. A concrete mixture as in claim **22**, wherein the foam admixture further comprises a fluorochemical surfactant comprising an oligomer having one or more hydrophilic nonionic monomer and one or more hydrophilic anionic monomer.

29. A concrete mixture as in claim **28**, wherein the fluorochemical surfactant has the formula:

$$R_f\text{-}E_a\text{-}(S)_b\text{-}[M_1]_x\text{-}[M_2]_y\text{-}H$$

wherein

R_f is (i) a straight chain, branched chain, or cyclic periluoroalkyl of 1 to about 20 carbon atoms, (ii) a perfluoroalkyl substituted with a perfluoroalkoxy of 2 to about 20 carbon atoms, (iii) a perfluoroalkyl oligomer or polymer of greater than 10 carbon atoms, or (iv) a combination thereof

E_a is (i) a direct bond, (ii) a branched, straight chain, or cyclic alkylene of 2 to about 20 carbon atoms, (iii) the alkylene of (ii) interrupted by one or more groups selected from the group consisting of —NR—, —O—,

—S—, —SO_2—, —COO—, —OOC—, —CONR—, —NRCO—, —SO_2NR—, —NRSO_2—, —SiR_2—; or (iv) the alkylene of (ii) terminated at the R_f end with —CONR— or —SO_2NR—;

R is independently hydrogen, an alkyl of 1-10 carbon atoms, or a hydroxyalkyl of 2 to 10 carbon atoms;

a and b are independently 0 or 1;

-$[M_1]$- represents a non-ionic hydrophilic monomer unit;

-$[M_2]$- represents an anionic hydrophilic monomer unit; and

x and y represent the number of monomer units present in the co-oligomers and are both greater than 0; the sum of x and y being between 5 and 200, and

y/(x+y) being between 0.01 and 0.98.

30. A cured concrete composition manufactured according to the method of claim **22**.

31. A concrete mixture as in claim **22**, wherein the concrete achieves a compressive strength of greater than 3000 psi in 28 days, when allowed to set.

* * * * *

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(12) **United States Patent**
Gray

(10) **Patent No.: US 7,670,426 B2**
(45) **Date of Patent: Mar. 2, 2010**

(54) **CONCRETE MIXTURES HAVING AQUEOUS FOAM ADMIXTURES**

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See application file for complete search history.

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(57) **ABSTRACT**

Flowable concrete mixtures have an aqueous foam admixture mixed therein to give the concrete mixture desired strength, flowability, and density. The concrete mixtures include a hydration stabilizer to stabilize the aqueous foam. The hydration stabilizer inhibits the reaction between the hydraulic cement and the water in the aqueous foam. The aqueous foam can be further stabilized using a fluorochemical surfactant. Preferred fluorochemical surfactants comprise an oligomer having at least one hydrophilic nonionic monomer and at least one hydrophilic anionic monomer.

42 Claims, No Drawings

CONCRETE MIXTURES HAVING AQUEOUS FOAM ADMIXTURES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Patent Application Ser. No. 60/715,458, filed Sep. 9, 2005, entitled "Concrete Mixtures Having Aqueous Foam Admixtures," the disclosure of which is incorporated herein in its entirety.

BACKGROUND OF THE INVENTION

1. The Field of the Invention

The present invention relates to flowable concrete mixtures and cured concrete obtained therefrom. More particularly, the present invention relates to concrete mixtures that have an aqueous based foam admixture and a hydration stabilizer that stabilizes the foam in the concrete.

2. Related Technology

Concrete mixtures are composite materials that are usually composed of water, cement, and aggregate. Common aggregates include sand, gravel, or crushed stone. Concrete is a well-known structural component with typical compressive strengths of about 2500 psi, when cured.

Admixtures are often added to concrete to give the concrete desired properties. Examples of suitable uses for concrete admixtures include lowering the concrete's density, improving the concrete's workability, improving the concrete's strength to weight ratio, giving the concrete insulating properties, and/or enhancing the acoustic properties of the concrete, among others. These beneficial properties are often accomplished by adding several different admixtures.

Air entraining agents are often used alone or in combination with other admixtures to give the concrete one or more of the foregoing properties. Air entraining admixtures are used to purposely trap microscopic air bubbles in the concrete. Air entrainment dramatically improves the durability of concrete exposed to moisture during cycles of freezing and thawing. In addition, entrained air greatly improves concrete's resistance to surface scaling caused by chemical deicers. Air entrainment also increases the workability of fresh concrete while eliminating or reducing segregation and bleeding.

There are several methods for entraining air in concrete. One approach is to generate bubbles or air pockets in situ. This approach can be accomplished using surfactants or other air entraining admixtures that generate bubbles as the concrete is mixed. Materials used to achieve these desired effects include non-ionic, cationic, and anionic surfactants, natural and synthetic resins, fatty acids, proteinaceous material, sulfonated hydrocarbons, and the like. This approach, while effective for entraining small amounts of air, is difficult to use for higher percentages of air because the bubble size, amount of bubbles, durability, and distribution of bubbles within the concrete are difficult to control.

Another approach for incorporating air in concrete is to add foam admixtures. When using a foam admixture, the cellular bubbles (i.e. the foam) is formed ex-situ and then mixed with the concrete. This method is advantageous because the foam is created in a controlled environment. The water, air, and foaming concentrates can be designed to produce foams having a desired size and composition.

Despite many advantages, the use of foam admixtures formed ex-situ have had limited use (e.g. in insulating, non-structural, or non-load-bearing bearing applications). Most commercially available foaming agents are not stable in cementitious media and the results of their use are often inconsistent. For example, with existing foam-concrete mixtures, the size and distribution of foam cells have been difficult to control and the cells have had a limited period of usefulness or lifetime. The foam cells have tended to agglomerate, coalesce, and recombine to give larger cells and a wide range of sizes. Long mixing times, such as those required for transportation from a concrete production facility to a construction site, have been precluded due to bubbles collapsing and air escaping from the mix. Even when additives have been used to stabilize these foams (e.g., U.S. Pat. Nos. 5,160,540 and 6,153,005, which are hereby incorporated by reference), the foam's stability and useful lifetime in the concrete prevents use in many applications, such as those requiring transportation of the concrete (e.g. ready mixed concrete).

BRIEF SUMMARY OF THE INVENTION

The present invention relates to flowable concrete mixtures comprising an aqueous foam. The concrete mixtures include (i) a hydraulic cement, (ii) a hydration stabilizer, and (iii) an aqueous foam. The hydration stabilizer inhibits hydration of the hydraulic cement thereby inhibiting deleterious interactions between the cement and the aqueous foam that can destroy the foam bubbles. The stabilizing effect of the hydration stabilizer allows the foam to be successfully combined with concrete mixtures and/or allows the foam to last longer in the concrete mixture.

The hydration stabilizers used to reduce the reaction between the cement and the foam includes a hydration retarder that can slow or stop hydration of the siliceous and/or aluminous component of hydraulic cements. Preferred hydration stabilizers are those that can bind calcium, such as derivatives of phosphonic acid and carboxylic acids having hydroxyl or amino groups. Because of the retarding effect that the hydration retarder can have on setting, the hydration stabilizer may also include an accelerator.

The inventor of the present invention has found that controlling the hydration of the cement has a significant stabilizing effect on aqueous based foams in concrete mixtures. The hydration stabilization of the present invention allows aqueous foams to be added to concrete that would otherwise not be stable in a concrete mixture. Furthermore, aqueous foams that are currently being used in concrete mixtures for certain applications (i.e. to make some precast structures) can be sufficiently stabilized such that they can be used in new applications that require longer initial set times (e.g. ready mix applications).

In a preferred embodiment, the present invention is used with foams that have a fluorochemical surfactant. Fluorochemical surfactants are known to stabilize and/or strengthen the air bubbles in aqueous foams. Fluorochemical surfactants have been used in firefighting foams to generate foam bubbles that have enough structural stability that they can be sprayed on a burning chemical and last long enough to smother the fire. The aqueous nature of these foams and the stability of the foam bubbles make these foams particularly useful in the concrete mixtures of the present invention. The use of at least one such foam in a concrete mixture is described in U.S. Pat. No. 6,153,005 to Welker et al., which is incorporated herein by reference.

The stabilizing effect of the fluorochemical surfactant is distinct and in addition to the stabilizing effect of the hydration stabilizer. The fluorochemical surfactant is a component of the foam bubble and provides stability within the bubble. In contrast, the hydration stabilizer is a component of the concrete mixture to prevent deleterious interactions between the cement and the aqueous foam.

Foams stabilized with fluorochemical surfactants are particularly benefited by the hydration stabilizers used in the concrete mixture of the present invention. Since fluorochemical stabilized foams have bubbles that are already particularly stable, it is believed to be the interactions between the cement and the foam that has previously prevented the use of these foams in concrete and/or has previously prevented their use in applications that require relatively long initial set times (e.g. ready mix applications). In the present invention the hydraulic cement is stabilized with respect to the aqueous foam, thereby allowing or improving their use in the concrete mix. The resulting concrete compositions have many improved properties, including decreased permeability, decreased shrinkage, decreased absorption and bleeding, improved acoustic properties, lower densities, and increased initial flowability. The concrete mixtures also have reduced water migration, which improves the hydration of cement and can improve the reaction between free lime and pozzolans. The concrete mixtures also have improved aesthetics due to reduced rock pockets.

The hydration stabilizer used in the present invention is also particularly advantageous when used with foams stabilized with fluorochemical oligomers comprising hydrophilic nonionic monomers and hydrophilic anionic monomers. Foams stabilized using these surfactants provide additional benefits because of the interaction between the oligomer in the foam and certain components of the concrete mixture (e.g. the cement and/or the aggregate). It is believed that the nonionic and anionic monomers are able to better disperse the cement particles and/or the aggregates uniformly in the concrete mixture. This dispersion of components in the mixtures of the present invention is believed to be the source of the added workability of these mixtures and the strength of the cured concrete resulting therefrom.

These and other features of the present invention will become more fully apparent from the following description and appended claims.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

I. Introduction

The present invention relates to flowable concrete mixtures having aqueous foam admixtures. The concrete mixtures of the present invention include (i) a hydraulic cement, (ii) a hydration stabilizer, and (iii) an aqueous foam. The hydration stabilizer controls hydration of the cement to inhibit the reaction between the cement and the aqueous foam, thereby preserving the foam bubbles for a desired amount of time.

For purposes of the present invention, the “initial set time” occurs when the concrete reaches a compressive strength of 500 psi.

For purposes of the present invention, the term “air” includes all gases including mixtures of gases and pure gasses, whether obtained from the atmosphere or generated by chemical reaction.

II. Concrete Mixtures

The concrete mixtures of the present invention can have very different compositions depending on the desired use for the concrete. However, in general, the concrete mixtures of the present invention include at least hydraulic cement, a hydration stabilizer, an aqueous foam admixture, and water (either from the foam or added separately). The concrete mixtures typically include an aggregate, which gives the concrete strength. Dispersants and other admixtures are also described below and can be included to give the concrete mixtures of the present invention desired properties.

A. Hydraulic Cement and Water

The cement included in the concrete mixtures of the present invention is a hydraulic material such as Portland cement, modified Portland cement, or masonry cement. For purposes of this invention, Portland cement includes all cementitious compositions which have a high content of tricalcium silicate, including Portland cement, cements that are chemically similar or analogous to Portland cement, and cements that fall within ASTM specification C-150-00. Other cementitious materials include ground granulated blast-furnace slag, hydraulic hydrated lime, white cement, slag cement, calcium aluminate cement, silicate cement, phosphate cement, high-alumina cement, magnesium oxychloride cement, and combinations of these and other similar materials.

Water is added to the concrete mixture in sufficient amounts to hydrate the cement. Those skilled in the art will recognize that the amount of water needed will depend on the desired flowability and on the amounts and types of admixtures included in the concrete composition. Many of these admixtures are discussed below. In general, suitable amounts of water for hydrating the cement ranges from about 1% to about 50%, more preferably about 5-50%, and most preferably about 10% to about 25% of the concrete mixture by weight.

B. Foam Admixtures

The foams used in the concrete mixtures of the present invention include water, air, and at least one foaming agent (e.g. surfactant). The foam admixtures comprise a plurality of cellular bubbles that trap air in the concrete and provide the uncured concrete with desired properties such as flowability and/or workability and provide the cured concrete with properties such as increased strength and/or resistance to cracking during freeze thaw cycles.

The foams of the present invention can be made from a foaming concentrate. A detailed description of how to make the aqueous foam admixture using a foaming concentrate, air, and water is described below in connection with the methods of the present invention and the examples.

The composition of the foaming concentrate is in large part responsible for the properties of the foam admixture. The following is a description of suitable foaming concentrate composition. The foaming concentrates typically include a foaming agent, solvents, and other surfactants, and/or additives that allow the foaming concentrate to form foam bubbles that can be added to concrete.

1. Foaming Concentrates

(a) Foaming Agents and Solvents

The foaming concentrates include at least one foaming agent suitable for forming an aqueous based foam. Typical foaming agents include ionic, cationic, anionic surfactants, natural and synthetic resins, fatty acids, proteinaceous material, sulfonated hydrocarbons, and the like. In an exemplary embodiment, the foaming concentrate comprises a combination of foaming agents, solvents and/or viscosity modifiers or other components. In a preferred embodiment, the foaming agents can be a non-fluorinated anionic surfactant preferably selected from the group consisting of C_8 to C_{18} anionic surfactants and most preferably, C_{10} to C_{18} alpha olefin sulfonates, as well as mixtures of these surfactants.

Suitable solvents include glycol ethers and fatty alcohols of about 8 to about 15 carbons or C_2 to C_8 aliphatic diols. Specifically preferred as the solvent, if used, is propylene glycol t-butyl ether. The preferred fatty alcohol comprises a mixture of equal parts n-dodecanol, n-tetra decanol and n-hexadecanol. Preferred as the anionic surfactant are mixtures of sodium alkenyl sulfonate, sodium tetradecene sulfonate, and sodium hexadecene sulfonate in a ratio of about 4:1:1.

Viscosity modifiers can also be added to the foam admixture. Suitable viscosity modifiers include those described below as admixtures to be added to the concrete mixture apart from the foam. Preferred viscosity modifiers include polysaccharide gums, preferably selected from the group consisting of rhamsan gums, xanthan gums, guar gums and locust bean gums. Viscosity modifiers such as polysaccharide gums can be useful in foams because they form a membrane on the surface of solvents that protects the rest of the foam from collapsing. The viscosity modifier in the foam can also aid in pumpability of the concrete mixture.

Other ingredients can be employed in the composition of the surfactant formulation to effect specific environmental or shelf-life concerns. Examples of such ingredients are freezing point depressants, such as ethylene glycol, and preservatives, such as that available under the trade name DOWICIDE (Dow Chemical Company).

There are many other known foaming concentrates that can be used with the present invention. Suitable foaming surfactant concentrates include cellulose based concentrates (e.g. "CELLUCON" (Romaroda Chemicals)) and hydrolyzed protein based concentrates (e.g. MEARL (The Mearl Corporation)).

The foam concentrates include surfactants and additives that lead to foams with sufficient mechanical stability to withstand the mixing involved in making concrete compositions. The foregoing concentrates, if needed, can be structurally strengthened (i.e. stabilized) using a fluorochemical surfactant as described below, or other similar stabilizing additive.

(b) Foam Stabilizing Surfactants

In an exemplary embodiment the foam concentrate includes a fluorochemical foam stabilizing surfactant. Fluorochemical foam stabilizing surfactants are well known in the art of fire fighting foams (e.g. U.S. Pat. Nos. 4,472,286; 4,717,744; and 4,859,349; which are incorporated herein by reference). Particularly useful fluorinated surfactants are those described in U.S. Pat. Nos. 4,460,480 and 5,218,021 to Kleine et al., and Clark et al., respectively, which are incorporated herein by reference, and which discloses an oligomer surfactant that includes (i) a fluorinated hydrocarbon monomer, (ii) a hydrophilic nonionic monomer, and (iii) a hydrophilic anionic monomer.

Examples of suitable fluorinated hydrocarbon monomer include (i) straight chain, branched chain, or cyclic perfluoroalkyls of 1 to about 20 carbon atoms, (ii) perfluoroalkyls substituted with perfluoroalkoxy groups of 2 to about 20 carbon atoms, (iii) a perfluoroalkyl oligomers or polymers of greater than 10 carbon atoms, or (iv) monomers of the like and/or combination thereof.

Many non-ionic hydrophilic monomers suitable for use in the present invention are known and commercially available. Particularly useful non-ionic hydrophilic monomers include acrylamide, methacrylamide, diacetone acrylamide, and 2-hydroxyethyl methacrylate. Other examples of such monomers include derivatives of acrylic, methacrylic, maleic, fumaric, and itaconic acids, such as hydroxyalkyl esters of acrylic acids; amides such as N-vinyl-pyrrolidone, N-(hydroxyalkyl)-acrylamides, or N-(hydroxyalkyl)-methacrylamides; and vinyl esters with 1-20 carbons in the ester group such as vinyl acetate, butyrate, laurate, or stearate. The above listed non-ionic hydrophilic monomers can be used alone or in combination with each other as well as in combination with suitable anionic hydrophilic monomers described below. Some non-ionic hydrophilic monomers may require a comonomer for polymerization, such as di(hydroxyalkyl) maleates with ethoxylated hydroxyalkyl maleates.

Many anionic hydrophilic monomers that co-oligomerize with non-ionic hydrophilic monomers are known and are commercially available. Particularly useful anionic hydrophilic monomers include acrylic and methacrylic acids and salts thereof. Other examples of such monomers include maleic, fumaric, and itaconic acids and salts thereof; acrylamidopropane sulfonic acid and salts thereof; and mono-olefinic sulfonic and phosphonic acids and salts thereof.

Oligomers made using the foregoing fluorinated hydrocarbon monomers and hydrophilic monomers are particularly advantageous when used with foams in the concrete mixtures of the present invention. These oligomers are particularly useful for dispersing and/or suspending the cement and/or aggregates in the concrete mixture. By dispersing and/or suspending these and other components of the concrete mixture, the resulting cured concrete has improved strength and resistance to cracking.

In an exemplary embodiment, the fluorochemical foam stabilizers of the present invention can be characterized by chemical moieties represented by the general formula, R_f-E_a-$(S)_b$-$[M_1]_x$-$[M_2]_y$-H (Formula I), and mixtures thereof, wherein:

R_f is (i) a straight chain, branched chain, or cyclic perfluoroalkyl of 1 to about 20 carbon atoms, (ii) a perfluoroalkyl substituted with a perfluoroalkoxy of 2 to about 20 carbon atoms, (iii) a perfluoroalkyl oligomer or polymer of greater than 10 carbon atoms (e.g. hexafluoropropylene oxide), or (iv) a mixture of perfluoroalkyl moieties;

E_a is (i) a direct bond, (ii) a branched, straight chain, or cyclic alkylene of 2 to about 20 carbon atoms, (iii) the alkylene of (ii) interrupted by one or more groups selected from the group consisting of —NR—, —O—, —S—, —SO_2—, —COO—, —OOC—, —CONR—, —NRCO—, —SO_2NR—, —NRSO_2—, —SiR_2—; or (iii) the alkylene of (ii) terminated at the R_f end with —CONR— or —SO_2NR—;

R is independently hydrogen, an alkyl of 1-10 carbon atoms, or a hydroxyalkyl of 2 to 10 carbon atoms; and

a and b are independently 0 or 1; -$[M_1]$- represents a non-ionic hydrophilic monomer unit; -$[M_2]$- represents an anionic hydrophilic monomer unit; and x and y represent the number of monomer units present in the co-oligomers and are both greater than 0; the sum of x and y being between 5 and 200, and y/(x+y) being between 0.01 and 0.98.

Formula (I) does not necessarily depict the actual sequence of the oligomer or macromer units since the units can be randomly distributed throughout. It is also assumed that the monomers for M_1 and M_2 are known as described above.

While the foams of the present invention preferably include a fluorochemical foam stabilizer, the present invention is not limited to these foams. The use of a hydration stabilizer with other aqueous based foams can advantageously stabilize and prolong the life of the foam in concrete.

(c) Example Foaming Concentrates

Table 1 below sets forth exemplary foaming concentrates according to the present invention. In Table 1, column 1 specifies the useful ranges for each component, column 2 specifies preferred ranges for each of the components and column 3 describes the highly preferred ranges for each of the components. In Table 1, all compositions are in parts by weight. The fluorochemical surfactant is normally supplied as a solution in an alcohol such as tert-butyl alcohol.

TABLE 1

	1	2	3
Solvent	0-50%	0-20%	1-10%
Fatty Alcohol	0.1-10%	0.1-1.0%	0.2-1.0%
Polysaccharide Gum	0.1-10%	0.1-5.0%	0.5-4.0%
Anionic Surfactant	0.1-50%	0.1-20%	0.5-8.0%
Fluorochemical	0.1-15%	0.1-5.0%	0.5-3.0%
Water	Balance	Balance	Balance

A particularly useful foaming concentrate that includes a fluorochemical surfactant is sold by Miracon Technologies, Inc. under the trademark Miracon®.

C. Hydration Stabilization

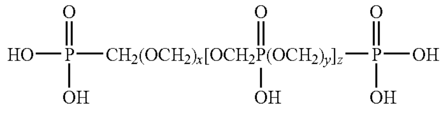
The hydration stabilizer (also known as an extended set retarder) of the present invention is used to inhibit the hydration of the hydraulic cement. The hydration stabilizer slows the rate of hydrate formation by tying up (i.e. chelating, complexing, or otherwise binding) calcium ions on the surface of cement particles. The hydration stabilizer includes a hydration retarder that forms a protective barrier around cementitious particles. The hydration retarder bonded to the cement particles acts as a dispersant preventing hydrates from flocculating and setting. This barrier prevents the hydraulic cement from obtaining initial set.

Another feature of the hydration stabilizer is that it degrades and/or is inactivated over time such that hydration of the cement eventually occurs. Preferably the release of the hydraulic cement is progressive over time so as to provide a controlled release of the cement and an ascertainable delay in set time.

The hydration stabilizer preferably comprises a calcium chelating compound such as a polyphosphonic acid or a carboxylic acid that contains hydroxyl and/or amino groups. Polyphosphonic acids and similar compounds can be particularly advantageous because of their controlled degradation in the concrete mixture over an extended period of time that allows for a timed setting of the concrete.

Suitable examples of hydration stabilizers include N-nitrilo tris(methylene phosphonic acid); 1,2-ethanediyl bis[nitrilo di(methylene phosphonic acid)]; 1,6-hexanediyl bis[nitrilo di(methylene phosphonic acid)] and the like.

Another class of suitable phosphonic acid hydration stabilizing compounds include polymethoxy polyphosphonic acids represented by the formula II



$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-CH_2(OCH_2)_x[OCH_2\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}(OCH_2)_y]_z-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-OH$$

wherein x and y are each an integer of from 1-3, and preferably 1, and z is an integer of 0 or 1. It is understood that when z is 0 the radical within the bracket is non-existent and, therefore $(OCH_2)_y$ is nonexistent. The preferred polymethoxy polyphosphonic acid compounds are represented by the above formula when z=0 and x is 1-3. Other suitable polymethoxy polyphosphoic acid compounds are disclosed in U.S. Pat. No. 5,215,585, which is incorporated herein by reference.

A particularly useful hydration stabilizer is amino tris (methylene phosphonic acid), which is a component of the commercially available hydration stabilizer sold by Master Builders under the trademark Delvo. Illustrative examples of

hydration stabilizers, including some of those mentioned above, are set forth in U.S. Pat. Nos. 5,427,617 and 5,203,919, which are incorporated herein by reference. Hydration retarders and accelerators suitable for use as hydration stabilizers are also disclosed in U.S. Pat. No. 6,858,074, which is also incorporated herein by reference.

As mentioned, the hydration stabilizer of the present invention prevents or inhibits setting and then degrades or is released from the cement to provide controlled setting. In some cases, it is necessary that the hydration stabilizer also comprise an accelerator to cause the controlled hydration of the cement. The amount of accelerator that needs to be added depends on several factors, such as the amount of hydration retarder, cement type and reactivity, ambient temperature, concrete mixture proportions, and the presence or absence of certain admixtures in the concrete mixture, such as water reducing polymers.

Accelerators that can be used to activate the hydraulic cement can be selected from conventional cement accelerators such as those classified as ASTM C 494 Type C admixtures. These include alkali metal halides (calcium chloride and the like), alkali metal nitrites (calcium nitrite and the like), alkali metal nitrates (calcium nitrate and the like), alkali metal formates (calcium formate and the like), alkali metal thiocyanates (sodium thiocyanate and the like), triethanolamine and the like. The particular set accelerator to be used will depend on the known nature of the accelerators and side effects of the agent. For example, where metal corrosion is not a problem, calcium chloride might be chosen, while if corrosion is a problem, the nitrite or nitrate salts might be better used. The preferred accelerators are calcium nitrate and the like.

The accelerating agent should be added in amounts which effectively cause the combined cement mixture to set and provide conventional 28 day strength for such compositions (e.g. mortars of about 2000-4000 psi; concrete of about 2,500 to 10,000 psi). The amount, based on cement content, should be from about 0.5 to about 6 weight percent, preferably from about 1 to about 5 percent.

The hydration stabilizer is mixed with the cement mixtures in amounts effective to prevent the hydraulic cement from reacting with the aqueous foam for a desired period of time. The specific effective amount depends on the amount and type of cement and the desired amount of stabilization. Preferably, a sufficient amount of hydration stabilizer is included in the concrete mixture to stabilize substantially all of the cement. Suitable amounts typically require from about 1.5 oz to about 8.0 oz per hundred lbs of cement, more preferably about 3.0 oz to about 6 oz, for a concrete mix having a 28 day cure time. The stabilization can be extended by adding about 4 oz of hydration stabilizer per 100 lbs cement per hour of extension.

Hydration stabilizers are known and used in the concrete industry for waste water reclamation and for reusing concrete mixtures. Currently, hydration stabilizers are added to concrete waste water so that the truck or other mixing machinery does not have to be washed out after use or so that the remaining concrete can be used on another job. The hydration stabilizer prevents setting until the cement can be reused. The inventor of the present invention has found that the properties and concentrations of hydration retarders used in these known hydration stabilizing compositions are surprisingly advantageous for stabilizing foam admixtures according to the present invention. Commercially available hydration stabilizers, in addition to Delvo mentioned above, include Recover (W. R. Grace), Delayed Set (Fritz-Pak Corp.), Stop-Set and

Stop-Set L (Axim Italcementi Group), and Polychem Renu (General Resource Technology).

D. Dispersants and/or Water-Reducers

Water reducers are used in concrete mixtures to lower the water content in the plastic concrete (i.e. uncured concrete) to increase its strength and to obtain higher slump without adding water. Water-reducers will generally reduce the required water content of a concrete mixture for a given slump and are useful for pumping concrete and in hot weather to offset the increased water demand. These admixtures disperse the cement particles in the concrete and make more efficient use of the hydraulic cement. This dispersion increases strength and/or allows the cement content to be reduced while maintaining the same strength. Water-reducers should meet the requirements for Type A in ASTM C 494 Specification.

Another class of water reducers includes mid-range water reducers. These water reducers have a greater ability to reduce the water content of the concrete and are often used because of their ability to improve the finishability of concrete flatwork. Mid-range water reducers should at least meet the requirements for Type A in ASTM C 494.

High range water-reducers (HRWR), also referred to as superplasticizers, are a special class of water-reducer. HRWRs reduce the water content of a given concrete mixture by about 12% to 30%. HRWRs are used to increase strength and reduce permeability of concrete by reducing the water content in the mixture or greatly increase the slump to produce “flowing” concrete without adding water. HRWRs are often used for high strength and high performance concrete mixture that contain higher contents of cementitious materials and mixtures containing silica fume. In a typical concrete mixture, adding a normal dosage of HRWRs to a concrete mixture with a slump of 3 to 4 inches (75 to 100 mm) will produce a concrete with a slump of about 8 inches (200 mm). Exemplary HRWRs that can be used in the present invention are covered by ASTM Specification C 494 and types F and G, and Types 1 and 2 in ASTM C 1017. Particularly advantageous dispersants include the HRWRS described in U.S. Pat. No. 6,858,074, which is incorporated herein by reference.

It is believed that water reducing dispersants may have a particularly beneficial effect on the concrete compositions of the present invention by working in conjunction with the hydration stabilizer to stabilize the foam admixtures of the present invention.

E. Aggregates

Aggregates are usually included in the concrete mixture to add bulk and to give the concrete strength. The aggregate can be a fine aggregate and/or a coarse aggregate. The fine aggregates are materials that pass through a Number 4 sieve (ASTM C125 and ASTM C33), such as silica sand. The coarse aggregate 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.

Whether an aggregate needs to be added can depend on the desired use of the cured concrete and on the type of aqueous foam admixture that is used. Some aqueous foam admixtures of the present invention are sufficiently stabilized to function as a foam aggregate. For example, the air bubbles in aqueous foams that are stabilized with a fluorochemical surfactant can have sufficient strength to act as a foam aggregate. In particular, foams stabilized with fluorochemical surfactants that include hydrophilic nonionic and hydrophilic anionic monomers are particularly suited to act as foam aggregates. It is believed that the anionic and nonionic monomers are able to

disperse the hydraulic cement around the foam bubbles thereby creating a cement matrix similar to the cement matrix that forms around aggregates.

The concrete mixtures of the present invention also include concrete mixtures that include traditional aggregates (i.e. coarse and fine aggregates) in combination with foam aggregates (e.g. aqueous foams stabilized with surfactants having nonionic and anionic monomers). Concrete mixtures of the present invention that incorporate a combination of foam aggregates with fine aggregates and/or coarse aggregates can be made to have superior compressive and flexural strength and/or can include ratios of aggregate sizes that are not possible with traditional concrete mixtures.

For example, ready mixed concrete used in flat work or foundation walls typically has a ratio of fine aggregates to coarse aggregates of 50:50. This ratio can be usually be modified to ratios from 60:40 to 40:60. Using the aqueous foams stabilized with a fluorochemical surfactant, the concrete mixtures of the present invention can be made using ratios of less than 40% of either fine aggregates or coarse aggregates while still maintaining ASTM standards for flexural and compressive strength. In an exemplary embodiment, the aggregate can comprise less than 40% fine aggregate, less than 30% fine aggregate, less than 20% fine aggregate or even substantially no fine aggregate. Alternatively, the aggregate can comprise less than 40% coarse aggregate, less than 30% coarse aggregate, less than 20% coarse aggregate, or even substantially no coarse aggregate. Even with these low percentages of coarse or fine aggregate, a compressive strength of greater than 2500 psi, more preferably greater than 3000 psi, or most preferably greater than 4000 psi can be achieved.

The use of only one size of aggregate is particularly beneficial in areas where both coarse and fine aggregates are not available or a particular size aggregate is in abundance. Also, the concrete mixtures of the present invention are particularly useful for incorporating certain aggregates sizes such as ⅜ inch gravel (i.e. pea gravel), that cannot be used in some concrete mixtures because it leads to lower quality concrete. With the concrete mixtures of the present invention, pea gravel can be used while still maintaining suitable compressive strength (e.g. 3000-4000 psi).

Thus, using the foam aggregates of the present invention, novel combinations of aggregates can be used to make concrete having suitable strength for ready mixed concrete and other applications.

F. Fly Ash

Fly ash is another admixture that can be included in the concrete mixtures of the present invention. ASTM C618 standard, which is incorporated herein by reference, recognizes two major classes of fly ashes for use in concrete—Class C and Class F. These two classes of fly ashes are derived from different kinds of coals that are a result of differences in the coal formation processes occurring over geological time periods. Class F fly ash is normally produced from burning anthracite or bituminous coal, whereas Class C fly ash is normally produced from lignite or sub-bituminous coal. The ASTM C618 standard differentiates Class F and Class C fly ashes primarily according to their pozzolanic properties. Accordingly, in the ASTM C618 standard, the major specification difference between the Class F fly ash and Class C fly ash is the minimum limit of $SiO_2+Al_2O_3+Fe_2O_3$ in the composition. The minimum limit of $SiO_2+Al_2O_3+Fe_2O_3$ for Class F fly ash is 70% and for Class C fly ash is 50%. Thus, Class F fly ashes are more pozzolanic than the Class C fly ashes. Although not explicitly recognized in the ASTM C618 standard, Class C fly ashes typically contain high calcium oxide content. Presence of high calcium oxide content makes

Class C fly ashes possess cementitious properties leading to the formation of calcium silicate and calcium aluminate hydrates when mixed with water. The use of Class C fly ash can be particularly useful to replace a portion of the cement in the concrete. Class C fly ash and Portland cement can be blended in weight ratios of ash to cement of about 0/100 to 150/100, preferably 75/100 to 125/100. In some reactive powder blends the portland cement is about 40 to 80 wt % and fly ash 20 to 60 wt %.

Because fly ash is obtained from coal combustion or found naturally, fly ash can include a certain amount of carbon. The amount of carbon in fly ash is measured according loss of ignition (LOI). Fly ash that has an LOI greater than about 1.5 is typically not suitable for use with concrete mixtures that have air entraining agents because the carbon destroys the air entrainment. The inventor of the present invention has found that the foam admixtures of the present invention that are stabilized with a fluorochemical surfactant are surprisingly resistant to destruction by high carbon fly ash. Thus, in one embodiment of the invention, the concrete mixture includes a fly ash having an LOI greater than about 1.5, more preferably greater than about 2, more preferably greater than 4, and most preferably greater than about 6. It has also been found that high carbon fly ash when used in combination with the fluorochemical stabilized foam admixtures of the present invention, increases the strength of the cured concrete over fly ash that is not high carbon.

G. Viscosity Modifiers

Viscosity modifying agents (VMA), also known as Theological modifiers or rheology modifying agents, can be added to the concrete mixture of the present invention. These additives are usually water-soluble polymers and function by increasing the apparent viscosity of the mix water. This enhanced viscosity facilitates uniform flow of the particles and reduces bleed, or free water formation, on the fresh paste surface.

Suitable viscosity modifiers that can be used in the present invention include, for example, cellulose ethers (e.g., hydroxyethyl cellulose (HEC), hydroxyproplmethyl cellulose (HPMC), sodium carboxymethyl cellulose (CMC), carboxymethylhydroxyethyl cellulose (CMHEC), and the like); synthetic polymers (e.g., polyacrylates, polyvinyl alcohol (PVA), polyethylene glycol (PEG), and the like); exopolysaccharides (also known as biopolymers, e.g., welan gum, xanthan, rhamsan, gellan, dextran, pullulan, curdlan, and the like); marine gums (e.g., algin, agar, carrageenan, and the like); plant exudates (e.g., locust bean, gum arabic, gum Karaya, tragacanth, Ghatti, and the like); seed gums (e.g., Guar, locust bean, okra, psyllium, mesquite, and the like); starch-based gums (e.g., ethers, esters, and related derivatized compounds). See, for example, Shandra, Satish and Ohama, Yoshihiko, "Polymers In Concrete", published by CRC press, Boca Ration, Ann Harbor, London, Tokyo (1994).

Viscosity modifying agents are typically used with water reducers in highly flowable mixtures to hold the mixture together. Viscosity modifiers can disperse and/or suspend components of the concrete thereby assisting in holding the concrete mixture together. This property of viscosity modifiers makes them useful for making self compacting concrete, which requires high flowability.

Some foam admixtures of the present invention (e.g. fluorochemical stabilized foams having nonionic and anionic monomers) can act as a viscosity modifying agent thereby reducing the need for a separate viscosity modifier in the concrete mix. Highly flowable and/or self-compacting concrete can be achieved with these foams of the present invention while substantially reducing the amount of viscosity modifier included separately in the concrete mix. In an exemplary embodiment, viscosity modifier is added to the concrete mix in an amount less than 12 oz/100 wt, more preferably less than 9 oz, even more preferably less than about 5 oz, and most preferably substantially no viscosity modifier is added apart from the foam admixture.

Even with no additional viscosity modifier added to the concrete mixture, the concrete mixtures of the present invention can be highly flowable. Water and Low-range, mid-range, and/or high range water reducers can be added to the concrete mixture to give the concrete mixture a high flowability without the concrete separating because the foam admixture acts as a very good viscosity modifier. Concrete according to the present invention can be manufactured to have a "flow spread" of greater than 24-36 inches (using a 12 inch slump cone). The high spread of the concrete composition of the present invention are particularly advantageous because the spread is homogenous. The foam admixtures of the present invention can suspend the aggregate and other components in the concrete mixture such that mixes that spread greater than about 24-36 inches are spread substantially homogenous.

H. Other Admixtures

Many other types of admixtures can be added to the concrete compositions of the present invention to give the concrete a desired property. As discussed below, other admixtures suitable for use in the concrete mixtures of the present invention include but are not limited to viscosity modifiers, corrosion inhibitors, pigments, wetting agents, water soluble polymers, strength enhancing agents, rheology modifying agents, water repellents, fibers, permeability reducers, pumping aids, fungicidal admixtures, germicidal admixtures, insecticidal admixtures, finely divided mineral admixtures, alkali reactivity reducer, bonding admixtures, and any other admixtures or additive that do not adversely affect the stabilized foam or hydration stabilizers of the present invention.

Corrosion inhibitors in concrete serve to protect embedded reinforcing steel from corrosion due to its highly alkaline nature. The high alkaline nature of the concrete causes a passive and noncorroding protective oxide film to form on the steel. However, carbonation or the presence of chloride ions from deicers or seawater can destroy or penetrate the film and result in corrosion. Corrosion-inhibiting admixtures chemically arrest this corrosion reaction. The materials most commonly used to inhibit corrosion are calcium nitrite, sodium nitrite, sodium benzoate, certain phosphates or fluorosilicates, fluoroaluminates, amines, organic based water repelling agents, and related chemicals.

Dampproofing admixtures reduce the permeability of concrete that have low cement contents, high water-cement ratios, or a deficiency of fines in the aggregate. These admixtures retard moisture penetration into dry concrete and include certain soaps, stearates, and petroleum products.

Permeability reducers are used to reduce the rate at which water under pressure is transmitted through concrete. Silica fume, fly ash, ground slag, natural pozzolans, water reducers, and latex can be employed to decrease the permeability of the concrete.

Pumping aids are added to concrete mixes to improve pumpability. These admixtures thicken the fluid concrete, i.e., increase its viscosity, to reduce de-watering of the paste while it is under pressure from the pump. Among the materials used as pumping aids in concrete are organic and synthetic polymers, hydroxyethylcellulose (HEC) or HEC blended with dispersants, organic flocculents, organic emulsions of paraffin, coal tar, asphalt, acrylics, bentonite and pyrogenic silicas, natural pozzolans, fly ash and hydrated lime.

Bacteria and fungal growth on or in hardened concrete may be partially controlled through the use of fungicidal, germicidal, and insecticidal admixtures. The most effective materials for these purposes are polyhalogenated phenols, dialdrin emulsions, and copper compounds.

Fibers can be distributed throughout a fresh concrete mixture to strengthen it. Upon hardening, this concrete is referred to as fiber-reinforced concrete. Fibers can be made of zirconium materials, carbon, steel, fiberglass, or synthetic materials, e.g., polypropylene, nylon, polyethylene, polyester, rayon, high-strength aramid, or mixtures thereof.

The shrinkage reducing agent which can be used in the present invention can include but is not limited to alkali metal sulfate, alkaline earth metal sulfates, alkaline earth oxides, preferably sodium sulfate and calcium oxide.

Alkali-reactivity reducers can reduce the alkali-aggregate reaction and limit the disruptive expansion forces in hardened concrete. Pozzolans (fly ash and silica fume), blast-furnace slag, salts of lithium, and barium are especially effective.

Bonding admixtures are usually added to hydraulic cement mixtures to increase the bond strength between old and new concrete and include organic materials such as rubber, polyvinyl chloride, polyvinyl acetate, acrylics, styrene butadiene copolymers, and other powdered polymers.

Natural and synthetic admixtures are used to color concrete for aesthetic and safety reasons. These coloring admixtures are usually composed of pigments and include carbon black, iron oxide, phthalocyanine, umber, chromium oxide, titanium oxide and cobalt blue.

Air entrainers can be included in the concrete mixtures of the present invention, although this is usually not necessary since the foam admixtures provide an air entraining features. Unlike foam, air entrainers are added to the concrete mixture in a liquid form (i.e. without the air entrapped).

III. Methods of Making and Using Concrete Mixtures

The present invention also includes methods for making foam and methods for incorporating those foams into concrete mixtures.

A. Method of Making Foam Admixtures

As discussed above, in an exemplary embodiment, the foam admixtures are manufactured from a foam concentrate. Foam production is performed by drawing water and the foam concentrate, in proper ratios, and injecting them into a chamber using high pressure air. The mixture is subjected to shearing forces that produce air bubbles (i.e. foam) in the chamber.

The ratio of water, foam concentrate, and air are controlled to produce air bubbles of a desired size and shape. In a preferred embodiment, the water and foam concentrate are mixed to form a diluted concentrate comprising between at least about 80% water, more preferably greater than about 90% water and more preferably greater than about 95% water. The amount of air injected into the diluted foam is controlled by the air pressure and volume of air.

In an exemplary embodiment, air bubbles are formed having an approximate size of about 0.3 ml to about 1.0 ml, more preferably from about 0.5 ml to about 0.7 ml. In a preferred embodiment, the bubbles are of uniform size and shape. It is believed that the uniform size and shape is beneficial for providing a uniform dispersion of cement and aggregate.

Any number of foam production devices can be used for producing the foam admixtures of the present invention, and the invention is not limited to any specific such device. Such devices are well known in the art. Whatever mechanism used, it should be adequate to produce a stream of bubbles suitable for introduction into the concrete mixtures of the present invention.

The following formula "Concentrate I," shown in the table below, illustrates a suitable concentrate for manufacturing a foam admixture according to the present invention.

CONCENTRATE I

COMPONENT	CAS NUMBER/TRADE NAME	w/w %
Sodium alkenyl sulfonates mixture)	68439-57-6, 11066-21-0, 11067-19-9	7.0
1-t-Butoxy-2-propanol	57018-52-7	5.0
Rhamsan gum	96949-21-2	2.0
Perfluoroethylthia acrylic telomere	Lodyne ™ K90'90 (Ciba-Geigy Corp.)	1.4
n-Alkanols (mixture)	112-53-8, 112-72-1, 36653-82-4	1.0
2-Methyl-2-propanol	75-65-0	0.2
Water	7732-18-5	balance

Concentrate I can be used to form a stable and resilient aqueous foam admixture by diluting Concentrate I to 2.5 w/w % water (39 parts water to one part Concentrate I) and then aerating it through a foam generating chamber at about 92 psi, thereby subjecting the diluted Concentrate I to shearing forces that produce an aqueous foam admixture.

B. Method of Mixing Concrete

The concrete mixtures of the present invention are manufacture by mixing proper amounts of a hydraulic cement, hydration stabilizer, water, and foam admixture. Typically the concrete mixture also includes aggregate. However, for some non-structural applications, aggregate may not be necessary. Dispersants and other admixtures can be added as needed to give the concrete mixture desired properties.

Typically the hydraulic cement, hydration stabilizer, water, and foam can be mixed together in any order so long as the water is added before the foam. The hydration stabilizer is preferably added to the cement before the cement is mixed with the foam to minimize the reaction of hydraulic cement and foam. It has also been found that adding the hydration stabilizer to the water before the water is mixed with the cement can also increase stability of the foam when the foam is mixed with the cement. Accelerator can be added to the concrete mixture at the same time that the hydration retarding agent is added, or the accelerator can be added at a later point in time, such as just before the concrete is to be poured.

The amount of foam mixed into the concrete mixture is selected to give the concrete a desired percent of air. In an exemplary embodiment, the foam admixture is included in the concrete mixture in an amount sufficient to provide greater than 5% air in the concrete, more preferably greater than 10% air, and most preferably greater than about 15% air by volume of the concrete mixture.

The limit on the amount of foam that can be added depends on the desired final strength of the concrete and the amount of cement in the mixture. In general, lower percentages of air and higher amounts of cement produce stronger cements. However, the concrete mixtures of the present invention can have very high compressive strengths with percentages of air above 5%, as compared with existing cements. Using the aqueous foams of the present invention, air can be entrained into the concrete mixture in percentages greater than 5%, 10%, and even 20% while maintaining compressive strengths of greater than about 2500 psi, and more preferably greater than about 3000 psi, in 28 days. For example, concrete mixtures according to the present invention having 12% air and

300 lbs/yd^3 of cement can achieve about 300-4000 psi in 28 days. In another example, concrete mixture according to the present invention having 22% air and 650 lbs/yd^3 cement can achieve a compressive strength of about 6500 psi in 28 days. Even at very high percentages of air, significant compressive strength can be achieved. For example, concrete mixtures of 85% air can achieve 90 psi in 28 days.

Because the cement is stabilized with respect to the foam using the hydration stabilizer, the air entrainment provided by the foam can last at least until the concrete sets.

Table 2 below provides 3 different exemplary ranges of typical amounts of the components needed to make concrete mixtures according to the present invention.

TABLE 2

	1	2	3
Portland Cement	1-50%	6-50%	10-25%
Washed Sand	0-75%	0-60%	0-40%
Coarse Aggregate	0-60%	0-50%	0-40%
Water	4-50%	5-50%	10-25%
Pozzolanic Material	0-50%	0-20%	0-5.0%
Foam Admixture	1-90%	1-85%	1-75%
Water Reducers	0-20 oz	0-6.0 oz	0-4.5 oz
Accelerators	0-20 oz	0-12 oz	0-8.0 oz
Hydration Stabilizer	0.5-20 oz	1.0-12 oz	1.5-6.0 oz

In the compositions described in Table 2, the foam admixture is manufactured as described above (e.g. Concentrate I diluted to 2.5 w/w % water and foamed at 92 psi). The weight of the foam admixture includes the weight of the water that makes up the foam. Water is also included as a separate component, which does not include the water in the aqueous foam admixture.

A sufficient amount of hydration stabilizer is included to stabilize the foam admixture for a desired amount of time. The sufficiency of the hydration stabilizer can depend in part on the type of concrete being made. For ready mixed concrete, where transportation is often needed, the hydration stabilizer can be added in greater amounts such that the stabilization lasts during transportation and until the concrete has set.

The amount of hydration stabilizer used in the concrete mixture is determined by the need to stabilize the cement with respect to the foam. A sufficient amount of hydration stabilizer will inhibit the reaction between the cement and the foam such that a majority or substantially all of the foam initially mixed into the concrete lasts until the concrete achieves initial set. Typically, less than 2% of the foam collapses within the first 2 hours.

Regardless of whether the concrete is designed to set in a short period (e.g. less than 1 hour) or over along period of time, the hydration stabilizer included in the concrete of the present invention can be very beneficial to stabilizing the foam admixture. The cement in a concrete mixture is most reactive, and thus most destructive to the foam admixture, when it is first mixed with the water. Consequently, the hydration stabilizer provides its greatest benefit during initial mixing of the cement, foam, and water, although significant benefits can still be realized by including the hydration stabilizer after initial mixing. The use of hydration stabilizer during the initial mixing of the concrete differs from most current practices, which add hydration stabilizer to waste concrete after a job is finished or during a job to preserve the concrete for later use. In the present invention, the hydration stabilizer is added to prevent the reaction of the foam and the cement. Accelerators can be added anytime during or after mixing to control set time, if needed.

Those skilled in the art will recognize that there are many applications in which the combination of hydration stabilizer, hydraulic cement, and foam according to the present invention can be easily incorporated into a concrete composition using the foregoing description. The following examples give specific formulations of aqueous foams and concrete composition that employ the concepts of the present invention.

IV. EXAMPLES

Examples 1-5 illustrate concrete compositions according to the present invention. In each formula, admixtures (e.g. water reducers WR) were added based on 100 lbs of cement (i.e. 100-wt cement). The concrete mixtures of Examples 1-3 had 12% air and produced cured concrete with a compressive strength of greater than 3000 psi at 28 days.

Example 1

COMPONENTS	AMOUNTS
Portland Cement	308 lbs/yd^3
Water	30 gal/yd^3
Hydration Stabilizer (Recover, W.R. Grace)	5.5 oz/100-wt
Fine Aggregate	1630 lbs/yd^3
Coarse Aggregate	1235 lbs/yd^3
Foam Admixture (Miracon)	2.8 ft^3/yd^3
Mid Range WR (997, Master Builders)	5 oz/100-wt
Low Range WR (27, W.R. Grace)	0.5 oz/100-wt

Example 2

COMPONENTS	AMOUNTS
Portland Cement	308 lbs/yd^3
Water	30 gal/yd^3
Hydration Stabilizer (Recover, W.R. Grace)	5.5 oz/100-wt
Fine Aggregate	1630 lbs/yd^3
Coarse Aggregate	1235 lbs/yd^3
Foam Admixture (Miracon)	2.8 ft^3/yd^3
High Range WR (Adva, W.R. Grace)	3.5 oz/100-wt
Low Range WR (27, W.R. Grace)	0.5 oz/100-wt

Example 3

COMPONENTS	AMOUNTS
Portland Cement	308 lbs/yd^3
Water	30 gal/yd^3
Hydration Stabilizer (Recover, W.R. Grace)	5.5 oz/100-wt
Fine Aggregate	1630 lbs/yd^3
Coarse Aggregate	1235 lbs/yd^3
Foam Admixture (Miracon)	2.8 ft^3/yd^3
High Range WR (Adva, W.R. Grace)	3 oz/100-wt
Mid Range WR (997, Master Builders)	6.5 oz/100-wt
Low Range WR (27, W.R. Grace)	0.5 oz/100-wt

Example 4

COMPONENTS	AMOUNTS
Holcim Cement	408.2 lbs/yd^3
Water	25.88 gal/yd^3
Hydration Stabilizer (Delvo, Master Builders)	2.52 oz/100-wt
Fine Aggregate (concrete sand)	1251 lbs/yd^3
Coarse Aggregate (#8 pea gravel)	830.8 lbs/yd^3
Fly Ash (Bridger)	164.1 lbs/yd^3
Foam Admixture (Miracon)	7.65 ft^3/yd^3
High Range WR (30/30, Master Builders)	6.3 oz/100-wt
Low Range WR (27, W.R. Grace)	1.17 oz/100-wt
Accelerator Calcium Chloride	32.32 oz/100-wt

The concrete prepared using Example 4 had 27.1% air and a compressive strength of 923 psi in 28 days and 1205 psi in 56 days.

Example 5

COMPONENTS	AMOUNTS
Cement (Ashgrove I/II)	352 lbs/yd^3
Water	21.8 gal/yd^3
Hydration Stabilizer (Recover,)	1.99 oz/100-wt
Fine Aggregate (concrete sand)	1316 lbs/yd^3
Coarse Aggregate (#8 pea gravel)	312 lbs/yd^3
Coarse Aggregate (#57 rock)	1581 lbs/yd^3
Fly Ash (San Juan Type F)	103 lbs/yd^3
Foam Admixture (Miracon)	1.5 ft^3/yd^3
High Range WR (30/30, Master Builders)	4.85 oz/100-wt
Low Range WR (27, W.R. Grace)	2.5 oz/100-wt
Accelerator Calcium	29.82 oz/100-wt

The concrete prepared using Example 5 had 5.8% air and a compressive strength of 3615 psi in 28 days and 4320 psi in 56 days.

Example 6

In Example 6, a concrete mixture was prepared using a standard air entraining agent and a second mixture was prepared using Miracon as an air entraining agent. Both had an air entrainment of 5.8%, a density of 139 lbs/ft^3 and used 5.5 sacks of cement. The following performance data compares the performance of the standard mixture and the mixture prepared according to the present invention.

		Standard Air Entrainment	Air Entrainment with Miracon
Bleeding, (%)		1.68%	1.11%
Initial Set (hr)		4.67	4.51
Compressive Strength (psi)	3 day	2130	2840
	7 day	2890	3610
	21 day	4110	4970
Flexural Strength (psi)	3 day	430	470
	7 day	490	610
	21 day	590	640

As can be seen from the comparison with standard air entrainment, concrete entrained using the hydration stabilizer and foams of the present invention achieve higher strength and decreased bleeding when compared with traditional air entraining agents.

The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

What is claimed is:

1. A concrete mixture, comprising:

(i) a hydraulic cement;

(ii) a hydration stabilizer that inhibits hydration of the hydraulic cement, the hydration stabilizer including a set retarder and an accelerator;

(iii) water;

(iv) a foam admixture comprising water and a fluorochemical surfactant, wherein the foam is stabilized in the presence of the hydraulic cement by the hydration stabilizer.

2. A concrete mixture as in claim **1**, wherein the hydration stabilizer includes a calcium binding agent.

3. A concrete mixture as in claim **2**, wherein the hydration stabilizer includes a derivative of a phosphonic acid.

4. A concrete mixture as in claim **1**, wherein the hydration stabilizer includes a molecule selected from the group consisting of N-nitrilo tris(methylene phosphonic acid), 1,2-ethanediyl bis[nitrilo di(methylene phosphonic acid)]; 1,6-hexanediyl bis[nitrilo di(methylene phosphonic acid)], amino tris(methylene phosphonic acid), polymethoxy polyphosphonic acids, and combinations thereof.

5. A concrete mixture as in claim **1**, wherein the fluorochemical surfactant comprises an oligomer comprising a hydrophilic nonionic monomer.

6. A concrete mixture as in claim **1**, wherein the fluorochemical surfactant comprises a hydrophilic anionic monomer.

7. A concrete mixture as in claim **1**, wherein the fluorochemical surfactant has the formula:

$$R_f\text{-}E_a\text{-}(S)_b\text{-}[M_1]_x\text{-}[M_2]_y\text{-}H$$

wherein

R_f is (i) a straight chain, branched chain, or cyclic perfluoroalkyl of 1 to about 20 carbon atoms, (ii) a perfluoroalkyl substituted with a perfluoroalkoxy of 2 to about 20 carbon atoms, (iii) a perfluoroalkyl oligomer or polymer of greater than 10 carbon atoms, or (iv) a combination thereof;

E_a is (i) a direct bond; (ii) a branched, straight chain, or cyclic alkylene of 2 to about 20 carbon atoms; (iii) the alkylene of (ii) interrupted by one or more groups selected from the group consisting of —NR—, —O—, —S—, —SO_2—, —COO—, —OOC—, —CONR—, —NRCO—, —SO_2NR—, —$NRSO_2$—, —SiR_2—; or (iv) the alkylene of (ii) terminated at the R_f end with —CONR— or —SO_2NR—;

R is independently hydrogen, an alkyl of 1-10 carbon atoms, or a hydroxyalkyl of 2 to 10 carbon atoms;

a and b are independently 0 or 1;

-[M_1]- represents a non-ionic hydrophilic monomer unit;

-[M_2]- represents an anionic hydrophilic monomer unit; and

x and y represent the number of monomer units present in the co-oligomers and are both greater than 0; the sum of x and y being between 5 and 200, and y/(x+y) being between 0.01 and 0.98.

8. A concrete mixture as in claim **7**, wherein:

-[M_1]- is selected from the group consisting of acrylamide, methacrylamide, diacetone acrylamide, 2-hydroxyethyl methacrylate, derivatives of acrylic, methacrylic, maleic, fumaric and itaconic acids, amides, and vinyl esters containing from 1 to about 20 carbon atoms in the ester group, and combinations thereof; and

-[M_2]- is selected from the group consisting of acrylic and methacrylic acids and salts thereof, maleic, fumaric and itaconic acids and salts thereof, acrylamidopropane sulfonic acid and salts thereof, and mono-olefinic sulfonic and phosphonic acids and salts thereof, and combinations thereof.

9. A concrete mixture as in claim **1**, wherein the foam comprises at least about 5% by volume of the concrete mixture.

10. A concrete mixture as in claim **1**, wherein the foam comprises at least about 10% by volume of the concrete mixture.

11. A concrete mixture as in claim **1**, wherein the hydration stabilizer is included in an amount sufficient to inhibit the reaction between the hydraulic cement and the water in the foam for greater than about 30 minutes.

12. A concrete mixture as in claim **1**, wherein the hydration stabilizer is included in an amount sufficient to inhibit the reaction between the hydraulic cement and the water in the foam for greater than about 1 hour.

13. A cured concrete manufactured by pouring the concrete mixture of claim **1** and allowing the concrete mixture to cure.

14. A concrete mixture as in claim **1** that achieves a compressive strength of greater than 2500 psi in 28 days, when allowed to set.

15. A concrete mixture as in claim **1** that achieves a compressive strength of greater than 3000 psi in 28 days, when allowed to set.

16. A concrete mixture as in claim **1** that achieves a compressive strength of greater than 4000 psi in 28 days, when allowed to set.

17. A concrete mixture, comprising:

(i) a hydraulic cement;

(ii) a hydration stabilizer that inhibits hydration of the hydraulic cement, the hydration stabilizer including a set retarder and an accelerator;

(iii) water;

(iv) a dispersant;

(v) aggregate; and

(vi) a foam comprising water, a nonionic surfactant, and a fluorochemical surfactant, wherein the foam comprises a plurality of air bubbles that are stabilized by the fluorochemical surfactant, the fluorochemical surfactant comprising an oligomer having at least one hydrophilic nonionic monomer or at least one hydrophilic anionic monomer.

18. A concrete mixture as in claim **17**, wherein the hydration stabilizer includes a derivative of a phosphoric acid.

19. A concrete mixture as in claim **17**, wherein

the foam comprises one or more fatty acid alcohols selected from the group consisting of straight and branched chain fatty acid alcohols of about 8 to about 16 carbon atoms;

the foam comprises an anionic polysaccharide selected from the group consisting of rhamsan gums, xanthan gums, guar gums, and locust bean gums; and

the foam comprises a non-fluorinated anionic surfactant having from about 8 to about 18 carbon atoms.

20. A concrete mixture as in claim **17**, wherein the composition and initial set time make the concrete mixture suitable for use in ready-mix applications.

21. A concrete mixture as in claim **17**, wherein the composition and initial set time make the concrete mixture suitable for use in precast applications.

22. A concrete mixture as in claim **17**, wherein:

-[M_1]- is selected from the group consisting of acrylamide, methacrylamide, diacetone acrylamide, 2-hydroxyethyl methacrylate, derivatives of acrylic, methacrylic, maleic, fumaric and itaconic acids, amides, and vinyl esters containing from 1 to about 20 carbon atoms in the ester group, and combinations thereof; and

-[M_2]- is selected from the group consisting of acrylic and methacrylic acids and salts thereof, maleic, fumaric and itaconic acids and salts thereof, acrylamidopropane sulfonic acid and salts thereof, and mono-olefinic sulfonic and phosphonic acids and salts thereof, and combinations thereof.

23. A concrete composition as in claim **17**, wherein the aggregate comprises less than 40% fine aggregate.

24. A concrete composition as in claim **17**, wherein the aggregate comprises less than 40% coarse aggregate.

25. A concrete mixture as in claim **17** that achieves a compressive strength of greater than 3000 psi in 56 days, when allowed to set.

26. A method for stabilizing a foam in a concrete mixture, comprising:

(i) providing an aqueous foam admixture comprising water, a fluorochemical surfactant, and a plurality of air bubbles;

(i) providing a cementitious mixture comprising hydraulic cement, water, and aggregate; and

(iii) mixing together the cementitious mixture, the aqueous foam admixture and a hydration stabilizer, wherein the hydration stabilizer includes a set retarder and an accelerator, the hydration stabilizer inhibiting the destruction of the air bubbles by the hydraulic cement.

27. A concrete mixture as in claim **26**, wherein the hydration stabilizer includes a calcium binding agent.

28. A concrete mixture as in claim **27**, wherein the hydration stabilizer includes a derivative of a phosphonic acid.

29. A concrete mixture as in claim **28**, wherein the hydration stabilizer includes a compound selected from the group consisting of N-nitrilo tris(methylene phosphonic acid), 1,2-ethanediyl bis[nitrilo di(methylene phosphonic acid)]; 1,6-hexanediyl bis[nitrilo di(methylene phosphonic acid)], amino tris(methylene phosphonic acid), polymethoxy polyphosphonic acids, and combinations thereof.

30. A method as in claim **26**, wherein the hydration stabilizer is mixed with the hydraulic cement before the water is mixed with the hydraulic cement.

31. A method as in claim **26**, wherein the hydration stabilizer is mixed with the water before the water is mixed with the hydraulic cement.

32. A method as in claim **26**, wherein the hydration stabilizer is mixed with the cement after the cement is mixed with the foam.

33. A method as in claim **26**, wherein the hydration stabilizer is mixed with the cement before the cement is mixed with the foam.

34. A method as in claim **26**, wherein providing the foam admixture comprises:

(i) providing a foaming concentrate comprising a nonionic surfactant; and

(ii) mixing the foaming concentrate with water and air under shear forces sufficient to form the plurality of air bubbles.

35. A method as in claim **34**, wherein

the foaming concentrate comprises one or more fatty acid alcohols selected from the group consisting of straight and branched chain fatty acid alcohols of about 8 to about 16 carbon atoms;

the foaming concentrate comprises an anionic polysaccharide selected from the group consisting of rhamsan gums, xanthan gums, guar gums, and locust bean gums; and

the foaming concentrate comprises a non-fluorinated anionic surfactant having from about 8 to about 18 carbon atoms.

36. A method as in claim **26**, wherein the fluorochemical surfactant comprises an oligomer comprising a hydrophilic nonionic monomer or a hydrophilic anionic monomer.

37. A method as in claim **26**, wherein the fluorochemical surfactant has the formula:

$$R_f\text{-}E_a\text{-}(S)_b\text{-}[M_1]_x\text{-}[M_2]_y\text{-}H$$

wherein

R_f is (i) a straight chain, branched chain, or cyclic perfluoroalkyl of 1 to about 20 carbon atoms, (ii) a perfluoroalkyl substituted with a perfluoroalkoxy of 2 to about 20 carbon atoms, (iii) a perfluoroalkyl oligomer or polymer of greater than 10 carbon atoms, or (iv) a combination thereof;

E_a is (i) a direct bond, (ii) a branched, straight chain, or cyclic alkylene of 2 to about 20 carbon atoms, (iii) the alkylene of (ii) interrupted by one or more groups selected from the group consisting of —NR—, —O—, —S—, —SO_2—, —COO—, —OOC—, —CONR—, —NRCO—, —SO_2NR—, —$NRSO_2$—, —SiR_2—; or (iv) the alkylene of (ii) terminated at the R_f end with —CONR— or —SO_2NR—;

R is independently hydrogen, an alkyl of 1-10 carbon atoms, or a hydroxyalkyl of 2 to 10 carbon atoms;

a and b are independently 0 or 1;

-$[M_1]$- represents a non-ionic hydrophilic monomer unit;

-$[M_2]$- represents an anionic hydrophilic monomer unit; and

x and y represent the number of monomer units present in the co-oligomers and are both greater than 0; the sum of x and y being between 5 and 200, and y/(x+y) being between 0.01 and 0.98.

38. A cured concrete composition manufacture according to the method of claim **26**.

39. A cured concrete as in claim **38** wherein the concrete achieves a compressive strength of greater than 3000 psi in 28 days.

40. A concrete mixture as in claim **1** further comprising a fly ash having a loss on ignition of at least about 4%.

41. A concrete mixture as in claim **1**, further comprising a fly ash having a loss on ignition of at least about 6%.

42. A method as in claim **26**, further comprising the step of mixing a fly ash with the cementitious material, the fly ash having a loss on ignition of at least about 6%.

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(54) **CONCRETE MIXTURES HAVING STABILIZED FOAM ADMIXTURE**

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(57) **ABSTRACT**

Flowable concrete mixtures have an aqueous foam admixture mixed therein to give the concrete mixture desired strength, flowability, and density. The concrete mixtures include a hydration stabilizer to stabilize the aqueous foam. The hydration stabilizer inhibits the reaction between the hydraulic cement and the water in the aqueous foam. The aqueous foam can be stabilized using a fluorochemical surfactant.

20 Claims, No Drawings

CONCRETE MIXTURES HAVING STABILIZED FOAM ADMIXTURE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a Continuation-In-Part of U.S. patent application Ser. No. 11/311,490, filed Dec. 19, 2005, entitled "Concrete Mixtures Having Aqueous Foam Admixtures" which claims the benefit of U.S. Provisional Patent Application Ser. No. 60/715,458, filed Sep. 9, 2005, entitled "Concrete Mixtures Having Aqueous Foam Admixtures," the disclosure of which is incorporated herein in its entirety.

BACKGROUND OF THE INVENTION

1. The Field of the Invention

The present invention relates to flowable concrete mixtures and cured concrete obtained therefrom. More particularly, the present invention relates to concrete mixtures that have an aqueous based foam admixture and a hydration stabilizer that stabilizes the foam in the concrete.

2. Related Technology

Concrete mixtures are composite materials that are usually composed of water, cement, and aggregate. Common aggregates include sand, gravel, or crushed stone. Concrete is a well-known structural component with typical compressive strengths of about 2500 psi, when cured.

Admixtures are often added to concrete to give the concrete desired properties. Examples of suitable uses for concrete admixtures include lowering the concrete's density, improving the concrete's workability, improving the concrete's strength to weight ratio, giving the concrete insulating properties, and/or enhancing the acoustic properties of the concrete, among others. These beneficial properties are often accomplished by adding several different admixtures.

Air entraining agents are often used alone or in combination with other admixtures to give the concrete one or more of the foregoing properties. Air entraining admixtures are used to purposely trap microscopic air bubbles in the concrete. Air entrainment dramatically improves the durability of concrete exposed to moisture during cycles of freezing and thawing. In addition, entrained air greatly improves concrete's resistance to surface scaling caused by chemical deicers. Air entrainment also increases the workability of fresh concrete while eliminating or reducing segregation and bleeding.

There are several methods for entraining air in concrete. One approach is to generate bubbles or air pockets in situ. This approach can be accomplished using surfactants or other air entraining admixtures that generate bubbles as the concrete is mixed. Materials used to achieve these desired effects include non-ionic, cationic, and anionic surfactants, natural and synthetic resins, fatty acids, proteinaceous material, sulfonated hydrocarbons, and the like. This approach, while effective for entraining small amounts of air, is difficult to use for higher percentages of air because the bubble size, amount of bubbles, durability, and distribution of bubbles within the concrete are difficult to control.

Another approach for incorporating air in concrete is to add foam admixtures. When using a foam admixture, the cellular bubbles (i.e. the foam) is formed ex-situ and then mixed with the concrete. This method is advantageous because the foam is created in a controlled environment. The water, air, and foaming concentrates can be designed to produce foams having a desired size and composition.

Despite many advantages, the use of foam admixtures formed ex-situ have had limited use (e.g. in insulating, non-structural, or non-load-bearing bearing applications). Most commercially available foaming agents are not stable in cementitious media and the results of their use are often inconsistent. For example, with existing foam-concrete mixtures, the size and distribution of foam cells have been difficult to control and the cells have had a limited period of usefulness or lifetime. The foam cells have tended to agglomerate, coalesce, and recombine to give larger cells and a wide range of sizes. Long mixing times, such as those required for transportation from a concrete production facility to a construction site, have been precluded due to bubbles collapsing and air escaping from the mix. Even when additives have been used to stabilize these foams (e.g., U.S. Pat. Nos. 5,160,540 and 6,153,005, which are hereby incorporated by reference), the foam's stability and useful lifetime in the concrete prevents use in many applications, such as those requiring transportation of the concrete (e.g. ready mixed concrete).

BRIEF SUMMARY OF THE INVENTION

The present invention relates to flowable concrete mixtures comprising an aqueous foam. The concrete mixtures include (i) a hydraulic cement, (ii) a hydration stabilizer, and (iii) an aqueous foam. The hydration stabilizer inhibits hydration of the hydraulic cement thereby inhibiting deleterious interactions between the cement and the aqueous foam that can destroy the foam bubbles. The stabilizing effect of the hydration stabilizer allows the foam to be successfully combined with concrete mixtures and/or allows the foam to last longer in the concrete mixture.

The hydration stabilizers used to reduce the reaction between the cement and the foam includes a hydration retarder that can slow or stop hydration of the siliceous and/or aluminous component of hydraulic cements. Preferred hydration stabilizers are those that can bind calcium, such as derivatives of phosphonic acid and carboxylic acids having hydroxyl or amino groups. Because of the retarding effect that the hydration retarder can have on setting, the hydration stabilizer may also include an accelerator.

The inventor of the present invention has found that controlling the hydration of the cement has a significant stabilizing effect on aqueous based foams in concrete mixtures. The hydration stabilization of the present invention allows aqueous foams to be added to concrete that would otherwise not be stable in a concrete mixture. Furthermore, aqueous foams that are currently being used in concrete mixtures for certain applications (i.e. to make some precast structures) can be sufficiently stabilized such that they can be used in new applications that require longer initial set times (e.g. ready mix applications).

In a preferred embodiment, the present invention is used with foams that have a fluorochemical surfactant. Fluorochemical surfactants are known to stabilize and/or strengthen the air bubbles in aqueous foams. Fluorochemical surfactants have been used in firefighting foams to generate foam bubbles that have enough structural stability that they can be sprayed on a burning chemical and last long enough to smother the fire. The aqueous nature of these foams and the stability of the foam bubbles make these foams particularly useful in the concrete mixtures of the present invention. The use of at least one such foam in a concrete mixture is described in U.S. Pat. No. 6,153,005 to Welker et al., which is incorporated herein by reference.

The stabilizing effect of the fluorochemical surfactant is distinct and in addition to the stabilizing effect of the hydration stabilizer. The fluorochemical surfactant is a component of the foam bubble and provides stability within the bubble. In contrast, the hydration stabilizer is a component of the concrete mixture to prevent deleterious interactions between the cement and the aqueous foam.

Foams stabilized with fluorochemical surfactants are particularly benefited by the hydration stabilizers used in the concrete mixture of the present invention. Since fluorochemical stabilized foams have bubbles that are already particularly stable, it is believed to be the interactions between the cement and the foam that has previously prevented the use of these foams in concrete and/or has previously prevented their use in applications that require relatively long initial set times (e.g. ready mix applications). In the present invention the hydraulic cement is stabilized with respect to the aqueous foam, thereby allowing or improving their use in the concrete mix. The resulting concrete compositions have many improved properties, including decreased permeability, decreased shrinkage, decreased absorption and bleeding, improved acoustic properties, lower densities, and increased initial flowability. The concrete mixtures also have reduced water migration, which improves the hydration of cement and can improve the reaction between free lime and pozzolans. The concrete mixtures also have improved aesthetics due to reduced rock pockets.

The hydration stabilizer used in the present invention is also particularly advantageous when used with foams stabilized with fluorochemical oligomers comprising hydrophilic nonionic monomers and hydrophilic anionic monomers. Foams stabilized using these surfactants provide additional benefits because of the interaction between the oligomer in the foam and certain components of the concrete mixture (e.g. the cement and/or the aggregate). It is believed that the nonionic and anionic monomers are able to better disperse the cement particles and/or the aggregates uniformly in the concrete mixture. This dispersion of components in the mixtures of the present invention is believed to be the source of the added workability of these mixtures and the strength of the cured concrete resulting therefrom.

These and other features of the present invention will become more fully apparent from the following description and appended claims.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

I. Introduction

The present invention relates to flowable concrete mixtures having aqueous foam admixtures. The concrete mixtures of the present invention include (i) a hydraulic cement, (ii) a hydration stabilizer, and (iii) an aqueous foam. The hydration stabilizer controls hydration of the cement to inhibit the reaction between the cement and the aqueous foam, thereby preserving the foam bubbles for a desired amount of time.

For purposes of the present invention, the “initial set time” occurs when the concrete reaches a compressive strength of 500 psi.

For purposes of the present invention, the term “air” includes all gases including mixtures of gases and pure gasses, whether obtained from the atmosphere or generated by chemical reaction.

II. Concrete Mixtures

The concrete mixtures of the present invention can have very different compositions depending on the desired use for the concrete. However, in general, the concrete mixtures of the present invention include at least hydraulic cement, a hydration stabilizer, an aqueous foam admixture, and water (either from the foam or added separately). The concrete mixtures typically include an aggregate, which gives the concrete strength. Dispersants and other admixtures are also described below and can be included to give the concrete mixtures of the present invention desired properties.

A. Hydraulic Cement and Water

The cement included in the concrete mixtures of the present invention is a hydraulic material such as Portland cement, modified Portland cement, or masonry cement. For purposes of this invention, Portland cement includes all cementitious compositions which have a high content of tricalcium silicate, including Portland cement, cements that are chemically similar or analogous to Portland cement, and cements that fall within ASTM specification C-150-00. Other cementitious materials include ground granulated blast-furnace slag, hydraulic hydrated lime, white cement, slag cement, calcium aluminate cement, silicate cement, phosphate cement, high-alumina cement, magnesium oxychloride cement, and combinations of these and other similar materials.

Water is added to the concrete mixture in sufficient amounts to hydrate the cement. Those skilled in the art will recognize that the amount of water needed will depend on the desired flowability and on the amounts and types of admixtures included in the concrete composition. Many of these admixtures are discussed below. In general, suitable amounts of water for hydrating the cement ranges from about 1% to about 50%, more preferably about 5-50%, and most preferably about 10% to about 25% of the concrete mixture by weight.

B. Foam Admixtures

The foams used in the concrete mixtures of the present invention include water, air, and at least one foaming agent (e.g. surfactant). The foam admixtures comprise a plurality of cellular bubbles that trap air in the concrete and provide the uncured concrete with desired properties such as flowability and/or workability and provide the cured concrete with properties such as increased strength and/or resistance to cracking during freeze thaw cycles.

The foams of the present invention can be made from a foaming concentrate. A detailed description of how to make the aqueous foam admixture using a foaming concentrate, air, and water is described below in connection with the methods of the present invention and the examples.

The composition of the foaming concentrate is in large part responsible for the properties of the foam admixture. The following is a description of suitable foaming concentrate composition. The foaming concentrates typically include a foaming agent, solvents, and other surfactants, and/or additives that allow the foaming concentrate to form foam bubbles that can be added to concrete.

1. Foaming Concentrates

(a) Foaming Agents and Solvents

The foaming concentrates include at least one foaming agent suitable for forming an aqueous based foam. Typical foaming agents include ionic, cationic, anionic surfactants, natural and synthetic resins, fatty acids, proteinaceous material, sulfonated hydrocarbons, and the like. In an exemplary embodiment, the foaming concentrate comprises a combination of foaming agents, solvents and/or viscosity modifiers or other components. In a preferred embodiment, the foaming agents can be a non-fluorinated anionic surfactant preferably selected from the group consisting of C_8 to C_{18} anionic surfactants and most preferably, C_{10} to C_{18} alpha olefin sulfonates, as well as mixtures of these surfactants.

Suitable solvents include glycol ethers and fatty alcohols of about 8 to about 15 carbons or C_2 to C_8 aliphatic diols. Specifically preferred as the solvent, if used, is propylene glycol t-butyl ether. The preferred fatty alcohol comprises a mixture of equal parts n-dodecanol, n-tetra decanol and n-hexadecanol. Preferred as the anionic surfactant are mixtures of sodium alkenyl sulfonate, sodium tetradecene sulfonate, and sodium hexadecene sulfonate in a ratio of about 4:1:1.

Viscosity modifiers can also be added to the foam admixture. Suitable viscosity modifiers include those described below as admixtures to be added to the concrete mixture apart from the foam. Preferred viscosity modifiers include polysaccharide gums, preferably selected from the group consisting of rhamsan gums, xanthan gums, guar gums and locust bean gums. Viscosity modifiers such as polysaccharide gums can be useful in foams because they form a membrane on the surface of solvents that protects the rest of the foam from collapsing. The viscosity modifier in the foam can also aid in pumpability of the concrete mixture.

Other ingredients can be employed in the composition of the surfactant formulation to effect specific environmental or shelf-life concerns. Examples of such ingredients are freezing point depressants, such as ethylene glycol, and preservatives, such as that available under the trade name DOWICIDE (Dow Chemical Company).

There are many other known foaming concentrates that can be used with the present invention. Suitable foaming surfactant concentrates include cellulose based concentrates (e.g. “CELLUCON” (Romaroda Chemicals)) and hydrolyzed protein based concentrates (e.g. MEARL (The Mearl Corporation)).

The foam concentrates include surfactants and additives that lead to foams with sufficient mechanical stability to withstand the mixing involved in making concrete compositions. The foregoing concentrates, if needed, can be structurally strengthened (i.e. stabilized) using a fluorochemical surfactant as described below, or other similar stabilizing additive.

(b) Foam Stabilizing Surfactants

In an exemplary embodiment the foam concentrate includes a fluorochemical foam stabilizing surfactant. Fluorochemical foam stabilizing surfactants are well known in the art of fire fighting foams (e.g. U.S. Pat. Nos. 5,218,021, 4,472,286; 4,717,744; and 4,859,349; 4,460,480; 4,387,032; and 4,020,903; which are incorporated herein by reference). Particularly useful fluorinated surfactants are oligomer surfactants that includes (i) a fluorinated hydrocarbon monomer, (ii) a hydrophilic nonionic monomer, and (iii) a hydrophilic anionic monomer.

Examples of suitable fluorinated hydrocarbon monomer include (i) straight chain, branched chain, or cyclic perfluoroalkyls of 1 to about 20 carbon atoms, (ii) perfluoroalkyls substituted with perfluoroalkoxy groups of 2 to about 20 carbon atoms, (iii) a perfluoroalkyl oligomers or polymers of greater than 10 carbon atoms, or (iv) monomers of the like and/or combination thereof.

Many non-ionic hydrophilic monomers suitable for use in the present invention are known and commercially available. Particularly useful non-ionic hydrophilic monomers include acrylamide, methacrylamide, diacetone acrylamide, and 2-hydroxyethyl methacrylate. Other examples of such monomers include derivatives of acrylic, methacrylic, maleic, fumaric, and itaconic acids, such as hydroxyalkyl esters of acrylic acids; amides such as N-vinyl-pyrrolidone, N-(hydroxyalkyl)-acrylamides, or N-(hydroxyalkyl)-methacrylamides; and vinyl esters with 1-20 carbons in the ester group such as vinyl acetate, butyrate, laurate, or stearate. The above listed non-ionic hydrophilic monomers can be used alone or in combination with each other as well as in combination with suitable anionic hydrophilic monomers described below. Some non-ionic hydrophilic monomers may require a co-monomer for polymerization, such as di(hydroxyalkyl) maleates with ethoxylated hydroxyalkyl maleates.

Many anionic hydrophilic monomers that co-oligomerize with non-ionic hydrophilic monomers are known and are commercially available. Particularly useful anionic hydrophilic monomers include acrylic and methacrylic acids and salts thereof. Other examples of such monomers include maleic, fumaric, and itaconic acids and salts thereof; acrylamidopropane sulfonic acid and salts thereof; and mono-olefinic sulfonic and phosphonic acids and salts thereof.

Oligomers made using the foregoing fluorinated hydrocarbon monomers and hydrophilic monomers are particularly advantageous when used with foams in the concrete mixtures of the present invention. These oligomers are particularly useful for dispersing and/or suspending the cement and/or aggregates in the concrete mixture. By dispersing and/or suspending these and other components of the concrete mixture, the resulting cured concrete has improved strength and resistance to cracking.

While the foams of the present invention preferably include a fluorochemical foam stabilizer, the present invention is not limited to these foams. The use of a hydration stabilizer with other aqueous based foams can advantageously stabilize and prolong the life of the foam in concrete.

(c) Example Foaming Concentrates

In one embodiment, the foaming concentrate is a firefighting foam concentrate suitable for extinguishing Class A fires or Class B fires. For purposes of this invention, firefighting foam concentrates are compositions that include the agents needed to extinguish a fire when applied thereto as specified by the Underwriter Laboratories specification 162. In one embodiment, the firefighting foam concentrate meets Class A, Class B, and/or Class D or other section of the UL162 specification in effect in 2006. The firefighting foam may include a fluorochemical surfactant or may substantially free of a fluorochemical surfactant. The concentrate may be an aqueous film forming foam (AFFF), a protein foam, a fluoroprotein foam (FP, or an alcohol resistant fluoroprotein foam (AR-FP, a film forming fluoroprotein (FFFP) or an alcohol-resistant film forming fluoroprotein (AR-FFFP) or wetting agent suitable for use in firefighting. An example of a suitable Class A fire-fighting foam concentrate is Pinnacle Class A Foam Concentrate available from Hazard Control Technologies, Inc. (Fayetteville, Ga.). Examples of firefighting concentrates include, but are not limited to those described in U.S. Pat. Nos. 7,172,709; 7,005,082; 7,011,763; 6,139,775; and 6,740,250, all of which are hereby incorporated herein by reference for their teachings of firefighting concentrates.

Table 1 below sets forth exemplary foaming concentrates according to the present invention. In Table 1, column 1 specifies the useful ranges for each component, column 2 specifies preferred ranges for each of the components and column 3 describes the highly preferred ranges for each of the components. In Table 1, all compositions are in parts by weight. The fluorochemical surfactant is normally supplied as a solution in an alcohol such as tert-butyl alcohol.

TABLE 1

	1	2	3
Solvent	0-50%	0-20%	1-10%
Fatty Alcohol	0.1-10%	0.1-1.0%	0.2-1.0%
Polysaccharide Gum	0.1-10%	0.1-5.0%	0.5-4.0%
Anionic Surfactant	0.1-50%	0.1-20%	0.5-8.0%
Fluorochemical	0.1-15%	0.1-5.0%	0.5-3.0%
Water	Balance	Balance	Balance

A particularly useful foaming concentrate that includes a fluorochemical surfactant is sold by Miracon Technologies, Inc. under the trademark Miracon®.

C. Hydration Stabilization

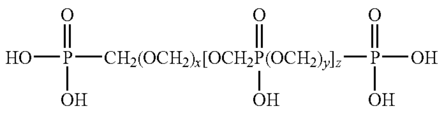
The hydration stabilizer (also known as an extended set retarder) of the present invention is used to inhibit the hydration of the hydraulic cement. The hydration stabilizer slows the rate of hydrate formation by tying up (i.e. chelating, complexing, or otherwise binding) calcium ions on the surface of cement particles. The hydration stabilizer includes a hydration retarder that forms a protective barrier around cementitious particles. The hydration retarder bonded to the cement particles acts as a dispersant preventing hydrates from flocculating and setting. This barrier prevents the hydraulic cement from obtaining initial set.

Another feature of the hydration stabilizer is that it degrades and/or is inactivated over time such that hydration of the cement eventually occurs. Preferably the release of the hydraulic cement is progressive over time so as to provide a controlled release of the cement and an ascertainable delay in set time.

The hydration stabilizer preferably comprises a calcium chelating compound such as a polyphosphonic acid or a carboxylic acid that contains hydroxyl and/or amino groups. Polyphosphonic acids and similar compounds can be particularly advantageous because of their controlled degradation in the concrete mixture over an extended period of time that allows for a timed setting of the concrete.

Suitable examples of hydration stabilizers include N-nitrilo tris(methylene phosphonic acid); 1,2-ethanediyl bis[nitrilo di(methylene phosphonic acid)]; 1,6-hexanediyl bis[nitrilo di(methylene phosphonic acid)] and the like.

Another class of suitable phosphonic acid hydration stabilizing compounds include polymethoxy polyphosphonic acids represented by the formula II



$$HO-\overset{O}{\underset{OH}{P}}-CH_2(OCH_2)_x[OCH_2\overset{O}{\underset{OH}{P}}(OCH_2)_y]_z-\overset{O}{\underset{OH}{P}}-OH$$

wherein x and y are each an integer of from 1-3, and preferably 1, and z is an integer of 0 or 1. It is understood that when z is 0 the radical within the bracket is non-existent and, therefore $(OCH_2)_y$ is nonexistent. The preferred polymethoxy polyphosphonic acid compounds are represented by the above formula when z=0 and x is 1-3. Other suitable polymethoxy polyphosphonic acid compounds are disclosed in U.S. Pat. No. 5,215,585, which is incorporated herein by reference.

A particularly useful hydration stabilizer is amino tris(methylene phosphonic acid), which is a component of the commercially available hydration stabilizer sold by Master Builders under the trademark Delvo. Illustrative examples of hydration stabilizers, including some of those mentioned above, are set forth in U.S. Pat. Nos. 5,427,617 and 5,203,919, which are incorporated herein by reference. Hydration retarders and accelerators suitable for use as hydration stabilizers are also disclosed in U.S. Pat. No. 6,858,074, which is also incorporated herein by reference.

As mentioned, the hydration stabilizer of the present invention prevents or inhibits setting and then degrades or is released from the cement to provide controlled setting. In some cases, it is necessary that the hydration stabilizer also comprise an accelerator to cause the controlled hydration of the cement. The amount of accelerator that needs to be added depends on several factors, such as the amount of hydration retarder, cement type and reactivity, ambient temperature, concrete mixture proportions, and the presence or absence of certain admixtures in the concrete mixture, such as water reducing polymers.

Accelerators that can be used to activate the hydraulic cement can be selected from conventional cement accelerators such as those classified as ASTM C 494 Type C admixtures. These include alkali metal halides (calcium chloride and the like), alkali metal nitrites (calcium nitrite and the like), alkali metal nitrates (calcium nitrate and the like), alkali metal formates (calcium formate and the like), alkali metal thiocyanates (sodium thiocyanate and the like), triethanolamine and the like. The particular set accelerator to be used will depend on the known nature of the accelerators and side effects of the agent. For example, where metal corrosion is not a problem, calcium chloride might be chosen, while if corrosion is a problem, the nitrite or nitrate salts might be better used. The preferred accelerators are calcium nitrate and the like.

The accelerating agent should be added in amounts which effectively cause the combined cement mixture to set and provide conventional 28 day strength for such compositions (e.g. mortars of about 2000-4000 psi; concrete of about 2,500 to 10,000 psi). The amount, based on cement content, should be from about 0.5 to about 6 weight percent, preferably from about 1 to about 5 percent.

The hydration stabilizer is mixed with the cement mixtures in amounts effective to prevent the hydraulic cement from reacting with the aqueous foam for a desired period of time. The specific effective amount depends on the amount and type of cement and the desired amount of stabilization. Preferably, a sufficient amount of hydration stabilizer is included in the concrete mixture to stabilize substantially all of the cement. Suitable amounts typically require from about 1.5 oz to about 8.0 oz per hundred lbs of cement, more preferably about 3.0 oz to about 6 oz, for a concrete mix having a 28 day cure time. The stabilization can be extended by adding about 4 oz of hydration stabilizer per 100 lbs cement per hour of extension.

Hydration stabilizers are known and used in the concrete industry for waste water reclamation and for reusing concrete mixtures. Currently, hydration stabilizers are added to concrete waste water so that the truck or other mixing machinery does not have to be washed out after use or so that the remaining concrete can be used on another job. The hydration stabilizer prevents setting until the cement can be reused. The inventor of the present invention has found that the properties and concentrations of hydration retarders used in these known hydration stabilizing compositions are surprisingly advantageous for stabilizing foam admixtures according to the present invention. Commercially available hydration stabilizers, in addition to Delvo mentioned above, include Recover (W.R. Grace), Delayed Set (Fritz-Pak Corp.), Stop-Set and Stop-Set L (Axim Italcementi Group), and Polychem Renu (General Resource Technology).

D. Dispersants and/or Water-Reducers

Water reducers are used in concrete mixtures to lower the water content in the plastic concrete (i.e. uncured concrete) to increase its strength and to obtain higher slump without adding water. Water-reducers will generally reduce the required water content of a concrete mixture for a given slump and are useful for pumping concrete and in hot weather to offset the increased water demand. These admixtures disperse the cement particles in the concrete and make more efficient use of the hydraulic cement. This dispersion increases strength and/or allows the cement content to be reduced while maintaining the same strength. Water-reducers should meet the requirements for Type A in ASTM C 494 Specification.

Another class of water reducers includes mid-range water reducers. These water reducers have a greater ability to reduce the water content of the concrete and are often used because of their ability to improve the finishability of concrete flatwork. Mid-range water reducers should at least meet the requirements for Type A in ASTM C 494.

High range water-reducers (HRWR), also referred to as superplasticizers, are a special class of water-reducer. HRWRs reduce the water content of a given concrete mixture by about 12% to 30%. HRWRs are used to increase strength and reduce permeability of concrete by reducing the water content in the mixture or greatly increase the slump to produce "flowing" concrete without adding water. HRWRs are often used for high strength and high performance concrete mixture that contain higher contents of cementitious materials and mixtures containing silica fume. In a typical concrete mixture, adding a normal dosage of HRWRs to a concrete mixture with a slump of 3 to 4 inches (75 to 100 mm) will produce a concrete with a slump of about 8 inches (200 mm). Exemplary HRWRs that can be used in the present invention are covered by ASTM Specification C 494 and types F and G, and Types 1 and 2 in ASTM C 1017. Particularly advantageous dispersants include the HRWRS described in U.S. Pat. No. 6,858,074, which is incorporated herein by reference.

It is believed that water reducing dispersants may have a particularly beneficial effect on the concrete compositions of the present invention by working in conjunction with the hydration stabilizer to stabilize the foam admixtures of the present invention.

E. Aggregates

Aggregates are usually included in the concrete mixture to add bulk and to give the concrete strength. The aggregate can be a fine aggregate and/or a coarse aggregate. The fine aggregates are materials that pass through a Number 4 sieve (ASTM C125 and ASTM C33), such as silica sand. The coarse aggregate 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.

Whether an aggregate needs to be added can depend on the desired use of the cured concrete and on the type of aqueous foam admixture that is used. Some aqueous foam admixtures of the present invention are sufficiently stabilized to function as a foam aggregate. For example, the air bubbles in aqueous foams that are stabilized with a fluorochemical surfactant can have sufficient strength to act as a foam aggregate. In particular, foams stabilized with fluorochemical surfactants that include hydrophilic nonionic and hydrophilic anionic monomers are particularly suited to act as foam aggregates. It is believed that the anionic and nonionic monomers are able to disperse the hydraulic cement around the foam bubbles thereby creating a cement matrix similar to the cement matrix that forms around aggregates.

The concrete mixtures of the present invention also include concrete mixtures that include traditional aggregates (i.e. coarse and fine aggregates) in combination with foam aggregates (e.g. aqueous foams stabilized with surfactants having nonionic and anionic monomers). Concrete mixtures of the present invention that incorporate a combination of foam aggregates with fine aggregates and/or coarse aggregates can be made to have superior compressive and flexural strength and/or can include ratios of aggregate sizes that are not possible with traditional concrete mixtures.

For example, ready mixed concrete used in flat work or foundation walls typically has a ratio of fine aggregates to coarse aggregates of 50:50. This ratio can be usually be modified to ratios from 60:40 to 40:60. Using the aqueous foams stabilized with a fluorochemical surfactant, the concrete mixtures of the present invention can be made using ratios of less than 40% of either fine aggregates or coarse aggregates while still maintaining ASTM standards for flexural and compressive strength. In an exemplary embodiment, the aggregate can comprise less than 40% fine aggregate, less than 30% fine aggregate, less than 20% fine aggregate or even substantially no fine aggregate. Alternatively, the aggregate can comprise less than 40% coarse aggregate, less than 30% coarse aggregate, less than 20% coarse aggregate, or even substantially no coarse aggregate. Even with these low percentages of coarse or fine aggregate, a compressive strength of greater than 2500 psi, more preferably greater than 3000 psi, or most preferably greater than 4000 psi can be achieved.

The use of only one size of aggregate is particularly beneficial in areas where both coarse and fine aggregates are not available or a particular size aggregate is in abundance. Also, the concrete mixtures of the present invention are particularly useful for incorporating certain aggregates sizes such as ⅜ inch gravel (i.e. pea gravel), that cannot be used in some concrete mixtures because it leads to lower quality concrete. With the concrete mixtures of the present invention, pea gravel can be used while still maintaining suitable compressive strength (e.g. 3000-4000 psi).

Thus, using the foam aggregates of the present invention, novel combinations of aggregates can be used to make concrete having suitable strength for ready mixed concrete and other applications.

F. Fly Ash

Fly ash is another admixture that can be included in the concrete mixtures of the present invention. ASTM C618 standard, which is incorporated herein by reference, recognizes two major classes of fly ashes for use in concrete—Class C and Class F. These two classes of fly ashes are derived from different kinds of coals that are a result of differences in the coal formation processes occurring over geological time periods. Class F fly ash is normally produced from burning anthracite or bituminous coal, whereas Class C fly ash is normally produced from lignite or sub-bituminous coal. The ASTM C618 standard differentiates Class F and Class C fly ashes primarily according to their pozzolanic properties. Accordingly, in the ASTM C618 standard, the major specification difference between the Class F fly ash and Class C fly ash is the minimum limit of SiO_2+Al_2O_3+Fe_2O_3 in the composition. The minimum limit of SiO_2+Al_2O_3+Fe_2O_3 for Class F fly ash is 70% and for Class C fly ash is 50%. Thus, Class F fly ashes are more pozzolanic than the Class C fly ashes. Although not explicitly recognized in the ASTM C618 standard, Class C fly ashes typically contain high calcium oxide content. Presence of high calcium oxide content makes Class C fly ashes possess cementitious properties leading to the formation of calcium silicate and calcium aluminate hydrates when mixed with water. The use of Class C fly ash can be particularly useful to replace a portion of the cement in the concrete. Class C fly ash and Portland cement can be blended in weight ratios of ash to cement of about 0/100 to 150/100, preferably 75/100 to 125/100. In some reactive powder blends the portland cement is about 40 to 80 wt % and fly ash 20 to 60 wt %.

Because fly ash is obtained from coal combustion or found naturally, fly ash can include a certain amount of carbon. The amount of carbon in fly ash is measured according loss of ignition (LOI). Fly ash that has an LOI greater than about 1.5 is typically not suitable for use with concrete mixtures that have air entraining agents because the carbon destroys the air entrainment. The inventor of the present invention has found that the foam admixtures of the present invention that are stabilized with a fluorochemical surfactant are surprisingly resistant to destruction by high carbon fly ash. Thus, in one embodiment of the invention, the concrete mixture includes a fly ash having an LOI greater than about 1.5, more preferably greater than about 2, more preferably greater than 4, and most preferably greater than about 6. It has also been found that high carbon fly ash when used in combination with the fluorochemical stabilized foam admixtures of the present invention, increases the strength of the cured concrete over fly ash that is not high carbon.

G. Viscosity Modifiers

Viscosity modifying agents (VMA), also known as rheological modifiers or rheology modifying agents, can be added to the concrete mixture of the present invention. These additives are usually water-soluble polymers and function by increasing the apparent viscosity of the mix water. This enhanced viscosity facilitates uniform flow of the particles and reduces bleed, or free water formation, on the fresh paste surface.

Suitable viscosity modifiers that can be used in the present invention include, for example, cellulose ethers (e.g., hydroxyethyl cellulose (HEC), hydroxypropylmethyl cellulose (HPMC), sodium carboxymethyl cellulose (CMC), carboxymethylhydroxyethyl cellulose (CMHEC), and the like); synthetic polymers (e.g., polyacrylates, polyvinyl alcohol (PVA), polyethylene glycol (PEG), and the like); exopolysaccharides (also known as biopolymers, e.g., welan gum, xanthan, rhamsan, gellan, dextran, pullulan, curdlan, and the like); marine gums (e.g., algin, agar, carrageenan, and the like); plant exudates (e.g., locust bean, gum arabic, gum Karaya, tragacanth, Ghatti, and the like); seed gums (e.g., Guar, locust bean, okra, psyllium, mesquite, and the like); starch-based gums (e.g., ethers, esters, and related derivatized compounds). See, for example, Shandra, Satish and Ohama, Yoshihiko, "Polymers In Concrete", published by CRC press, Boca Ration, Ann Harbor, London, Tokyo (1994).

Viscosity modifying agents are typically used with water reducers in highly flowable mixtures to hold the mixture together. Viscosity modifiers can disperse and/or suspend components of the concrete thereby assisting in holding the concrete mixture together. This property of viscosity modifiers makes them useful for making self compacting concrete, which requires high flowability.

Some foam admixtures of the present invention (e.g. fluorochemical stabilized foams having nonionic and anionic monomers) can act as a viscosity modifying agent thereby reducing the need for a separate viscosity modifier in the concrete mix. Highly flowable and/or self-compacting concrete can be achieved with these foams of the present invention while substantially reducing the amount of viscosity modifier included separately in the concrete mix. In an exemplary embodiment, viscosity modifier is added to the concrete mix in an amount less than 12 oz/100 wt, more preferably less than 9 oz, even more preferably less than about 5 oz, and most preferably substantially no viscosity modifier is added apart from the foam admixture.

Even with no additional viscosity modifier added to the concrete mixture, the concrete mixtures of the present invention can be highly flowable. Water and Low-range, mid-range, and/or high range water reducers can be added to the concrete mixture to give the concrete mixture a high flowability without the concrete separating because the foam admixture acts as a very good viscosity modifier. Concrete according to the present invention can be manufactured to have a "flow spread" of greater than 24-36 inches (using a 12 inch slump cone). The high spread of the concrete composition of the present invention are particularly advantageous because the spread is homogenous. The foam admixtures of the present invention can suspend the aggregate and other components in the concrete mixture such that mixes that spread greater than about 24-36 inches are spread substantially homogenous.

H. Other Admixtures

Many other types of admixtures can be added to the concrete compositions of the present invention to give the concrete a desired property. As discussed below, other admixtures suitable for use in the concrete mixtures of the present invention include but are not limited to viscosity modifiers, corrosion inhibitors, pigments, wetting agents, water soluble polymers, strength enhancing agents, rheology modifying agents, water repellents, fibers, permeability reducers, pumping aids, fungicidal admixtures, germicidal admixtures, insecticidal admixtures, finely divided mineral admixtures, alkali reactivity reducer, bonding admixtures, and any other admixtures or additive that do not adversely affect the stabilized foam or hydration stabilizers of the present invention.

Corrosion inhibitors in concrete serve to protect embedded reinforcing steel from corrosion due to its highly alkaline nature. The high alkaline nature of the concrete causes a passive and noncorroding protective oxide film to form on the steel. However, carbonation or the presence of chloride ions from deicers or seawater can destroy or penetrate the film and result in corrosion. Corrosion-inhibiting admixtures chemically arrest this corrosion reaction. The materials most commonly used to inhibit corrosion are calcium nitrite, sodium nitrite, sodium benzoate, certain phosphates or fluorosilicates, fluoroaluminates, amines, organic based water repelling agents, and related chemicals.

Dampproofing admixtures reduce the permeability of concrete that have low cement contents, high water-cement ratios, or a deficiency of fines in the aggregate. These admixtures retard moisture penetration into dry concrete and include certain soaps, stearates, and petroleum products.

Permeability reducers are used to reduce the rate at which water under pressure is transmitted through concrete. Silica fume, fly ash, ground slag, natural pozzolans, water reducers, and latex can be employed to decrease the permeability of the concrete.

Pumping aids are added to concrete mixes to improve pumpability. These admixtures thicken the fluid concrete, i.e., increase its viscosity, to reduce de-watering of the paste while it is under pressure from the pump. Among the materials used as pumping aids in concrete are organic and synthetic polymers, hydroxyethylcellulose (HEC) or HEC blended with dispersants, organic flocculents, organic emulsions of paraffin, coal tar, asphalt, acrylics, bentonite and pyrogenic silicas, natural pozzolans, fly ash and hydrated lime.

Bacteria and fungal growth on or in hardened concrete may be partially controlled through the use of fungicidal, germicidal, and insecticidal admixtures. The most effective materials for these purposes are polyhalogenated phenols, dialdrin emulsions, and copper compounds.

Fibers can be distributed throughout a fresh concrete mixture to strengthen it. Upon hardening, this concrete is referred to as fiber-reinforced concrete. Fibers can be made of zirconium materials, carbon, steel, fiberglass, or synthetic materials, e.g., polypropylene, nylon, polyethylene, polyester, rayon, high-strength aramid, or mixtures thereof.

The shrinkage reducing agent which can be used in the present invention can include but is not limited to alkali metal sulfate, alkaline earth metal sulfates, alkaline earth oxides, preferably sodium sulfate and calcium oxide.

Alkali-reactivity reducers can reduce the alkali-aggregate reaction and limit the disruptive expansion forces in hardened concrete. Pozzolans (fly ash and silica fume), blast-furnace slag, salts of lithium, and barium are especially effective.

Bonding admixtures are usually added to hydraulic cement mixtures to increase the bond strength between old and new concrete and include organic materials such as rubber, polyvinyl chloride, polyvinyl acetate, acrylics, styrene butadiene copolymers, and other powdered polymers.

Natural and synthetic admixtures are used to color concrete for aesthetic and safety reasons. These coloring admixtures are usually composed of pigments and include carbon black, iron oxide, phthalocyanine, umber, chromium oxide, titanium oxide and cobalt blue.

Air entrainers can be included in the concrete mixtures of the present invention, although this is usually not necessary since the foam admixtures provide an air entraining features. Unlike foam, air entrainers are added to the concrete mixture in a liquid form (i.e. without the air entrapped).

III. Methods of Making and Using Concrete Mixtures

The present invention also includes methods for making foam and methods for incorporating those foams into concrete mixtures.

A. Method of Making Foam Admixtures

As discussed above, in an exemplary embodiment, the foam admixtures are manufactured from a foam concentrate. Foam production is performed by drawing water and the foam concentrate, in proper ratios, and injecting them into a chamber using high pressure air. The mixture is subjected to shearing forces that produce air bubbles (i.e. foam) in the chamber.

The ratio of water, foam concentrate, and air are controlled to produce air bubbles of a desired size and shape. In a preferred embodiment, the water and foam concentrate are mixed to form a diluted concentrate comprising between at least about 80% water, more preferably greater than about 90% water and more preferably greater than about 95% water. The amount of air injected into the diluted foam is controlled by the air pressure and volume of air.

In an exemplary embodiment, air bubbles are formed having an approximate size of about 0.3 ml to about 1.0 ml, more preferably from about 0.5 ml to about 0.7 ml. In a preferred embodiment, the bubbles are of uniform size and shape. It is believed that the uniform size and shape is beneficial for providing a uniform dispersion of cement and aggregate.

Any number of foam production devices can be used for producing the foam admixtures of the present invention, and the invention is not limited to any specific such device. Such devices are well known in the art. Whatever mechanism used, it should be adequate to produce a stream of bubbles suitable for introduction into the concrete mixtures of the present invention.

The following formula "Concentrate I," shown in the table below, illustrates a suitable concentrate for manufacturing a foam admixture according to the present invention.

CONCENTRATE I

COMPONENT	CAS NUMBER/TRADE NAME	w/w %
Sodium alkenyl sulfonates mixture)	68439-57-6, 11066-21-0, 11067-19-9	7.0
1-t-Butoxy-2-propanol	57018-52-7	5.0
Rhamsan gum	96949-21-2	2.0
Perfluoroethylthia acrylic telomere	Lodyne ™ K90'90 (Ciba-Geigy Corp.)	1.4
n-Alkanols (mixture)	112-53-8, 112-72-1, 36653-82-4	1.0
2-Methyl-2-propanol	75-65-0	0.2
Water	7732-18-5	balance

Concentrate I can be used to form a stable and resilient aqueous foam admixture by diluting Concentrate 1 to 2.5 w/w % water (39 parts water to one part Concentrate I) and then aerating it through a foam generating chamber at about 92 psi, thereby subjecting the diluted Concentrate I to shearing forces that produce an aqueous foam admixture.

B. Method of Mixing Concrete

The concrete mixtures of the present invention are manufacture by mixing proper amounts of a hydraulic cement, hydration stabilizer, water, and foam admixture. Typically the concrete mixture also includes aggregate. However, for some non-structural applications, aggregate may not be necessary. Dispersants and other admixtures can be added as needed to give the concrete mixture desired properties.

Typically the hydraulic cement, hydration stabilizer, water, and foam can be mixed together in any order so long as the water is added before the foam. The hydration stabilizer is preferably added to the cement before the cement is mixed with the foam to minimize the reaction of hydraulic cement and foam. It has also been found that adding the hydration stabilizer to the water before the water is mixed with the cement can also increase stability of the foam when the foam is mixed with the cement. Accelerator can be added to the concrete mixture at the same time that the hydration retarding agent is added, or the accelerator can be added at a later point in time, such as just before the concrete is to be poured.

The amount of foam mixed into the concrete mixture is selected to give the concrete a desired percent of air. In an exemplary embodiment, the foam admixture is included in the concrete mixture in an amount sufficient to provide greater than 5% air in the concrete, more preferably greater than 10% air, and most preferably greater than about 15% air by volume of the concrete mixture.

The limit on the amount of foam that can be added depends on the desired final strength of the concrete and the amount of cement in the mixture. In general, lower percentages of air and higher amounts of cement produce stronger cements. However, the concrete mixtures of the present invention can have very high compressive strengths with percentages of air above 5%, as compared with existing cements. Using the aqueous foams of the present invention, air can be entrained into the concrete mixture in percentages greater than 5%, 10%, and even 20% while maintaining compressive strengths of greater than about 2500 psi, and more preferably greater than about 3000 psi, in 28 days. For example, concrete mixtures according to the present invention having 12% air and 300 lbs/yd^3 of cement can achieve about 3000-4000 psi in 28 days. In another example, concrete mixture according to the present invention having 22% air and 650 lbs/yd^3 cement can achieve a compressive strength of about 6500 psi in 28 days. Even at very high percentages of air, significant compressive strength can be achieved. For example, concrete mixtures of 85% air can achieve 90 psi in 28 days.

Because the cement is stabilized with respect to the foam using the hydration stabilizer, the air entrainment provided by the foam can last at least until the concrete sets.

Table 2 below provides 3 different exemplary ranges of typical amounts of the components needed to make concrete mixtures according to the present invention.

TABLE 2

	1	2	3
Portland Cement	1-50%	6-50%	10-25%
Washed Sand	0-75%	0-60%	0-40%
Coarse Aggregate	0-60%	0-50%	0-40%
Water	4-50%	5-50%	10-25%
Pozzolanic Material	0-50%	0-20%	0-5.0%
Foam Admixture	1-90%	1-85%	1-75%
Water Reducers	0-20 oz	0-6.0 oz	0-4.5 oz
Accelerators	0-20 oz	0-12 oz	0-8.0 oz
Hydration Stabilizer	0.5-20 oz	1.0-12 oz	1.5-6.0 oz

In the compositions described in Table 2, the foam admixture is manufactured as described above (e.g. Concentrate I diluted to 2.5 w/w % water and foamed at 92 psi). The weight of the foam admixture includes the weight of the water that makes up the foam. Water is also included as a separate component, which does not include the water in the aqueous foam admixture.

A sufficient amount of hydration stabilizer is included to stabilize the foam admixture for a desired amount of time. The sufficiency of the hydration stabilizer can depend in part on the type of concrete being made. For ready mixed concrete, where transportation is often needed, the hydration stabilizer can be added in greater amounts such that the stabilization lasts during transportation and until the concrete has set.

The amount of hydration stabilizer used in the concrete mixture is determined by the need to stabilize the cement with respect to the foam. A sufficient amount of hydration stabilizer will inhibit the reaction between the cement and the foam such that a majority or substantially all of the foam initially mixed into the concrete lasts until the concrete achieves initial set. Typically, less than 2% of the foam collapses within the first 2 hours.

Regardless of whether the concrete is designed to set in a short period (e.g. less than 1 hour) or over along period of time, the hydration stabilizer included in the concrete of the present invention can be very beneficial to stabilizing the foam admixture. The cement in a concrete mixture is most reactive, and thus most destructive to the foam admixture, when it is first mixed with the water. Consequently, the hydration stabilizer provides its greatest benefit during initial mixing of the cement, foam, and water, although significant benefits can still be realized by including the hydration stabilizer after initial mixing. The use of hydration stabilizer during the initial mixing of the concrete differs from most current practices, which add hydration stabilizer to waste concrete after a job is finished or during a job to preserve the concrete for later use. In the present invention, the hydration stabilizer is added to prevent the reaction of the foam and the cement. Accelerators can be added anytime during or after mixing to control set time, if needed.

Those skilled in the art will recognize that there are many applications in which the combination of hydration stabilizer, hydraulic cement, and foam according to the present invention can be easily incorporated into a concrete composition using the foregoing description. The following examples give specific formulations of aqueous foams and concrete composition that employ the concepts of the present invention.

IV. Examples

Examples 1-5 illustrate concrete compositions according to the present invention. In each formula, admixtures (e.g. water reducers WR) were added based on 100 lbs of cement (i.e. 100-wt cement). The concrete mixtures of Examples 1-3 had 12% air and produced cured concrete with a compressive strength of greater than 3000 psi at 28 days.

Example 1

COMPONENTS	AMOUNTS
Portland Cement	308 lbs/yd^3
Water	30 gal/yd^3
Hydration Stabilizer (Recover, W. R. Grace)	5.5 oz/100-wt
Fine Aggregate	1630 lbs/yd^3
Coarse Aggregate	1235 lbs/yd^3
Foam Admixture (Miracon)	2.8 ft^3/yd^3
Mid Range WR (997, Master Builders)	5 oz/100-wt
Low Range WR (27, W. R. Grace)	0.5 oz/100-wt

Example 2

COMPONENTS	AMOUNTS
Portland Cement	308 lbs/yd^3
Water	30 gal/yd^3
Hydration Stabilizer (Recover, W. R. Grace)	5.5 oz/100-wt
Fine Aggregate	1630 lbs/yd^3
Coarse Aggregate	1235 lbs/yd^3
Foam Admixture (Miracon)	2.8 ft^3/yd^3
High Range WR (Adva, W. R. Grace)	3.5 oz/100-wt
Low Range WR (27, W. R. Grace)	0.5 oz/100-wt

Example 3

COMPONENTS	AMOUNTS
Portland Cement	308 lbs/yd^3
Water	30 gal/yd^3
Hydration Stabilizer (Recover, W. R. Grace)	5.5 oz/100-wt
Fine Aggregate	1630 lbs/yd^3
Coarse Aggregate	1235 lbs/yd^3
Foam Admixture (Miracon)	2.8 ft^3/yd^3
High Range WR (Adva, W. R. Grace)	3 oz/100-wt
Mid Range WR (997, Master Builders)	6.5 oz/100-wt
Low Range WR (27, W. R. Grace)	0.5 oz/100-wt

Example 4

COMPONENTS	AMOUNTS
Holcim Cement	408.2 lbs/yd^3
Water	25.88 gal/yd^3
Hydration Stabilizer (Delvo, Master Builders)	2.52 oz/100-wt
Fine Aggregate (concrete sand)	1251 lbs/yd^3
Coarse Aggregate (#8 pea gravel)	830.8 lbs/yd^3
Fly Ash (Bridger)	164.1 lbs/yd^3
Foam Admixture (Miracon)	7.65 ft^3/yd^3
High Range WR (30/30, Master Builders)	6.3 oz/100-wt
Low Range WR (27, W. R. Grace)	1.17 oz/100-wt
Accelerator Calcium Chloride	32.32 oz/100-wt

The concrete prepared using Example 4 had 27.1% air and a compressive strength of 923 psi in 28 days and 1205 psi in 56 days.

Example 5

COMPONENTS	AMOUNTS
Cement (Ashgrove I/II)	352 lbs/yd^3
Water	21.8 gal/yd^3
Hydration Stabilizer (Recover,)	1.99 oz/100-wt
Fine Aggregate (concrete sand)	1316 lbs/yd^3
Coarse Aggregate (#8 pea gravel)	312 lbs/yd^3
Coarse Aggregate (#57 rock)	1581 lbs/yd^3
Fly Ash (San Juan Type F)	103 lbs/yd^3
Foam Admixture (Miracon)	1.5 ft^3/yd^3
High Range WR (30/30, Master Builders)	4.85 oz/100-wt
Low Range WR (27, W. R. Grace)	2.5 oz/100-wt
Accelerator Calcium	29.82 oz/100-wt

The concrete prepared using Example 5 had 5.8% air and a compressive strength of 3615 psi in 28 days and 4320 psi in 56 days.

Example 6

In Example 6, a concrete mixture was prepared using a standard air entraining agent and a second mixture was prepared using Miracon as an air entraining agent. Both had an air entrainment of 5.8%, a density of 139 lbs/ft^3 and used 5.5 sacks of cement. The following performance data compares the performance of the standard mixture and the mixture prepared according to the present invention.

		Standard Air Entrainment	Air Entrainment with Miracon
Bleeding, (%)		1.68%	1.11%
Initial Set (hr)		4.67	4.51
Compressive Strength	3 day	2130	2840
(psi)	7 day	2890	3610
	21 day	4110	4970
Flexural Strength	3 day	430	470
(psi)	7 day	490	610
	21 day	590	640

As can be seen from the comparison with standard air entrainment, concrete entrained using the hydration stabilizer and foams of the present invention achieve higher strength and decreased bleeding when compared with traditional air entraining agents.

The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

What is claimed is:

1. A concrete mixture, comprising:

(i) a hydraulic cement;

(ii) a hydration stabilizer comprising one or more calcium chelating agents;

(iii) water; and

(iv) a foam admixture comprising water and a fluorochemical surfactant, wherein the foam is stabilized in the presence of the hydraulic cement by the hydration stabilizer.

2. A concrete mixture as in claim **1**, wherein the calcium chelating agent comprises a molecule selected from the group consisting of N-nitrilo tris(methylene phosphonic acid), 1,2-ethanediyl bis[nitrilo di(methylene phosphonic acid)]; 1,6-hexanediyl bis[nitrilo di(methylene phosphonic acid)], amino tris(methylene phosphonic acid), polymethoxy polyphosphonic acids, and combinations thereof.

3. A concrete mixture as in claim **1**, wherein the foam admixture comprises at least about 5% by volume of the concrete mixture.

4. A concrete mixture as in claim **1**, wherein the foam admixture comprises at least about 10% by volume of the concrete mixture.

5. A concrete mixture as in claim **1**, wherein the hydration stabilizer is included in an amount sufficient to inhibit the reaction between the hydraulic cement and the water in the foam for greater than about 30 minutes.

6. A concrete mixture as in claim **1**, wherein the hydration stabilizer is included in an amount sufficient to inhibit the reaction between the hydraulic cement and the water in the foam for greater than about 1 hour.

7. A cured concrete manufactured by pouring the concrete mixture of claim **1** and allowing the concrete mixture to cure.

8. A concrete mixture as in claim **1** that achieves a compressive strength of greater than 2500 psi in 28 days, when allowed to set.

9. A concrete mixture as in claim **1** that achieves a compressive strength of greater than 3000 psi in 28 days, when allowed to set.

10. A method for manufacturing an initial concrete mixture having stable air entrainment, comprising:

(i) preparing a foam admixture by mixing together a foam concentrate comprising a fluorochemical surfactant, water, and air under shear forces sufficient to form a plurality of air bubbles;

(ii) providing a hydration stabilizing including a calcium chelating agent; and

(iii) forming an initial concrete mixture by mixing together the foam admixture, a hydraulic cement, water, aggregate, and the hydration stabilizer, wherein the hydration stabilizer inhibits the destruction of the air bubbles by the hydraulic cement during at least a portion of the initial mixing.

11. A method as in claim **10**, wherein the calcium chelating agent comprises a molecule selected from the group consisting of N-nitrilo tris(methylene phosphonic acid), 1,2-ethanediyl bis[nitrilo di(methylene phosphonic acid)]; 1,6-hexanediyl bis[nitrilo di(methylene phosphonic acid)], amino tris(methylene phosphonic acid), polymethoxy polyphosphonic acids, and combinations thereof.

12. A method as in claim **10**, wherein the foam admixture comprises at least about 5% by volume of the concrete mixture.

13. A method as in claim **10**, wherein the hydration stabilizer is included in an amount sufficient to inhibit the reaction between the hydraulic cement and the water in the foam for greater than about 30 minutes.

14. A method for making a concrete structure comprising pouring the concrete mixture of claim **10** into a form and allowing the concrete mixture to cure.

15. A method as in claim **14**, wherein the cured concrete achieves a compressive strength of greater than 2500 psi in 28 days.

16. A method as in claim **10**, further comprising the step of mixing a fly ash with the cementitious material, the fly ash having a loss on ignition of at least about 6%.

17. A method for manufacturing an initial concrete mixture having stable air entrainment, comprising:

(i) providing a firefighting foam concentrate;

(ii) preparing a foam admixture by mixing together the firefighting foam concentrate, water, and air under shear forces sufficient to form a plurality of air bubbles;

(ii) providing a hydration stabilizer including a calcium chelating agent; and

(iii) forming an initial concrete mixture by mixing together the foam admixture, a hydraulic cement, water, aggregate, and the hydration stabilizer, wherein the hydration stabilizer inhibits the destruction of the air bubbles by the hydraulic cement during at least a portion of the initial mixing.

18. A method as in claim **17**, wherein the firefighting foam concentrate is a aqueous film forming foam, a protein foam, a fluoroprotein foam, an alcohol resistant fluoroprotein foam, a film forming fluoroprotein, and/or an alcohol-resistant film forming fluoroprotein (AR-FFFP).

19. A method as in claim **18**, wherein the calcium chelating agent comprises a molecule selected from the group consisting of N-nitrilo tris(methylene phosphonic acid), 1,2-ethanediyl bis[nitrilo di(methylene phosphonic acid)]; 1,6-hexanediyl bis[nitrilo di(methylene phosphonic acid)], amino tris(methylene phosphonic acid), polymethoxy polyphosphonic acids, and combinations thereof.

20. A method for making a concrete structure comprising pouring the concrete mixture of claim **18** into a form and allowing the concrete mixture to cure, wherein the cured concrete achieves a compressive strength of greater than 3000 psi in 28 days.

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(54) **CONCRETE MIXTURES INCLUDING CARBON ENCAPSULATING ADMIXTURE**

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(57) **ABSTRACT**

Concrete mixtures for use with air entraining agents and supplementary cementitious materials are achieved using a carbon encapsulating agent. The carbon encapsulating agent can include a nitrilotrisethanol aliphatic soap.

21 Claims, No Drawings

CONCRETE MIXTURES INCLUDING CARBON ENCAPSULATING ADMIXTURE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional application 61/450,614 filed Mar. 8, 2011, titled "CONCRETE MIXTURES INCLUDING CARBON ENCAPSULATING ADMIXTURE", which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

1. The Field of the Invention

The present invention relates to flowable concrete mixtures and cured concrete obtained therefrom. More particularly, the present invention relates to concrete mixtures that have an aqueous based carbon encapsulating admixture.

2. Related Technology

Concrete mixtures are composite materials that are usually composed of water, cement, and aggregate. Common aggregates include sand, gravel, or crushed stone. Concrete is a well-known structural component with typical compressive strengths of about 2500 psi, when cured.

Admixtures are often added to concrete to give the concrete desired properties. Examples of suitable uses for concrete admixtures include lowering the concrete's density, improving the concrete's workability, improving the concrete's strength to weight ratio, giving the concrete insulating properties, and/or enhancing the acoustic properties of the concrete, among others. These beneficial properties are often accomplished by adding several different admixtures.

Air entraining agents are often used alone or in combination with other admixtures to give the concrete one or more of the foregoing properties. Air entraining admixtures are used to purposely trap microscopic air bubbles in the concrete. Air entrainment dramatically improves the durability of concrete exposed to moisture during cycles of freezing and thawing. In addition, entrained air greatly improves concrete's resistance to surface scaling caused by chemical deicers. Air entrainment also increases the workability of fresh concrete while eliminating or reducing segregation and bleeding.

There are several methods for entraining air in concrete. One approach is to generate bubbles or air pockets in situ. This approach can be accomplished using surfactants or other air entraining admixtures that generate bubbles as the concrete is mixed. Materials used to achieve these desired effects include non-ionic, cationic, and anionic surfactants, natural and synthetic resins, fatty acids, proteinaceous material, sulfonated hydrocarbons, and the like.

Another trend in concrete is to incorporate supplementary cementitious materials such as fly ash and pozzolans. However, many SCMs are known to reduce air entrainment and/or cause great variability in air entrainment, thereby making it difficult to achieve consistent results in the performance of the concrete (both wet and cured).

The desire to use SCMs such as fly ash in concrete is quite compelling due to cost reduction. There has been extensive research over a long period of time to mitigate the detrimental effects that fly ash and other SCMs can have on air entrainment. Despite this long felt need, there still does not exist a simple and economical solution to solve the variability in air entrainment when using fly ash.

DESCRIPTION OF THE INVENTION

I. Concrete Mixtures

The composition of the concrete mixtures of the present invention can vary depending on the desired use for the concrete. In general, the concrete mixtures of the present invention include at least (i) a hydraulic cement, (ii) water, (iii) an SCM that includes carbon, (iv) an air entraining agent, and (v) a carbon encapsulating agent. The concrete mixtures typically include one or more aggregates, which gives the concrete strength. Dispersants and other admixtures are also described below and can be included to give the concrete mixtures of the present invention desired properties.

The carbon encapsulating agent is a surfactant that includes hydrophilic and lipophilic groups. In one embodiment the encapsulating agent is insoluble in the mixture of water and air-entraining agent. The encapsulating agent coats the carbon particles rather than the micro-air bubbles. This allows the concentration of the encapsulating agent to be selected independent of the air entraining agent. Thus, the concentration of the carbon encapsulating agent can be selected according to the concentration of SCM in the concrete mixture (and thus the amount of deleterious carbon), while the concentration of the air entraining agent is selected to produce the desired concentration of air.

The mixtures and methods of the present invention provided important control over the manufacture of concretes with SCMs that include carbon. Because the encapsulating agent and air entraining agent work separately, the cost of each can be minimized. Experimental data shows that small amounts of encapsulating agent can have drastic affects on the amount of air entraining agent needed to reach the desired level of air entrainment. In addition, the use of lower amounts of air entraining agent allows water to be added without causing large changes in the air entrainment, which can be very detrimental to strength and finishability of the concrete.

A. Hydraulic Cement and Water

The cement included in the concrete mixtures of the present invention is a hydraulic material such as Portland cement, modified Portland cement, or masonry cement. For purposes of this invention, Portland cement includes all cementitious compositions which have a high content of tricalcium silicate, including Portland cement, cements that are chemically similar or analogous to Portland cement, and cements that fall within ASTM specification C-150-00. Other cementitious materials include ground granulated blast-furnace slag, hydraulic hydrated lime, white cement, slag cement, calcium aluminate cement, silicate cement, phosphate cement, high-alumina cement, magnesium oxychloride cement, and combinations of these and other similar materials.

Water is added to the concrete mixture in sufficient amounts to hydrate the cement. Those skilled in the art will recognize that the amount of water needed will depend on the desired flowability and on the amounts and types of admixtures included in the concrete composition. Many of these admixtures are discussed below. In general, suitable amounts of water for hydrating the cement ranges from about 1% to about 50%, more preferably about 5-50%, and most preferably about 10% to about 25% of the concrete mixture by weight.

B. Supplementary Cementing Material

The supplementary cementitious material (SCM) can be a natural or synthetic pozzolan that can react with excess calcium from a hydraulic cement to form a cementitious material. In a preferred embodiment, the SCM may include, but is not limited to, fly ash such as coal ash. ASTM C618 standard, which is incorporated herein by reference, recognizes two major classes of fly ashes for use in concrete—Class C and Class F. These two classes of fly ashes are derived from different kinds of coals that are a result of differences in the coal formation processes occurring over geological time periods. Class F fly ash is normally produced from burning anthracite or bituminous coal, whereas Class C fly ash is normally produced from lignite or sub-bituminous coal. The ASTM C618 standard differentiates Class F and Class C fly ashes primarily according to their pozzolanic properties. Accordingly, in the ASTM C618 standard, the major specification difference between the Class F fly ash and Class C fly ash is the minimum limit of $SiO_2+Al_2O_3+Fe_2O_3$ in the composition. The minimum limit of $SiO_2+Al_2O_3+Fe_2O_3$ for Class F fly ash is 70% and for Class C fly ash is 50%. Thus, Class F fly ashes are more pozzolanic than the Class C fly ashes. Although not explicitly recognized in the ASTM C618 standard, Class C fly ashes typically contain high calcium oxide content. Presence of high calcium oxide content makes Class C fly ashes possess cementitious properties leading to the formation of calcium silicate and calcium aluminate hydrates when mixed with water. The use of Class C fly ash can be particularly useful to replace a portion of the cement in the concrete. Class C fly ash and Portland cement can be blended in weight ratios of ash to cement of about 0/100 to 150/100, preferably 75/100 to 125/100. In some reactive powder blends the portland cement is about 40 to 80 wt % and fly ash 20 to 60 wt %.

Because fly ash is obtained from coal combustion or found naturally, fly ash typically includes a certain amount of carbon. The amount of carbon in fly ash is measured according loss on ignition (LOI). Fly ash that has an LOI greater than about 1.5 can be difficult to work with in concrete mixtures that have air entraining agents because the carbon destroys the air entrainment. The inventor of the present invention has found that the carbon encapsulating agents described herein are surprisingly effective at sequestering the carbon in fly ash.

Thus, in one embodiment of the invention, the concrete mixture includes a fly ash having an LOI greater than or equal to 1.0, 1.5, 2, 4, or 6 as measured using ASTM standard procedures and less than 20, 15, or 10 or within a range of the foregoing. It has also been found that high carbon fly ash when used in combination with the carbon encapsulating agents of the present invention, increases the strength of the cured concrete as compared to fly ash that is not high carbon (i.e., the carbon in combination with the carbon encapsulating agent can be beneficial).

C. Carbon Encapsulating Agents

The carbon encapsulating agent is a composition including one or more non-foaming surfactants that can sequester carbon and thereby isolate the carbon from the air entraining agent. In one embodiment, the encapsulating agent may form a micelle around carbon particles. In some embodiments the micelle may be a spherical micelle. The encapsulation or formation of a micelle is achieved by selecting a surfactant that can form micelles with a hydrophobic interior that are sufficiently large to encapsulate the carbon particles. Forming micelles with a hydrophobic interior that is sufficiently large to encapsulate carbon can be achieved using surfactant molecules with water-insoluble aliphatic groups such as long chain aliphatic acids and/or alcohols.

In a preferred embodiment, the carbon encapsulating agent is a non-foaming surfactant. The use of a non-foaming surfactant inhibits the miscibility of the carbon encapsulating agent and the air entraining agent, which allows them to function separately within the same mixture.

In addition, it may be desirable for the encapsulating agent to have a hydrophobicity in which the carbon encapsulating agent has a greater affinity for the carbon particles than a mixture of water and air entraining agent. In one embodiment, the encapsulating agent may be insoluble or have less than 5% or 1% solubility in a mixture of the water and air entraining agent at a pH and temperature suitable for the hydrating cement.

The encapsulating agent can include one or more active agents and/or solvents to allow the agent to be dispersed in the concrete during mixing.

In a preferred embodiment the carbon encapsulating agent has a molecular weight of at least 200, 300, 400, 500, 750, or 1000 Da and/or less than 20,000, 10,000, or 5,000 Da or a range thereof. In one embodiment, the agent includes a hydrocarbon moiety of at least 200, 300, 400, or 500 Da. In one embodiment the encapsulating agent forms micelles in cement paste that have a molecular weight greater than 10,000, 25,000, or 50,000 Da.

The encapsulating agent may be an amphipathic molecule or surfactant that includes a plurality of aliphatic groups. The aliphatic groups may be formed from water insoluble aliphatic alcohols or acids.

The encapsulating agent can include one or more of the following components: (i) one or more solvents, (ii) nitrilotrisethanol aliphatic soap; (iii) alkyl ether amine reacted with one or more aliphatic acids; (iiv) and/or an aliphatic alcohol. Preferably the carbon encapsulating agent includes at least nitrilotrisethanol aliphatic soap and most preferably a 2,2,2-nitrilotrisethanol aliphatic acid soap. The nitrilotrisethanol can be included in the encapsulating agent at a weight percent of 0.25-18 wt %, 0.5-9 wt %, or 0.1-4.5 wt %.

The concentration of the alkyl ether amine reacted with one or more aliphatic acids may be in a range from 10%-70%, more preferably 25%-55% by weight of the encapsulating agent.

The encapsulating agent can include an aliphatic alcohol having a branched straight chain, substitute or unsubstituted carbon chain of 6, 8, 10, 12, 14, or 16 carbons and/or less than 32, 24, 20, 18, or 16 carbons or a combination thereof. In one embodiment, the aliphatic alcohol is non-soluble. Non-soluble alcohols can produce reaction products that readily form micelles that can encapsulate carbon (i.e., create a micelle around the carbon).

The linear aliphatic alcohol may have a concentration in a range from 1%-20% by weight of the carbon encapsulating agent, preferably 3-10%.

In an example of a suitable carbon encapsulating agent having the foregoing properties is F-500 encapsulating agent, Pinnacle firefighting foam, HydroLock, and C-Sync products, which are manufactured by Hazard Control Technologies, Inc of Fayetteville, Ga., USA. Additional details about suitable encapsulating agents that can be used are disclosed in U.S. Pat. No. 5,945,026, which is incorporated herein by reference.

F-500 encapsulating agent is a well-known and widely distributed non-foaming firefighting agent. The ability of F-500 to provide consistency in air entrainment across a wide range of carbon content and/or concentrations of SCMs while allowing independent control of the air entrainment using an air entraining agent is a surprising and unexpected result.

The carbon encapsulating agents can be included in the concrete mixture in a concentration of from 0.5-100 oz of encapsulating agent per 100 lbs of cement or binder, alternatively 0.5-30 oz/100 wt cement or binder, or 1.0-10 oz/100 wt cement or binder. Typically the amount of encapsulating agent is selected according to the amount of SCM used. In one embodiment the encapsulating agent is included in a concrete mix at a concentration of 0.5, 0.75, 1.0, 1.25, or 1.5 oz per 100 wt of SCM, and less than 30, 15, 10, 7.5, or 5.0 oz per 100 wt of SCM, where the SCM has a LOI as described above. In one embodiment, the carbon encapsulating agent is selected so as to be in sufficient quantity to encapsulate a majority of the carbon provided by an SCM. A sufficient quantity can be determined by testing air entrainment and adding encapsulating agent until the difference in the amount of air entraining agent to achieve the same level of air entrainment as compared to a mix with no SCM is less than half the extra amount of entraining agent needed to achieve the same level of air entrainment when using the SCM. The air entrainment can be included sufficient to encapsulate at least 75%, 90%, 95%, or even 99% or more of the carbon included in the mix with the SCM.

D. Air Entraining Agents

The concrete mixtures of the invention may also include an air entraining agent. Air-entraining agents are compounds that entrain microscopic air bubbles in cementitious compositions, which then harden into concrete having microscopic air voids. Entrained air dramatically improves the durability of concrete exposed to moisture during freeze thaw cycles and greatly improves a concrete's resistance to surface scaling caused by chemical deicers. Air-entraining agents can also reduce the surface tension of a fresh cementitious composition at low concentration. Air entrainment can also increase the workability of fresh concrete and reduce segregation and bleeding. Examples of suitable air-entraining agents include wood resin, sulfonated lignin, petroleum acids, proteinaceous material, fatty acids, resinous acids, alkylbenzene sulfonates, sulfonated hydrocarbons, vinsol resin, anionic surfactants, cationic surfactants, nonionic surfactants, natural rosin, synthetic rosin, inorganic air entrainers, synthetic detergents, the corresponding salts of these compounds, and mixtures of these compounds. Air entrainers are added in an amount to yield a desired level of air in a cementitious composition. Generally, the amount of air entraining agent in a cementitious composition ranges from about 0.2 to about 30 fluid ounces per hundred pounds of dry cement or binder, alternatively 0.5-15, or 1.0-10. Weight percentages of the primary active ingredient of the air-entraining agents (i.e., the compound that provides the air entrainment) are about 0.001% to about 0.3%, based on the weight of dry cementitious material. The particular amount used will depend on materials, mix proportion, temperature, and mixing action.

Air entraining agents that may also be used include foams formed ex-situ, including stabilized foams such as, but not limited to foams described in Applicants co-pending U.S. patent application Ser. No. 12/701,398, filed Feb. 5, 2010, which is incorporated herein by reference in its entirety.

D. Aggregates

Aggregates are usually included in the concrete mixture to add bulk and to give the concrete strength. The aggregate can be a fine aggregate and/or a coarse aggregate. The fine aggregates are materials that pass through a Number 4 sieve (ASTM C125 and ASTM C33), such as silica sand. The coarse aggregate 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. Whether an aggregate needs to be added can depend on the desired use of the cured concrete. Aggregate sizing and selection for particular types of concrete (e.g., flowable fill and self consolidating concrete) is known in the art. The concrete mixtures of the present invention can include traditional aggregates such as coarse and fine aggregates.

E. Dispersants and/or Water-Reducers

Water reducers are used in concrete mixtures to lower the water content in the plastic concrete (i.e. uncured concrete) to increase its strength and to obtain higher slump without adding water. Water-reducers will generally reduce the required water content of a concrete mixture for a given slump and are useful for pumping concrete and in hot weather to offset the increased water demand. These admixtures disperse the cement particles in the concrete and make more efficient use of the hydraulic cement. This dispersion increases strength and/or allows the cement content to be reduced while maintaining the same strength. Water-reducers should meet the requirements for Type A in ASTM C 494 Specification.

Another class of water reducers includes mid-range water reducers. These water reducers have a greater ability to reduce the water content of the concrete and are often used because of their ability to improve the finishability of concrete flatwork. Mid-range water reducers should at least meet the requirements for Type A in ASTM C 494.

High range water-reducers (HRWR), also referred to as superplasticizers, are a special class of water-reducer. HRWRs reduce the water content of a given concrete mixture by about 12% to 30%. HRWRs are used to increase strength and reduce permeability of concrete by reducing the water content in the mixture or greatly increase the slump to produce "flowing" concrete without adding water. HRWRs are often used for high strength and high performance concrete mixture that contain higher contents of cementitious materials and mixtures containing silica fume. In a typical concrete mixture, adding a normal dosage of HRWRs to a concrete mixture with a slump of 3 to 4 inches (75 to 100 mm) will produce a concrete with a slump of about 8 inches (200 mm). Exemplary HRWRs that can be used in the present invention are covered by ASTM Specification C 494 and types F and G, and Types 1 and 2 in ASTM C 1017. Particularly advantageous dispersants include the HRWRS described in U.S. Pat. No. 6,858,074, which is incorporated herein by reference.

F. Viscosity Modifiers

Viscosity modifying agents (VMA), also known as rheological modifiers or rheology modifying agents, can be added to the concrete mixture of the present invention. These additives are usually water-soluble polymers and function by increasing the apparent viscosity of the mix water. This enhanced viscosity facilitates uniform flow of the particles and reduces bleed, or free water formation, on the fresh paste surface.

Suitable viscosity modifiers that can be used in the present invention include, for example, cellulose ethers (e.g., hydroxyethyl cellulose (HEC), hydroxyproplmethyl cellulose (HPMC), sodium carboxymethyl cellulose (CMC), carboxymethylhydroxyethyl cellulose (CMHEC), and the like); synthetic polymers (e.g., polyacrylates, polyvinyl alcohol (PVA), polyethylene glycol (PEG), and the like); exopolysaccharides (also known as biopolymers, e.g., welan gum, xanthan, rhamsan, gellan, dextran, pullulan, curdlan, and the like); marine gums (e.g., algin, agar, carrageenan, and the like); plant exudates (e.g., locust bean, gum arabic, gum Karaya, tragacanth, Ghatti, and the like); seed gums (e.g., Guar, locust bean, okra, psyllium, mesquite, and the like); starch-based gums (e.g., ethers, esters, and related derivatized compounds). See, for example, Shandra, Satish and Ohama, Yoshihiko, "Polymers In Concrete", published by CRC press, Boca Ration, Ann Harbor, London, Tokyo (1994).

Viscosity modifying agents are typically used with water reducers in highly flowable mixtures to hold the mixture together. Viscosity modifiers can disperse and/or suspend components of the concrete thereby assisting in holding the concrete mixture together. This property of viscosity modifiers makes them useful for making self compacting concrete, which requires high flowability.

G. Other Admixtures

Many other types of admixtures can be added to the concrete compositions of the present invention to give the concrete a desired property. As discussed below, other admixtures suitable for use in the concrete mixtures of the present invention include but are not limited to viscosity modifiers, corrosion inhibitors, pigments, wetting agents, water soluble polymers, strength enhancing agents, rheology modifying agents, water repellents, fibers, permeability reducers, pumping aids, fungicidal admixtures, germicidal admixtures, insecticidal admixtures, finely divided mineral admixtures, alkali reactivity reducer, bonding admixtures, and any other admixtures or additive that do not adversely affect the carbon encapsulating compounds.

Corrosion inhibitors in concrete serve to protect embedded reinforcing steel from corrosion due to its highly alkaline nature. The high alkaline nature of the concrete causes a passive and noncorroding protective oxide film to form on the steel. However, carbonation or the presence of chloride ions from deicers or seawater can destroy or penetrate the film and result in corrosion. Corrosion-inhibiting admixtures chemically arrest this corrosion reaction. The materials most commonly used to inhibit corrosion are calcium nitrite, sodium nitrite, sodium benzoate, certain phosphates or fluorosilicates, fluoroaluminates, amines, organic based water repelling agents, and related chemicals.

Dampproofing admixtures reduce the permeability of concrete that have low cement contents, high water-cement ratios, or a deficiency of fines in the aggregate. These admixtures retard moisture penetration into dry concrete and include certain soaps, stearates, and petroleum products.

Permeability reducers are used to reduce the rate at which water under pressure is transmitted through concrete. Silica fume, fly ash, ground slag, natural pozzolans, water reducers, and latex can be employed to decrease the permeability of the concrete.

Pumping aids are added to concrete mixes to improve pumpability. These admixtures thicken the fluid concrete, i.e., increase its viscosity, to reduce de-watering of the paste while it is under pressure from the pump. Among the materials used as pumping aids in concrete are organic and synthetic polymers, hydroxyethylcellulose (HEC) or HEC blended with dispersants, organic flocculents, organic emulsions of paraffin, coal tar, asphalt, acrylics, bentonite and pyrogenic silicas, natural pozzolans, fly ash and hydrated lime.

Bacteria and fungal growth on or in hardened concrete may be partially controlled through the use of fungicidal, germicidal, and insecticidal admixtures. The most effective materials for these purposes are polyhalogenated phenols, dialdrin emulsions, and copper compounds.

Fibers can be distributed throughout a fresh concrete mixture to strengthen it. Upon hardening, this concrete is referred to as fiber-reinforced concrete. Fibers can be made of zirconium materials, carbon, steel, fiberglass, or synthetic materials, e.g., polypropylene, nylon, polyethylene, polyester, rayon, high-strength aramid, or mixtures thereof.

The shrinkage reducing agent which can be used in the present invention can include but is not limited to alkali metal sulfate, alkaline earth metal sulfates, alkaline earth oxides, preferably sodium sulfate and calcium oxide.

Alkali-reactivity reducers can reduce the alkali-aggregate reaction and limit the disruptive expansion forces in hardened concrete. Pozzolans (fly ash and silica fume), blast-furnace slag, salts of lithium, and barium are especially effective.

Bonding admixtures are usually added to hydraulic cement mixtures to increase the bond strength between old and new concrete and include organic materials such as rubber, polyvinyl chloride, polyvinyl acetate, acrylics, styrene butadiene copolymers, and other powdered polymers.

Natural and synthetic admixtures are used to color concrete for aesthetic and safety reasons. These coloring admixtures are usually composed of pigments and include carbon black, iron oxide, phthalocyanine, umber, chromium oxide, titanium oxide and cobalt blue.

III. Methods for Making and using Concrete Mixtures

The concrete mixtures are prepared by selecting appropriates amounts of hydraulic cement, water, aggregate, air entraining agent, an SCM that includes at least 0.5%, 1%, 1.5%, 4%, 6%, or 8% carbon, and carbon encapsulating agent to sequester at least 60%, 80%, 90%, 95%, or 99% of the carbon in SCM. The encapsulating agent sequesters the carbon without itself entraining air. Thus, the air entrainment is controlled by the dosing of the air entraining agent and the dosing can be more silimar to traditional concentrations of air entrainment. This is in contrast to the technique used in prior art methods where the carbon is saturated using the air engraining agent. In the methods of the prior art, the air entraining agent is still interacting with the carbon, but an excess of air entraining agent creates the air. Obtaining proper dosing can be very difficult since proper dosing requires proper estimation of the carbon in the SCM, which can be highly variable. In contrast, by encapsulating the carbon, a majority to substantially all of the carbon can be sequestered and the variability in the air entrainment caused by the carbon can be significantly reduced or eliminated.

The amount of cement, water, aggregate, and SCM will typically be selected according to the design strength of the concrete and the materials available. The design strength of the concrete will depend on the particular application. The compositions of the invention can include wall mixes, sidewalk mixes, foundation mixes, flowable fill mixes, self consolidating concrete mixes, and the like. In one embodiment the design strength of the concrete is at least 500 psi, 1000 psi, 2000 psi, 3000 psi, 4000 psi, 5000 psi, 7000 psi, or 10,000 psi (or an approximation of the metric equivalent thereof). The concrete can have a design strength according to a range created from any of the foregoing strengths as endpoints. In some embodiments, the design strength can be less than 3000, 2000, or even 1000. This is advantageous for making flowable fill or excavateable concrete, which tends to have a very high air content.

Although not required, the present invention can be particularly useful for flowable fill concretes or self consolidating concrete where high flow and/or high air content is important. In one embodiment, the composition has an air content of at least 2%, 2.5%, 5%, 7.5%, or 10%.

The SCM content can be in a range from 0%-75% by weight of the binder content (i.e., as a percentage of the hydraulic cement and SCM fraction). In a preferred embodiment, the SCM is at least 5%, 10%, 15%, 20%, 25%, 30%, or 35% and less than 60%, 50%, 40%, or 35%, or a range between these endpoints. Higher SCM content can be advantageous for cost and performance reasons. The use of the carbon encapsulating material allows for the use of higher quantities of SCM while achieving the same or better air entrainment as compared to concrete composition that include a Portland cement and air entraining agent without the carbon encapsulating agent.

The carbon encapsulating agent is included in a concentration that allows the desired air entrainment (i.e., by sequestering the carbon in the SCM) while minimizing the amount of agent that is used. The carbon encapsulating agent is typically added as a concentrate of 25%-80% (preferably 40-50%) active agent of the concentrate. The concentrate can be added in amounts of 0.25-100 oz per hundred weight cement, 0.5-30, or 1-10 oz/100 wt cement or binder. Those skilled in the art will recognize that the optimal dosage will depend on the materials being used, the carbon content of the fly ash, the amount of fly ash used, and the desired air entrainment. Those skilled in the art are familiar with dosing admixtures to determine a desired amount for a particular application.

The air entrained by the air entraining agent in the presence of the carbon encapsulating agent can have a surface area that meets or exceeds ASTM standards available in March of 2011.

The compositions can be prepared using equipment known in the art. For example, in one embodiment, the compositions of the invention may be prepared at a ready mix plant and distributed in a local area.

IV. Examples

Example 1 illustrates a flowable fill concrete compositions according to the present invention. In each formula, admixtures (e.g. water reducers WR) were added based on 100 lbs of cement (i.e. 100-wt cement). The concrete mixture of Examples 1 achieved 12% air.

Example 1

COMPONENTS	AMOUNTS
Portland Cement	80 lbs/yd^3
Class F Fly Ash (LOI 4.0)	150 lbs/yd^3
Water	42 gal/yd^3
Aggregate	2929 lbs/yd^3
MICRO-AE (Air Entraining Agent)	10 oz/100-wt
F-500 (Hazard Control Technologies)	4.9 oz/100-wt

Examples 2-19 illustrates the performance of concrete mixtures including a carbon encapsulating agent, an air entraining agent, and fly ash, aggregate, Portland cement and water. The SCM was a class F fly ash included in an amount of 20% of the cementitious material (by weight). In Examples 2, 4, 6, 8, 10, 12, 14, 16, and 18, no encapsulating agent was added. In Examples 3, 5, 7, 9, 11, 13, 15, 17, and 19, the mixes included 2 oz of encapsulating agent (F-500) per 100 wt of fly ash. The amount of air entraining agent (Micro Air) was used in a sufficient concentration to achieve at least 6% air entrainment (AE).

Examples 2-19

Examples	2	3	4	5	6	7	8	9	10	11
F-500 agent	0	2	0	2	0	2	0	2	0	2
Water	32	39.1	32	39.7	32.75	40.1	34	39.7	34	40.5
Micro Air	15.1	1.4	16	1.3	22	0.8	23	0.5	23	0.5
W/C Ratio	0.46	0.56	0.46	0.57	0.47	0.58	0.49	0.57	0.49	0.58
Slump	3	4.25	3.25	5.25	3	4.5	3.25	4.25	3	4.5
Test AE %	6.2	7.2	6.5	9.4	6.5	7.7	6.5	6.2	6.5	6.4
3 day	2792	2506	2664	1984	2695	2410	2422	2703	2869	2381
7 day	3381	3789	3665	2861	3448	3280	3022	3688	3797	3644
14 day	4526	4990	4367	3788	4069	4642	3777	4942	4612	5002
28 day average	5461	6663	5272	4947	5210	5663	4906	6501	5816	6631
56 day	6343	6641	5987	5369	6293	617	6023	6562	6781	6643
PSI Per LB-28	9.42	11.49	9.09	8.53	8.98	9.76	8.46	11.21	10.03	11.43
PSI Per LB-56	10.94	11.45	10.32	9.257	10.85	1.064	10.38	11.31	11.69	11.45

Examples	12	13	14	15	16	17	18	19
F-500 Agent	0	2	0	2	0	2	0	2
Water	34	39.8	34	40.4	31	34.2	31	34.9
Micro Air	24	0.5	22.1	0.5	3.5	4	4.25	4
W/C Ratio	0.49	0.57	0.49	0.58	0.45	0.49	0.45	0.50
Slump	3	4.25	3.5	4.25	3.5	4	4.25	4.25
Test AE %	7.5	6.2	8.0	6.1	6.5	5.9	6.9	7.6
3 day	2153	2651	2192	2742	2785	3026	3246	3038
7 day	2933	3835	3053	4273	3451	4253	4371	4306
14 day	3514	5174	3723	5657	4609	4831	5286	5321
28 day average	4352	6447	4878	6464	5981	6627	6464	6289
56 day	4819	6878	5465	7046	7514	7034	7409	6292
PSI Per LB-28	7.50	11.12	8.41	11.14	10.31	11.43	11.14	10.84
PSI Per LB-56	8.309	11.86	9.422	12.15	12.96	12.13	12.77	10.85
Set Times	N/A	N/A	385 m	363 m	315 m	310 m	305 m	284 m

As can be seen from a comparison of even examples (no carbon encapsulating agent) to odd examples (2 oz of F-500 encapsulating agent), small quantities of encapsulating agent can allow for a substantial reduction in the amount of air entraining agent needed to achieve at least 6% air in concrete. This is a surprising and unexpected result.

Data also shows that the voids created by the air entrainment in the presence of the encapsulating agent are the same or superior to air entrainment without the carbon encapsulating agent, thereby suggesting the void spaces will produce durable concrete. In one embodiment, the specific surface area of voids in concrete manufactured according to the invention was 565 and the spacing factor was 0.006 as calculated using ASTM standards known in the art.

The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

What is claimed is:

1. A concrete mixture, comprising:

(i) a hydraulic cement;

(ii) a supplementary cementitious material including at least 1.0 wt % carbon;

(iii) water;

(iv) an air entraining agent in a concentration of at least 0.2 oz/100 wt % of cementitious material; and

(iv) a carbon encapsulating agent including a non-foaming surfactant including a nitrilotrisethanol aliphatic soap in sufficient concentration to sequester a majority of the carbon in the supplementary cementitious material.

2. A method as in claim **1**, wherein the surfactant is non-foaming and insoluble in air bubbles formed by the air entraining agent and water in the wet concrete mix.

3. A concrete mixture as in claim **1**, wherein the carbon encapsulating agent includes nitrilotrisethanol aliphatic soap, alkyl ether amine reacted with one or more aliphatic acids and/or a linear aliphatic alcohol.

4. A concrete mixture as in claim **3**, wherein the alkyl ether amine reacted with one or more aliphatic acids is Poly(oxy-1,2-ethanediyl) (iminodi-2,1-ethanediyl) bishydroxy fatty alkyl ether reaction products with one or more aliphatic acids.

5. A concrete mixture as in claim **3**, wherein the concentration of the alkyl ether amine reacted with one or more aliphatic acids is 25%-55% by weight of the carbon encapsulating agent.

6. A concrete mixture as in claim **3**, wherein the linear aliphatic alcohol has a concentration in a range from 3-10% of the encapsulating agent.

7. A concrete mixture as in claim **1**, wherein the surfactant is a nitrilotrisethanol aliphatic soap.

8. A concrete mixture as in claim **7**, wherein the concentration of nitrilotrisethanol aliphatic soap is 1-4.5% by weight of the carbon encapsulating agent.

9. A concrete mixture as in claim **1**, wherein the surfactant is non-foaming and has a weight greater than 500.

10. A concrete mixture as in claim **1**, wherein the carbon encapsulating agent is included in the composition in a range from 0.5-10.0 oz/100 wt % of supplementry cementitious material.

11. A concrete composition as in claim **1** wherein the air content is at least 5%.

12. A concrete composition as in claim **1**, wherein the supplementry cementitious material is a fly ash.

13. A cured concrete formed by allowing the concrete composition of claim **1** to harden.

14. A method for making an air entrained concrete, comprising:

providing a supplementary cementitious material comprising at least 1 wt % carbon; and

mixing together a hydraulic cement and the supplementary cementitious material with aggregate, water, an air entraining agent, and a carbon encapsulating agent to form a wet cementitious concrete, wherein the carbon encapsulating agent includes a non-foaming surfactant including a nitrilotrisethanol aliphatic soap and wherein the encapsulating agent is included in sufficient quantity to sequester at least a majority of the carbon.

15. A method as in claim **14**, wherein the supplementry cementitious material includes at least 4 wt % carbon and the carbon encapsulating agent is included in a concentration sufficient to sequester at least 98% of the carbon.

16. A method as in claim **14**, wherein the carbon encapsulating agent includes nitrilotrisethanol aliphatic soap, alkyl ether amine reacted with one or more aliphatic acids and/or a linear aliphatic alcohol.

17. A method as in claim **14**, wherein the active agent in the surfactant is insoluble in air bubbles formed by the air entraining agent and water in the wet concrete mix.

18. A method as in claim **14**, wherein the surfactant is a nitrilotrisethanol aliphatic soap.

19. A method as in claim **14**, wherein the surfactant is non-foaming and has a molecular weight greater than 500.

20. A method as in claim **14**, wherein the carbon encapsulating agent is included in the composition in a range from 0.5-10.0 oz/100 wt % of supplementry cementitious material.

21. A concrete mixture as in claim **1**, wherein the supplementry cementitious material includes at least 4 wt % carbon and the carbon encapsulating agent is included in a concentration sufficient to encapsulate at least 98% of the carbon.

* * * * *

JS 44 (Rev. 12/12)

CIVIL COVER SHEET

The JS 44 civil cover sheet and the information contained herein neither replace nor supplement the filing and service of pleadings or other papers as required by law, except as provided by local rules of court. This form, approved by the Judicial Conference of the United States in September 1974, is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. *(SEE INSTRUCTIONS ON NEXT PAGE OF THIS FORM.)*

I. (a) PLAINTIFFS

MIRACON TECHNOLOGIES, LLC

(b) County of Residence of First Listed Plaintiff Dallas County
(EXCEPT IN U.S. PLAINTIFF CASES)

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SPANGLER LAW, PC -208 N. Green, #300, Longview, TX/ 903-753-9300

DEFENDANTS

CRH, PLC, et al.

County of Residence of First Listed Defendant Ireland
(IN U.S. PLAINTIFF CASES ONLY)

NOTE: IN LAND CONDEMNATION CASES, USE THE LOCATION OF THE TRACT OF LAND INVOLVED.

Attorneys *(If Known)*

II. BASIS OF JURISDICTION *(Place an "X" in One Box Only)*

- ☐ 1 U.S. Government Plaintiff
- ☒ 3 Federal Question *(U.S. Government Not a Party)*
- ☐ 2 U.S. Government Defendant
- ☐ 4 Diversity *(Indicate Citizenship of Parties in Item III)*

III. CITIZENSHIP OF PRINCIPAL PARTIES *(Place an "X" in One Box for Plaintiff and One Box for Defendant)*

(For Diversity Cases Only)

	PTF	DEF		PTF	DEF
Citizen of This State	☒ 1	☐ 1	Incorporated *or* Principal Place of Business In This State	☒ 4	☐ 4
Citizen of Another State	☐ 2	☒ 2	Incorporated *and* Principal Place of Business In Another State	☐ 5	☒ 5
Citizen or Subject of a Foreign Country	☐ 3	☒ 3	Foreign Nation	☐ 6	☒ 6

IV. NATURE OF SUIT *(Place an "X" in One Box Only)*

CONTRACT
- ☐ 110 Insurance
- ☐ 120 Marine
- ☐ 130 Miller Act
- ☐ 140 Negotiable Instrument
- ☐ 150 Recovery of Overpayment & Enforcement of Judgment
- ☐ 151 Medicare Act
- ☐ 152 Recovery of Defaulted Student Loans (Excludes Veterans)
- ☐ 153 Recovery of Overpayment of Veteran's Benefits
- ☐ 160 Stockholders' Suits
- ☐ 190 Other Contract
- ☐ 195 Contract Product Liability
- ☐ 196 Franchise

REAL PROPERTY
- ☐ 210 Land Condemnation
- ☐ 220 Foreclosure
- ☐ 230 Rent Lease & Ejectment
- ☐ 240 Torts to Land
- ☐ 245 Tort Product Liability
- ☐ 290 All Other Real Property

TORTS

PERSONAL INJURY
- ☐ 310 Airplane
- ☐ 315 Airplane Product Liability
- ☐ 320 Assault, Libel & Slander
- ☐ 330 Federal Employers' Liability
- ☐ 340 Marine
- ☐ 345 Marine Product Liability
- ☐ 350 Motor Vehicle
- ☐ 355 Motor Vehicle Product Liability
- ☐ 360 Other Personal Injury
- ☐ 362 Personal Injury - Medical Malpractice

PERSONAL INJURY
- ☐ 365 Personal Injury - Product Liability
- ☐ 367 Health Care/ Pharmaceutical Personal Injury Product Liability
- ☐ 368 Asbestos Personal Injury Product Liability

PERSONAL PROPERTY
- ☐ 370 Other Fraud
- ☐ 371 Truth in Lending
- ☐ 380 Other Personal Property Damage
- ☐ 385 Property Damage Product Liability

CIVIL RIGHTS
- ☐ 440 Other Civil Rights
- ☐ 441 Voting
- ☐ 442 Employment
- ☐ 443 Housing/ Accommodations
- ☐ 445 Amer. w/Disabilities - Employment
- ☐ 446 Amer. w/Disabilities - Other
- ☐ 448 Education

PRISONER PETITIONS

Habeas Corpus:
- ☐ 463 Alien Detainee
- ☐ 510 Motions to Vacate Sentence
- ☐ 530 General
- ☐ 535 Death Penalty

Other:
- ☐ 540 Mandamus & Other
- ☐ 550 Civil Rights
- ☐ 555 Prison Condition
- ☐ 560 Civil Detainee - Conditions of Confinement

FORFEITURE/PENALTY
- ☐ 625 Drug Related Seizure of Property 21 USC 881
- ☐ 690 Other

LABOR
- ☐ 710 Fair Labor Standards Act
- ☐ 720 Labor/Management Relations
- ☐ 740 Railway Labor Act
- ☐ 751 Family and Medical Leave Act
- ☐ 790 Other Labor Litigation
- ☐ 791 Employee Retirement Income Security Act

IMMIGRATION
- ☐ 462 Naturalization Application
- ☐ 465 Other Immigration Actions

BANKRUPTCY
- ☐ 422 Appeal 28 USC 158
- ☐ 423 Withdrawal 28 USC 157

PROPERTY RIGHTS
- ☐ 820 Copyrights
- ☒ 830 Patent
- ☐ 840 Trademark

SOCIAL SECURITY
- ☐ 861 HIA (1395ff)
- ☐ 862 Black Lung (923)
- ☐ 863 DIWC/DIWW (405(g))
- ☐ 864 SSID Title XVI
- ☐ 865 RSI (405(g))

FEDERAL TAX SUITS
- ☐ 870 Taxes (U.S. Plaintiff or Defendant)
- ☐ 871 IRS—Third Party 26 USC 7609

OTHER STATUTES
- ☐ 375 False Claims Act
- ☐ 400 State Reapportionment
- ☐ 410 Antitrust
- ☐ 430 Banks and Banking
- ☐ 450 Commerce
- ☐ 460 Deportation
- ☐ 470 Racketeer Influenced and Corrupt Organizations
- ☐ 480 Consumer Credit
- ☐ 490 Cable/Sat TV
- ☐ 850 Securities/Commodities/ Exchange
- ☐ 890 Other Statutory Actions
- ☐ 891 Agricultural Acts
- ☐ 893 Environmental Matters
- ☐ 895 Freedom of Information Act
- ☐ 896 Arbitration
- ☐ 899 Administrative Procedure Act/Review or Appeal of Agency Decision
- ☐ 950 Constitutionality of State Statutes

V. ORIGIN *(Place an "X" in One Box Only)*

- ☒ 1 Original Proceeding
- ☐ 2 Removed from State Court
- ☐ 3 Remanded from Appellate Court
- ☐ 4 Reinstated or Reopened
- ☐ 5 Transferred from Another District *(specify)*
- ☐ 6 Multidistrict Litigation

VI. CAUSE OF ACTION

Cite the U.S. Civil Statute under which you are filing ***(Do not cite jurisdictional statutes unless diversity)***:
35 USC 1 et seq.; 28 USC 1331 and 1338(a); 28 USC 1332; 28 USC 2201 and 2202

Brief description of cause:
Patent Infringement; breach of contract; misappropriation of trade secrets; fraud; conspiracy; declaratory judgment

VII. REQUESTED IN COMPLAINT:

☐ CHECK IF THIS IS A **CLASS ACTION** UNDER RULE 23, F.R.Cv.P.

DEMAND $

CHECK YES only if demanded in complaint:
JURY DEMAND: ☐ Yes ☐ No

VIII. RELATED CASE(S) IF ANY

(See instructions): JUDGE DOCKET NUMBER

DATE
01/09/2015

SIGNATURE OF ATTORNEY OF RECORD
/s/ Andrew W. Spangler

FOR OFFICE USE ONLY

RECEIPT # AMOUNT APPLYING IFP JUDGE MAG. JUDGE

Print Save As... Reset

INSTRUCTIONS FOR ATTORNEYS COMPLETING CIVIL COVER SHEET FORM JS 44

Authority For Civil Cover Sheet

The JS 44 civil cover sheet and the information contained herein neither replaces nor supplements the filings and service of pleading or other papers as required by law, except as provided by local rules of court. This form, approved by the Judicial Conference of the United States in September 1974, is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. Consequently, a civil cover sheet is submitted to the Clerk of Court for each civil complaint filed. The attorney filing a case should complete the form as follows:

I.(a) **Plaintiffs-Defendants.** Enter names (last, first, middle initial) of plaintiff and defendant. If the plaintiff or defendant is a government agency, use only the full name or standard abbreviations. If the plaintiff or defendant is an official within a government agency, identify first the agency and then the official, giving both name and title.

(b) **County of Residence.** For each civil case filed, except U.S. plaintiff cases, enter the name of the county where the first listed plaintiff resides at the time of filing. In U.S. plaintiff cases, enter the name of the county in which the first listed defendant resides at the time of filing. (NOTE: In land condemnation cases, the county of residence of the "defendant" is the location of the tract of land involved.)

(c) **Attorneys.** Enter the firm name, address, telephone number, and attorney of record. If there are several attorneys, list them on an attachment, noting in this section "(see attachment)".

II. **Jurisdiction.** The basis of jurisdiction is set forth under Rule 8(a), F.R.Cv.P., which requires that jurisdictions be shown in pleadings. Place an "X" in one of the boxes. If there is more than one basis of jurisdiction, precedence is given in the order shown below.
United States plaintiff. (1) Jurisdiction based on 28 U.S.C. 1345 and 1348. Suits by agencies and officers of the United States are included here.
United States defendant. (2) When the plaintiff is suing the United States, its officers or agencies, place an "X" in this box.
Federal question. (3) This refers to suits under 28 U.S.C. 1331, where jurisdiction arises under the Constitution of the United States, an amendment to the Constitution, an act of Congress or a treaty of the United States. In cases where the U.S. is a party, the U.S. plaintiff or defendant code takes precedence, and box 1 or 2 should be marked.
Diversity of citizenship. (4) This refers to suits under 28 U.S.C. 1332, where parties are citizens of different states. When Box 4 is checked, the citizenship of the different parties must be checked**.** (See Section III below**; NOTE: federal question actions take precedence over diversity cases.**)

III. **Residence (citizenship) of Principal Parties.** This section of the JS 44 is to be completed if diversity of citizenship was indicated above. Mark this section for each principal party.

IV. **Nature of Suit.** Place an "X" in the appropriate box. If the nature of suit cannot be determined, be sure the cause of action, in Section VI below, is sufficient to enable the deputy clerk or the statistical clerk(s) in the Administrative Office to determine the nature of suit. If the cause fits more than one nature of suit, select the most definitive.

V. **Origin.** Place an "X" in one of the six boxes.
Original Proceedings. (1) Cases which originate in the United States district courts.
Removed from State Court. (2) Proceedings initiated in state courts may be removed to the district courts under Title 28 U.S.C., Section 1441. When the petition for removal is granted, check this box.
Remanded from Appellate Court. (3) Check this box for cases remanded to the district court for further action. Use the date of remand as the filing date.
Reinstated or Reopened. (4) Check this box for cases reinstated or reopened in the district court. Use the reopening date as the filing date.
Transferred from Another District. (5) For cases transferred under Title 28 U.S.C. Section 1404(a). Do not use this for within district transfers or multidistrict litigation transfers.
Multidistrict Litigation. (6) Check this box when a multidistrict case is transferred into the district under authority of Title 28 U.S.C. Section 1407. When this box is checked, do not check (5) above.

VI. **Cause of Action.** Report the civil statute directly related to the cause of action and give a brief description of the cause. **Do not cite jurisdictional statutes unless diversity.** Example: U.S. Civil Statute: 47 USC 553 Brief Description: Unauthorized reception of cable service

VII. **Requested in Complaint.** Class Action. Place an "X" in this box if you are filing a class action under Rule 23, F.R.Cv.P.
Demand. In this space enter the actual dollar amount being demanded or indicate other demand, such as a preliminary injunction.
Jury Demand. Check the appropriate box to indicate whether or not a jury is being demanded.

VIII. **Related Cases.** This section of the JS 44 is used to reference related pending cases, if any. If there are related pending cases, insert the docket numbers and the corresponding judge names for such cases.

Date and Attorney Signature. Date and sign the civil cover sheet.