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(57) **Abrégé/Abstract:**

A method of preparing a blended cement composition is provided. The method comprises intergrinding a composition comprised of a major amount by weight of portland cement clinker, a minor amount by weight of a pozzolanic material and a grinding aid in an amount of from about 0.1 % to about 5 % based on the total weight of portland cement clinker and pozzolanic material, said grinding aid being comprised of a naphthalenesulfonate formaldehyde condensate.



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(21) International Application Number: PCT/US96/19145 (22) International Filing Date: 6 December 1996 (06.12.96) (30) Priority Data: 60/008,545 13 December 1995 (13.12.95) US 08/755,433 22 November 1996 (22.11.96) US (71) Applicant: HENKEL CORPORATION [US/US]; Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US). (72) Inventors: FLEMING, Joseph, P.; 8 Watchung Road, East Brunswick, NJ 08816 (US). HIZNAY, Joseph, J.; 2568 Candytuft Drive, Jamison, PA 18929 (US). SAVOLY, Arpad; 1072 Dellwood Road, Martinsville, NJ 08836 (US). (74) Agent: WOOD, Daniel, J.; Henkel Corporation, Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US).		(81) Designated States: CA, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: METHOD OF MAKING BLENDED CEMENT COMPOSITONS (57) Abstract A method of preparing a blended cement composition is provided. The method comprises intergrinding a composition comprised of a major amount by weight of portland cement clinker, a minor amount by weight of a pozzolanic material and a grinding aid in an amount of from about 0.1 % to about 5 % based on the total weight of portland cement clinker and pozzolanic material, said grinding aid being comprised of a naphthalenesulfonate formaldehyde condensate.		

METHOD OF MAKING BLENDED CEMENT COMPOSITIONS

Field of the Invention

This invention relates to a method of making a blended cement composition comprised of a portland cement and a pozzolanic material.

5 Background Art

The term cement is used to designate many different kinds of agents useful to bind materials together. The present invention is directed to hydraulic

cements useful to form structural elements, such as those of roads, bridges, buildings and the like. Hydraulic cements are powder material which, when mixed with water, alone or with aggregate, form rock-hard products, such as paste, mortar or concrete. Paste is formed by mixing water with a hydraulic cement.

5 Mortar is formed by mixing a hydraulic cement with small aggregate (e.g. sand) and water. Concrete is formed by mixing a hydraulic cement with small aggregate, large aggregate (e.g. 0.2-1 inch stone) and water. For example, portland cement is a commonly used hydraulic cement material with particular standard specifications established in the various countries of the world. Further,

10 various organizations, such as American Society for Testing and Materials (ASTM), American Association of State Highway and Transportation Officials, as well as other governmental agencies, have established certain minimum standards for hydraulic cements which are based on principal chemical composition requirements of the clinker used to form the cement powder and

15 principal physical property requirements of the final cement mix.

Generally, hydraulic cements are prepared by sintering a mixture of components including calcium carbonate (as limestone), aluminum silicate (as clay or shale), silicon dioxide (as sand), and miscellaneous iron oxides. During the sintering process, chemical reactions take place wherein hardened nodules,

20 commonly called clinkers, are formed. Portland cement clinker is formed by the reaction of calcium oxide with acidic components to give, primarily tricalcium silicate, dicalcium silicate, tricalcium aluminate, and a ferrite solid solution phase approximating tetracalcium aluminoferrite. The conventional cement chemists notation uses the following abbreviations: $\text{CaO} = \text{C}$; $\text{SiO}_2 = \text{S}$; $\text{Al}_2\text{O}_3 = \text{A}$ and

$\text{Fe}_2\text{O}_3 = \text{F}$. Thus, tricalcium silicate = C3S; dicalcium silicate = C2S; tricalcium aluminate = C3A; and tetracalcium aluminoferrite = C4AF.

After the clinker has cooled, it is then pulverized together with a small amount of gypsum (calcium sulfate) in a finish grinding mill to provide a fine, homogeneous powdery product. In certain instances other materials may be added or the clinker composition may be modified to provide a particular desired type of hydraulic cement. For example, in certain instances limestone, granulated blast furnace slag, pozzolans and the like are substituted for a portion of the expensive clinker material. These materials are generally inert and are used in cements where economy is of prime consideration and some diminution in strength is acceptable. The term "blended cement" refers to hydraulic cements having between 5 and 80% (more conventionally 5-60%) clinker substitute material as part of its composition. Other hydraulic cements include, for example, moderate heat portland cement, fly ash portland cement, portland blast furnace cement and the like.

Due to the extreme hardness of the clinkers, a large amount of energy is required to properly mill them into a suitable powder form. Energy requirements for finish grinding can vary from about 33 to 77 kWh/ton depending upon the nature of the clinker. Several materials such as glycols, alkanolamines, aromatic acetates, etc., have been shown to reduce the amount of energy required and thereby improve the efficiency of the grinding of the hard clinkers. These materials, commonly known as grinding aids, are processing additives which are introduced into the mill in small dosages and interground with the clinker to attain a uniform powdery mixture.

One of the major classes of grinding aids used today is the oligomers of lower alkylene glycols, such as diethylene glycol. They are used because of their availability and low cost. These glycols have had their grinding effectiveness enhanced by the inclusion of polyglycerols, lower fatty acids and sulfonated lignin
5 (U.S. Patent No. 4,204,877); unsaturated aliphatic acid and amines (French Patent No. 2,337,699); a C3 aliphatic acid salt and an amine (U.S. Patent No. 3,615,785); as well as alcohols and amides (U.S. Pat. No. 5,125,976).

U.S. Patent No. 5,429,675 discloses a grinding aid composition suitable for grinding clinker into hydraulic cement powder, which grinding aid composition
10 is composed of a mixture of at least one alkylene ether glycol and particulate carbon.

U.S. Patent No. 3,856,542 discloses an aqueous solution of melamine formaldehyde condensation product is sprayed over dry cement product in the fine grinding compartment of a cement grinding mill at a uniform rate essentially
15 throughout the grinding process in concentration and amount chosen to evaporate all the aqueous solvent during the normal cement grinding process and introduce an aggregate of 0.1 to 2.0 weight per cent of condensation product solid in relation to the dry cement product being ground. By means of the disclosed process, two previously necessary operation steps are spared, (1)
20 spray drying of the solution of the condensation product and (2) the mixing of the pulverulent condensation product with the ground cement.

U.S. Patent No. 4,306,912 discloses a process for producing a binder (cement) to be used in slurry, mortar, or concrete having a low water-to-cement ratio. As raw-material for the binder is used at least 50% by weight of a hydraulic

material, such as slag, technical pozzolanas and/or natural pozzolanas. The hydraulic material is ground to a specific surface of at least 400 m²/kg. To the raw-material is added 0.1 to 5% by weight of a plasticizing material, such as a sulphonated polyelectrolyte, e.g. formaldehyde-naphthalene condensation products. To the raw-material are also added in total 0.5 to 8% by weight of sodium carbonate and/or sodium hydroxide. It is also disclosed that if it is desirable to add clinker to the binder or to the concrete, the clinker should preferably be ground separately while using the same admixtures.

10 Summary of the Invention

This invention relates a method of preparing a blended cement composition which comprises intergrinding a composition comprised of a major amount by weight of portland cement clinker, a minor amount by weight of a pozzolanic material and a grinding aid in an amount of from about 0.1% to about 5% based on the total weight of portland cement clinker and pozzolanic material, said grinding aid being comprised of a naphthalenesulfonate formaldehyde condensate.

20 Detailed Description of the Invention

Naphthaleneformaldehyde sulfonic acid is also known as the naphthalenesulfonic acid-formaldehyde condensates, formalin condensates of beta-naphthalenesulfonic acid, condensation products of naphthalenesulfonic acid with formaldehyde. Naphthaleneformaldehyde sulfonic acid may be

prepared by reacting a mixture of naphthalene, formaldehyde and sulfuric acid. It may be prepared by the processes described in U.S. Pat. No. 2,141,569 (Tucker et al, issued Dec. 27, 1938), U.S. Pat. No. 3,193,575 (Nebel et al, issued July 6, 1965), and U.S. Pat. No. 3,277,162 (Johnson, issued Oct. 4, 1966).

5 Naphthaleneformaldehyde sulfonic acid is a mixture of condensation products of naphthalenesulfonic acid and formaldehyde. It can be chromatographed by size exclusion chromatography through a column containing pore sizes which selectively separate molecular volumes according to size. The solvent chosen for the acid in chromatography should minimize
10 solute-packing interaction and solute-solute interaction. The chromatogram gives a true molecular volume profile when the eluents are displayed on a detector-strip chart recorder display. For example, if the chromatogram for a sample of the sulfonic acid is the same as that for the sodium naphthaleneformaldehyde sulfonate in U.S. Pat. No. 3,954,491 (Adrian et al,
15 issued May 4, 1976), the two anionic materials are identical. That is, the anionic materials from the acid have the same profile as the anionic materials from the sodium naphthaleneformaldehyde sulfonate having lowest elution volumes of from above 61 to about 70% of the total elution volume and equivalent elution volumes of from about 61 to about 70% of the total elution volume. The
20 teachings in U.S. Pat. No. 3,954,491 relating to chromatography are incorporated by reference herein. The naphthaleneformaldehyde sulfonic acid resin can be in the acid form but is preferably in an essentially neutralized form, e.g. as a water soluble salt. The counter ion of the neutralized resin can be a metal selected from the group consisting of sodium, calcium, magnesium, lithium, zinc,

and mixtures of two or more of said metals. Naphthalenesulfonate formaldehyde condensate resins available from Henkel Corporation, Ambler, Pennsylvania, as Lomar D, are particularly preferred.

5 The concentration of the grinding aid composition in the blend of cement clinker and pozzolanic material may vary, but will generally be less than about 5%, typically from about 0.1% to about 5%, preferably from about 1% to about 2% (by the sum of weights of portland cement clinker and pozzolanic material).

10 The portland cement clinker used in the process of this invention is an intermediate produced in the process of manufacturing finished portland cements. As is well known in the art, a portland cement is a hydraulic cement produced by pulverizing clinker which predominantly comprises hydraulic calcium silicates, and usually contains one or more of the forms of calcium sulfate. e.g. gypsum, as an interground addition present in a few percent by weight, typically 4% to 6% by weight. The clinker is prepared by heating a mixture of limestone and clay or shale, or other calcareous and argillaceous materials to a fused state. 15 As noted in U.S. Pat. No. 4,105,459, a portland cement will typically comprise about 60 to about 69% by weight of combined and uncombined calcium oxide.

20 ASTM C 150, Standard Specification for Portland Cement, covers 8 types of portland cement, all of which may be employed in accordance with the present invention; ASTM C 150 is hereby incorporated by reference in its entirety. Type I is for use when the special properties specified for any other type are not required; no limits are imposed on any of the four principal compounds. Type IA is air-entrained Type I cement, for use where air entrainment is desired (e.g., for making frost-resistant concrete). Type II is for general use, more especially when

moderate sulfate resistance or moderate heat of hydration is desired; since C3A and C3S produce high heats of hydration, the specification limits the C3A content of the cement to maximum 8 percent, and has an optional limit of maximum 58 percent on the sum of C3S and C3A (this limit applies when a moderate heat of hydration is required and test data for heat of hydration are not available). Type IIA is air-entraining Type II cement. Type III is for use when high early strength is desired; to ensure that the high strength is not due mainly to the hydration products of C3A, the specification limits the C3A content of the cement to maximum 15 percent. Type IIIA is air-entraining Type III cement. Type IV is for use when a low heat of hydration is desired; since C3A and C3S produce high heats of hydration, but C2S produces much less heat, the specification calls for maximum limits of 35 and 7 percent on C2S and C3A, respectively, and requires a minimum of 40 percent C2S in the cement. Type V is for use when high sulfate resistance is desired; the specification calls for a maximum limit of 5 percent on C3A which applies when the sulfate expansion test is not required. Types I, II and III are the most commonly used cements, and clinkers for such cements are particularly preferred for use in accordance with the present invention.

In addition to the portland cement clinker, the material to be ground will also contain a pozzolanic material. A pozzolanic material is defined as a siliceous or siliceous and aluminous material which in itself possesses insufficient cementing property to form a structurally useful material, but will in a finely divided form and in the presence of moisture chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. Thus, the cement produced by the process of this invention will be

a blended cement. Examples of pozzolanic materials include natural pozzolans, fly ash, ground granulated blast furnace slag (GGBF slag), and silica fume.

ASTM C 595, Standard Specification for Blended Hydraulic Cements, covers five classes of blended cements; ASTM C 595 is hereby incorporated by reference in its entirety. For purposes of the instant disclosure, a blended cement which is typically produced by the present invention may be characterized as a cement which meets the specifications of ASTM C 595 for Type IS, Type I(SM), Type IP or Type I(PM) cement. A blended cement may, in general, be produced by intergrinding portland cement clinker with other materials, blending the components together or both intergrinding and blending them together. In the method of this invention, the portland cement clinker, pozzolanic material and grinding aid are all ground together.

Type I(PM) is a pozzolan-modified portland cement produced either by intergrinding portland cement clinker and pozzolan, or by blending portland cement and finely divided pozzolan, in which the pozzolan content is less than 15% by weight of the pozzolan-modified portland cement composition. Type IP is a portland-pozzolan cement produced either by intergrinding portland Cement clinker and pozzolan or by blending portland cement and finely divided pozzolan, in which the pozzolan constituent comprises about 15-40 weight-% of the portland-pozzolan composition.

ASTM C 618, Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete, provides additional details concerning the chemical and physical properties of pozzolans and fly ashes. ASTM C 618 is hereby incorporated by reference in its

entirety. The materials comprised within the specifications of ASTM C 618 are divided into three classes. Class N comprises raw or calcined natural pozzolans such as some diatomaceous earths, opaline cherts and shales, tuffs and volcanic ashes or pumicites, and various materials requiring calcination to induce satisfactory properties (such as some clays and shales. Class F comprises fly ash normally produced from burning anthracite or bituminous coal. Class C comprises fly ash normally produced from lignite or subbituminous coal; in addition to having pozzolanic properties, this class of fly ash also has some cementitious properties. For purposes of the present invention, all three classes of materials defined in ASTM C 618 are considered suitable for use in preparation of blended portland cements meeting the requirements of ASTM C 595; therefore, a Type IP or Type I(PM) blended portland cement for purposes of the present invention may comprise Class N, Class F and/or Class C materials in addition to the portland cement.

15 Type I(SM) cement is an intimate and uniform blend of portland cement and fine granulated blast furnace slag produced by intergrinding portland cement clinker and granulated blast-furnace slag, by blending portland cement and finely ground granulated blast-furnace slag, or a combination of intergrinding and blending in which the slag constituent is less than 25% of the weight of the slag-modified portland cement. Type IS is an intimate and uniform blend of portland cement and fine granulated blast-furnace slag in which the slag constituent is between 25 and 70% of the weight of portland blast-furnace slag cement. Blast-furnace slag is a nonmetallic product consisting essentially of silicates and aluminosilicates of calcium and other bases. Granulated slag is the

glassy or non-crystalline product which is formed when molten blast furnace slag is rapidly chilled, as by immersion in water. ASTM C 989, Standard Specification for Ground Granulated Blast-Furnace Slag for Use in Concrete and Mortars, provided additional details concerning the chemical and physical properties of blast furnace slags; ASTM C 989 is hereby incorporated by reference in its entirety.

Compared to conventional pozzolans, finely ground granulated blast-furnace slag is self-cementing; that is, it does not require calcium hydroxide to form cementitious products such as C-S-H. However, when granulated blast-furnace slag hydrates by itself, the amount of cementitious products formed and the rates of formation are insufficient for application of the material to structural purposes. When used in combination with portland cement, the hydration of slag is accelerated in the presence of calcium hydroxide and gypsum. During the hydration of Type IS cement, some calcium hydroxide produced by the portland cement is consumed by the slag constituent of the cement.

While the description of blended cements discussed above all allow for the intermixing of pozzolanic material with finished portland cement, in the method of this invention, the portland cement clinker, pozzolanic material and grinding aid are all ground together.

The product of this invention will be useful in preparing cementitious compositions such as hydraulic cements, mortars, or concrete mixes which include concretes, mortars, neat paste compositions, oil well cement slurries, grouting compositions and the like. Cementitious compositions are discussed in

the encyclopedia article "Cement" cited below. Portland cements and blended Portland cements are well known and are described in "Cement", Encyclopedia of Chemical Technology, (Kirk-Othmer, eds, John Wiley & Sons, Inc., N.Y., N.Y., 4th ed., 1993), vol. 5, pp. 564-598, the disclosure of which is incorporated by reference herein. Portland cement is by far the most widely used hydraulic cement. The term "hydraulic cement" as used herein includes those inorganic cements which, when mixed with water, set and harden as a result of chemical reactions between the water and the compounds present in the cement. The term "concrete" as used herein includes a mixture of such hydraulic cements and inert aggregates. Typical aggregates include conventional aggregates such as gravel, sand, granite, limestone, and quartz sieve. Conventional hydraulic cement concretes, e.g. Portland cement concretes, employ major amounts, i.e. over 50%, usually up to about 75% by volume of such aggregates in the set product. The cements may be used to prepare concrete mixes containing 100 parts by weight of cement, from about 140 to about 260 parts by weight of sand, from about 100 to about 200 parts by weight of gravel, from about 20 to about 80 parts by weight of water and an amount of the blend composition of the invention effective to entrain the desired amount of air into the cementitious composition upon mixing with air. Preferred concrete mixes contain 100 parts by weight of cement, from about 160 to about 240 parts by weight of sand, from about 120 to about 180 parts by weight of gravel, from about 35 to about 60 parts by weight of water and an amount of the blend of this invention effective to entrain the desired amount of air into said composition. After preparation, these cementitious compositions are then allowed to harden to obtain a hardened cement mass.

While the invention has been described with reference to certain specific embodiments thereof, it is understood that it is not to be so limited since alterations and changes may be made therein which are within the full intended scope of the appended claims. All quantities, proportions and percentages are by weight and all references to temperature are °C unless otherwise indicated. As used herein, the terms "major" and "minor", applied to amounts, shall mean at least 50% by weight and less than 50% by weight, respectively.

Examples

10 Example 1

In a two-compartment mill (air-separating mill with coarse and fine compartments; throughput capacity 16 to 18 tons of cement per hour with a specific surface area of the cement of about 4,800 cm²/g measured by Blaine air permeability apparatus used to measure the surface area of a finely ground substance), 50 kg of an aqueous naphthalenesulfonate formaldehyde condensation product (commercially available as Lomar® D, from Henkel Corporation) having a solids content of 20% is sprayed into the fine grinding compartment per 1 ton of a blend of 75% portland cement clinker and 25% fly ash, at a uniform rate over the cement production period. The finished blended cement contains the calculated quantity of 1% condensation product with respect to total weight of cement/fly ash blend and distributed uniformly therein.

Example 2

The process of example 1 is repeated, except that the aqueous

naphthalenesulfonate formaldehyde condensation product is sprayed into the coarse grinding compartment instead of the fine grinding compartment.

What is claimed is:

1. A method of preparing a blended cement composition which comprises intergrinding a composition comprised of a major amount by weight of portland cement clinker, a minor amount by weight of a pozzolanic material and a grinding aid in an amount of from about 0.1% to about 5% based on the total weight of portland cement clinker and pozzolanic material, said grinding aid being comprised of a naphthalenesulfonate formaldehyde condensate.
2. The method of claim 1 wherein said amount of said grinding aid is from about 1% to about 2% based on the total weight of portland cement clinker and pozzolanic material.
3. The method of claim 1 wherein said amount of said pozzolanic material is from about 15% to about 40% of the total weight of portland cement clinker and pozzolanic material.
4. The method of claim 1 wherein said grinding aid consists essentially of said naphthalenesulfonate formaldehyde condensate.
5. A method of preparing a blended cement composition which comprises intergrinding a composition consisting essentially of a major amount by weight of portland cement clinker, a pozzolanic material in an amount by weight of from about 15% to about 40% of the total weight of portland cement clinker and

pozzolanic material, and a grinding aid in an amount of from about 1% to about 2% based on the total weight of portland cement clinker and pozzolanic material, said grinding aid consisting essentially of a naphthalenesulfonate formaldehyde condensate.