



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C04B 24/42, 28/02 // 103:52	A1	(11) International Publication Number: WO 00/39047 (43) International Publication Date: 6 July 2000 (06.07.00)
(21) International Application Number: PCT/US99/31013 (22) International Filing Date: 23 December 1999 (23.12.99) (30) Priority Data: PI 9805844-4 29 December 1998 (29.12.98) BR (71) Applicant: DOW CORNING CORPORATION [US/US]; 2200 West Salzburg Road, Midland, MI 48611 (US). (72) Inventor: LOPES DA CUNHA, Sebastiao, Walter, Jr.; Rua Drive Aristides, Lemos, 67, Vila Teixeira, CEP-Campinas, SP (BR). (74) Agent: GEARHART, Richard, I.; Dow Corning Corporation, Patent Department-C01232, P.O. Box 994, Midland, MI 48686-0994 (US).	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: SILICON CONTAINING GRINDING AIDES FOR CLINKER		
(57) Abstract		
<p>The present invention is directed to a novel grinding aid for forming hydraulic cement powder from clinker raw material and to the method of forming an improved hydraulic cement product. The grinding aid is selected from the group consisting of a cyclic siloxane, a functionalized polydiorganosiloxane, or mixtures thereof. Additional silicon containing materials may be added to the grinding aid as well.</p>		

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SILICON CONTAINING GRINDING AIDES FOR CLINKER**FIELD OF THE INVENTION**

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The present invention is directed to a novel grinding aid for forming hydraulic cement powder from clinker raw material and to a method of forming an improved hydraulic cement product.

BACKGROUND OF THE INVENTION

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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. 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 (See “Cement Standards of the World”, Cembureau, Paris, France).

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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. It is common that the mixture to be sintered contains as a component up to 80% slag. The components lose their separate identity and are chemically transformed during the sintering process. During the sintering process, chemical reactions take place wherein hardened nodules, commonly called clinkers, are formed.

30

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= C_3S ; dicalcium silicate= C_2S ; tricalcium aluminate= C_3A ; and tetracalcium aluminoferrite= C_4AF .

35

5 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, fly ash, pozzolans and the like are
10 substituted for a portion of the expensive clinker material: This use of slag and other
pozzolans is distinguished from their optional use as a component in the mixture to be
sintered to form clinker described above. 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
15 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
20 vary from about 33 to 77 kWh/metric 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
25 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 (U.S. Pat. No. 4,204,877); unsaturated
30 aliphatic acid and amines (FR 2,337,699); a C₃ aliphatic acid salt and an amine (U.S. Pat. No.
3,615,785); as well as alcohols and amides (U.S. Pat. No. 5,125,976). Although the time
required (and thereby energy consumed) is lessened when clinkers are ground in the presence
of glycol grinding aids, the resultant powder cements do not exhibit any beneficial effect over
cements formed without such grinding aid.

35 Silicon containing grinding aids other than those of the present invention have been
disclosed in the art. For example, Zadak, Zezulka and Vesely in *Adsorption of Vapors of*

5 *Liquid Grinding Aids on Cement Clinker* (Puvodni Prace, May 7, 1971) teach that short trimethyl endblocked polydimethylsiloxanes can be used as grinding aids. However, this article does not disclose the particular polymers of this invention, and the compositions of the present invention represent improvements over the technology described therein.

10 Silanes and their condensation products have also been disclosed for use as masonry additives, e.g., as in WO 81/01703 entitled "Process for the Preparation of a Mortar and the Product Thereby Obtained". However, this patent application does not disclose the use of silanes as a grinding aid for cement clinker.

15 It would be desirable to be able to form a hydraulic cement powder product having enhanced properties, such as strength and stability, by grinding in the presence of a grinding aid capable of causing an improved product.

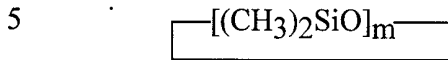
SUMMARY OF THE INVENTION

20 The present invention is directed to a novel grinding aid for forming hydraulic cement powder from clinker raw material and to the method of forming an improved hydraulic cement product. The grinding aid is selected from the group consisting of a cyclic siloxane, a functionalized polydiorganosiloxane, or mixtures thereof. Additional silicon containing materials may be added to the grinding aid as well. The compositions improve grinding efficiency of the clinker by reducing energy consumption during the grinding process, and the resulting concrete exhibits improved short and long term compression strength and improved graveling.

DETAILED DESCRIPTION OF THE INVENTION

30 The grinding aid of the present invention is added to the cement clinker to reduce the energy consumed during grinding and/or to improve the properties of the hydraulic cement product. The grinding aid can be a cyclic siloxane, a functionalized polydiorganosiloxane, or mixtures thereof. Each of these components will be described herein in detail.

35 The cyclic siloxanes used as grinding aids can be used alone or with the other components, some which are described below. Cyclic siloxanes are well known in the art, and may have functional groups such as vinyl, hydroxy, alkoxy or SiH disposed thereon or may be non-functional, such as those cyclic siloxanes defined by the formula:

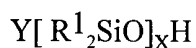


where m has a value of 3 to 8 inclusive.

Specific cyclic siloxanes are respectively hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane and dodecamethylcyclohexasiloxane. The cyclic siloxanes employed according to this invention are relatively volatile materials having boiling points below about 250° C at 760 mm Hg. The cyclic siloxanes may be employed as the individual compounds or as mixtures of two or more different cyclic siloxanes.

The functional polydiorganosiloxanes useful in the invention are preferably linear polydiorganosiloxanes, but branched polydiorganosiloxanes would work as well. By functional siloxane, it is meant a polydiorganosiloxane having at least one pendant or terminal functional group, such as hydroxyl, alkoxy, vinyl, amine, etc. The functional polydiorganosiloxane could also be terminated with hydrogen atoms. The organic groups along the backbone of the siloxane can be methyl, ethyl or phenyl, with methyl being most preferred. The polymers are preferably short chain molecules having from 1 to 50 repeating silicon units and are well known in the art. The functional polydiorganosiloxanes preferably have an average of at least two functional groups per molecule and the most preferred functional groups are hydroxyl groups situated at the terminal positions of the polydiorganosiloxane.

The hydroxyl terminated polydiorganosiloxanes useful in this invention are represented by the general formula



in which Y is a methyl or hydroxyl, R¹ is alkyl or aromatic group having 1 to 8 carbon atoms, and the chain length, x, has an average value which ranges from 2 to 1,000. Hydroxyl terminated polydiorganosiloxanes are well known hydroxylated siloxanes that can be prepared by conventional methods.

The chain length of the siloxane polymer preferably has an average number of siloxane units per polymer molecule of at least 2. Thus, for example, the hydroxylated siloxane can vary from thin fluids to non-flowable gums. Preferred R¹ groups are methyl, ethyl or phenyl, with methyl being most preferred. Accordingly, it is often preferred to employ a mixture of lower and higher molecular weight siloxanes in the compositions used in

5 this invention.

The polydiorganosiloxane can be completely hydroxyl terminated or a portion of the polymer chains can be terminated on one end by a methyl radical. It is preferred that siloxane is hydroxyl terminated and that all Y groups in the general formula are hydroxyl radicals.

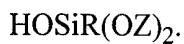
10 It will be apparent to the skilled artisan that mixtures and combinations of the materials can also be employed to achieve the results of the invention, such as mixtures of different cyclic siloxanes or hydroxyl terminated polydiorganosiloxanes, or combinations of cyclic siloxanes and hydroxyl terminated polydiorganosiloxanes, etc.

15 In addition other types of silicon containing additives may be added to the grinding aid, such as alkoxy silanes, trimethyl end blocked polydiorganosiloxane, siliconates, or polydiorganosiloxanates. Both of the latter types of additives by definition contain an ionic silanolate group, $\equiv \text{SiO}^-$.

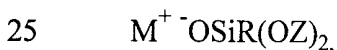
The use of any of these additives as the only grinding aid rather than as an additive to the grinding aids described above is outside the scope of the invention.

20 Preferably the trimethyl end blocked polydiorganosiloxanes have a viscosity in the range of 0.65 cst to 20 (mm)²/s.

Siliconates are defined as a salt of a silanol of the following structure:



The cation, M^+ , of this salt may be either an alkaline metal cation or a quaternary ammonium or phosphonium cation. Thus, siliconates contain the following structure:



where R is any organic group and OZ designates either an additional salt group, $\text{OZ} = \text{O}^+ \text{M}$, a non-reacted silanol, or an alkoxy group. If some self-condensation has occurred, then the SiOZ structure may be a disiloxane or a higher oligomer. If cross-condensation with a polydiorganosiloxane has occurred, then the SiOZ structure links the siliconate salt to a polydiorganosiloxane. Preferred siliconates include potassium alkylsiliconates and sodium alkylsiliconates, most preferred being potassium methylsiliconate and sodium methylsiliconate.

30

The polydiorganosiloxanates (abbreviated as siloxanates) are defined as salts of the terminal silanol or silanols of a polydiorganosiloxane, and include the same range of

5 cations as do the siliconates.

Preferred siloxanates include dipotassium and disodium polydialkylsiloxanates, the most preferred being dipotassium or disodium polydimethylsiloxanolate, K or NaO(Me₂SiO)_xK or Na.

The alkoxy silanes useful for this invention are represented by the general formula



wherein R is a methyl, ethyl, propyl or methoxyethyl radical, R² is a monovalent hydrocarbon or halogen substituted hydrocarbon radical having from 1 to 4 carbon atoms, and n has a value of 3 or 4. Thus specific examples include N-(2-aminoethyl)-3-

aminopropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane,

15 3[2(vinylbenzylamino) ethylamino]propyltrimethoxysilane,

3-glycidoxypropyltrimethoxysilane, triacetoxylvinylsilane,

tris-(2-methoxyethoxy)vinylsilane, 3-chloropropyltrimethoxysilane, 1-trimethoxysilyl-2-

(p,m-chloromethyl)phenyl-ethane, 3-chloropropyltriethoxysilane,

N-(aminoethylaminomethyl)phenyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyl tris(2-

20 ethylhexoxy)silane, 3-aminopropyltrimethoxysilane, trimethoxysilylpropyl

diethylenetriamine, beta (3,4-epoxycyclohexyl) ethyltrimethoxysilane,

3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane,

3-mercaptopropylmethyl dimethoxysilane, bis(2-hydroxyethyl)-3-

aminopropyltrimethoxysilane, 1,3 divinyltetramethyldisilazane, vinyltrimethoxysilane, 2-

25 (diphenylphosphino)ethyltriethoxysilane, 2-methacryloxyethyl dimethyl[3-

trimethoxysilylpropyl]ammonium chloride, 3-isocyanatopropyl dimethylethoxysilane, N-(3-

acryloxy-2-hydroxypropyl)-3-aminopropyltriethoxysilane, vinyl tris(t-butylperoxy)silane, 4-

aminobutyltriethoxysilane, methyltrimethoxysilane, ethyltrimethoxysilane,

phenyltrimethoxysilane, and phenyltriacetoxysilane.

30 Other silane compounds which are considered alkoxy silanes for the purpose of the present application include methyltrimethoxysilane, phenyltrimethoxysilane,

ethylorthosilicate, phenyltriethoxysilane and n-propylorthosilicate. In addition to the

monomeric alkoxy silanes, oligomeric products from partial hydrolysis and condensation of the alkoxy silanes can also be used in the compositions of this invention.

35 Generally, hydraulic cements are prepared by sintering a mixture of components

5 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, 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
10 solution phase approximating tetracalcium aluminoferrite. The cement is formed by adding
gypsum with the clinker and grinding the mixture. The grinding aids of the present invention
may be added to the clinker/gypsum mixture at any time during the grinding process but is
preferably added just prior to the commencement of the grinding. The grinding aid will be
added in the amount of 10 to 20,000 grams per metric ton of clinker.

15 The cyclic siloxane, functional siloxane, or mixtures thereof may be dispersed in
appropriate solvents such as hydrocarbons derived products like xylene, toluene, mineral
spirits, mineral oils, naphtha, isoparaffin and others that can dilute siloxane based products.
In addition, the grinding aids may be emulsified and thereafter added to the clinker.

As shown in the below examples, the compositions of the present invention improve
20 grinding efficiency of the clinker during grinding, thus reducing the amount of energy
consumed during the grinding process. In addition, concrete made from the clinker
containing the additive shows better short and long term compression strength over concrete
made from clinker using other grinding aids or having no grinding aid. It is also expected
that the present compositions will produce cement having a reduced tendency for graveling.
25 Given that the invention unexpectedly provides increased grinding efficiency and anti-
graveling, other anticipated benefits include greater production throughput during and after
grinding while handling powdered clinker or cement, and improved resistance to water
damage of cured cement or concrete made from the ground clinker.

30 EXAMPLES

In the examples below, the grinding aides were tested to show how they improved
both the efficiency of clinker. Cements were made using the clinker mixtures and their
compression strength was tested. The grinding aides showed improved efficiency in
grinding, as well as improved compression strength in the resulting concretes.

35 The grinding aides used in the experiments are described below:

5

Comp 1 is 100% trimethyl silyl endblocked dimethyl siloxane, having a viscosity of 10 (mm)²/s.

DCC 1 is a commercially available mixture of cyclic siloxanes comprising 4% decamethyl cyclopentasiloxane and 96% octamethylcyclotetrasiloxane.

10 DCC 2 is a commercially available mixture of cyclic and linear siloxanes comprising 45% dimethylcyclosiloxanes and 55% hydroxyl terminated dimethyl siloxane.

DCC 3 is a commercially available hydroxyl terminated polydimethylsiloxane having a viscosity of 55 to 90 (mm)²/s at 25°C and having a hydroxyl content of 1.0 to 2.5 wt%.

15 DCC 4 is made from two components. The first component is used in an amount of 80% and has a viscosity of 2.2 to 3 (mm)²/s. It is a mixture of cyclic siloxanes, comprising about 22% by weight decamethylcyclopentasiloxane and 77% by weight octamethylcyclotetrasiloxane and trace amounts of other dimethylcyclosiloxanes. The second component is used in an amount of 20% and is 32% by weight of sodium methyl silicate in water. The two immiscible liquids are mixed in a high shear mixer for 30 minutes, and
20 allowed to separate overnight. The clear supernatant is recovered by decantation and the underlying aqueous layer is discarded. The supernatant is primarily a mixture of the cyclic siloxanes but is also thought to contain some sodium polydimethylsiloxanolate formed by the attack of sodium methylsilicate to cleave some of the cyclics.

25 The grinding aids were added to the clinker that commonly is produced with a mixture of 3 - 5 parts of limestone and 1 part of clay. This mixture is burned with iron ore and sand in a cement kiln with temperature around 1500 deg. Celsius generating the material named clinker. The clinker used in this work was produced by a Brazilian cement producer named Soeicom S.A. located at Vespasiano in Minas Gerais state. The amount of grinding aids added was 200 grams/metric ton of clinker. Chrome alloy balls of the following sizes were
30 used in the single chamber mill: 29.8 % were 20 mm in diameter, and the remainder were equally divided between diameters of 40, 50, 60 and 70 mm.

The mixtures were then ground for 120 minutes in the ball mill with an average ball mill surface area of about 20 m²/ton and filling about 42% of the total void space of ball mill. The rotational speed of the ball mill was around 65% of its critical rotational speed. A
35 sample of the milled product was analysed.

5 Cement was made from 100% clinker. The cement for the example was prepared by milling 5.0 kg of clinker in a laboratory ball mill.

The specific surface area of milled clinker, designated as the Blaine in m²/Kg, was measured using NBR 7224. The average value of 3 different samples was taken and values with more than 5% variation from the average were discarded, following standards defined by
 10 Brazilian Portland Cement Association ABCP and also accepted by cement producers. Blaine is correlated directly with the strength of the resulting cement.

The percent of retained material in screen 200 mesh was measured by using standard NBR 11579 and for screen 325 mesh by using standard NBR 9202 (we took the average value of 3 different samples and discarded the values with more than 5% variation of the
 15 average, following standards defined by Brazilian Portland Cement Association ABCP and also accepted by cement producers). Larger mesh numbers correspond to smaller mesh openings through which particles can pass.

The primary purpose of grinding is to reduce the size of the particles being ground. Smaller particles have higher specific surface area and also pass more readily through finer
 20 mesh screens. The progress of grinding can be followed by periodically measuring the specific surface area or by measuring the percent of particles that pass through mesh screens. We quantitate the percent improvement in grinding efficiency by the following:

With respect to Blaine:

$$\frac{(\text{SURFACE AREA WITH GRINDING AID}) \times 100\%}{(\text{SURFACE AREA WITHOUT GRINDING AID})} - 100\%$$

25
$$\frac{(\text{SURFACE AREA WITH GRINDING AID})}{(\text{SURFACE AREA WITHOUT GRINDING AID})}$$

With respect to passing through a screen (often called "Grinding Efficiency"):

$$100\% - \frac{(\% \text{RETENTION WITH GRINDING AID}) \times 100\%}{(\% \text{RETENTION WITHOUT GRINDING AID})}$$

$$\frac{(\% \text{RETENTION WITH GRINDING AID})}{(\% \text{RETENTION WITHOUT GRINDING AID})}$$

30 Measurement of improvement in Blaine or in passage through a mesh screen depends on grinding time. Of course, the measurement based on screen passage also depends on the screen size.

5 The results of the grinding tests for 100% clinker are shown in Table 1 below:

Table 1

Additive	Surface Area	Efficiency	
	Blaine (m ² /kg) NBR 7224	% Retained on 200 mesh screen	% Retained on 325 mesh screen
No additive		8.5	35.2
Comp 1	257	8.0	35.2
DCC 1	305	7.6	30.2
DCC 2	308	8.2	27.8
DCC 3	316	5.2	23.8
DCC 4	322	7.2	27.0

10 The results in Table 1 show that all the silicon containing grinding aides of the invention improve the Blaine up to 20% and the efficiency up to 39% when compared to the values obtained without these grinding aides. The Blaine was improved by up to 25% and the efficiency by up to 35% when compared to values obtained by use of the silicon-containing grinding aide of the prior art (Comp 1).

Compressive Strength of Concrete

15 Compressive strength was measured using methods defined by ABNT (standard NBR 7215) for cure ages of 1, 3 and 28 days and the same results are shown below in Table 2 for 100% clinker. The standard NBR 7215 is related to the measurement of compressive strength of cylindrical samples having diameter of 50 mm and height of 100 mm. These samples are prepared with a rendering mortar having the following composition (by weight): one part of
20 cement, three parts of standard sand (defined by ABNT standard NBR 7214:1982) and with a water/cement ratio of 0.48. This rendering mortar is blended with a mechanical mixer and is manually compacted inside a mold using a standard procedure. The molds with the samples are kept in a wet environment for the initial cure and after some time the samples are released from the molds and cured in hydrated lime saturated water until the date of the test. The
25 compressive strength method and specification of the machine used to perform this test is defined by ABNT standard NBR 6156:1983 and the specification for the wet chambers and

5 tanks for the cure of rendering mortar and concrete samples is defined by ABNT standard NBR 9479:1994. Note that 1.0 Mega-Pascal (MPa) = 10 kgf/cm². The results of the compressive strength for 100% clinker are shown in Table 2 below:

Table 2

Additive	Surface Area Blaine (m ² /kg) NBR 7224	Compressive Strength (MPa) 1 day	Compressive Strength (MPa) 3 days	Compressive Strength (MPa) 28 days
No Additive	268	3.6	7.9	22.9
Comp 1	257	3.9	7.0	21.2
DCC 1	305	4.6	9.0	27.4
DCC 2	308	4.0	9.4	26.9
DCC 3	316	5.3	11.9	29.8
DCC 4	322	5.0	9.9	30.8

10 The additives of the present invention also improve the compressive strength of the resulting cement made from 100% clinker when compared to the values obtained with no grinding aide by up to 47%, 51%, and 34% after 1, 3, and 28 days or curing, respectively. They also improve the compressive strength when compared to the values obtained with the silicon containing grinding aide of the prior art (Comp 1) by up to 36%, 70%, and 45% after
15 1, 3, and 28 days of curing, respectively.

Another type of cement was also prepared with a chemical composition that meets Brazilian Portland Cement Specifications. Type CP I 32 is a General purpose Portland Cement defined by standard EB-1/NBR 5732 created by Brazilian Technical Standards Association (ABNT).
20 According to this standard cement type CP I 32 has 100% of clinker plus gypsum (normally in the range from 3.0 % to 5.0 %) on its formulation. This cement belongs to a compressive strength class of 32 MPa after 28 days of age, having a lower control limit of 32 MPa and an upper control limit of 49 MPa. The results of grinding laboratory tests of CP I 32 are shown on the Tables 3 and 4 below.

5

Table 3

Additive	Surface Area	Efficiency	
	Blaine (m ² /kg) NBR 7224	% Retained on 200 mesh screen	% Retained on 325 mesh screen
No additive		8.4	36.5
Comp 1	260	8.0	33.5
DCC 1	300	9.0	29.9
DCC 2	290	8.0	26.3
DCC 3	310	5.1	21.8
DCC 4	311	6.4	26.0

10 The results in Table 3 show that all the silicon containing grinding aides of the invention, when used to make the type CP I 32 cement, improve the Blaine up to 20% and the efficiency up to 40% when compared to the values obtained without these grinding aides. The Blaine was improved by up to 20% and the efficiency by up to 36% when compared to values obtained by use of the silicon-containing grinding aide of the prior art (Comp 1).

The results of the compressive strength for cement type CP I 32 are shown in Table 4 below:

15

Table 4

Additive	Surface Area Blaine (m ² /kg) NBR 7224	Compressive Strength (MPa) 1 day	Compressive Strength (MPa) 3 days	Compressive Strength (MPa) 28 days
No Additive	260	3.0	7.5	22.8
Comp 1	260	2.7	6.0	23.1
DCC 1	300	3.7	7.7	27.4
DCC 2	290	3.8	7.7	28.9
DCC 3	310	4.5	9.0	31.0
DCC 4	311	4.0	9.0	27.8

5 The additives of the present invention also improve the compressive strength of the resulting
cement when compared to the values obtained with no grinding aide by up to 50%, 20%, and
36% after 1, 3, and 28 days or curing, respectively. They also improve the compressive
strength when compared to the values obtained with the silicon containing grinding aide of
the prior art (Comp 1) by up to 67%, 50%, and 34% after 1, 3, and 28 days of curing,
10 respectively.

5 What is claimed:

1. A composition comprising:

clinker treated with a grinding aid selected from the group consisting of a cyclic siloxane, a functionalized polydiorganosiloxane, or mixtures thereof.

10 2. The composition of claim 1, wherein the grinding aid is present in an amount from 10 grams to 20,000 grams per metric ton of clinker.

3. The composition of claim 1, further comprising a trimethyl endblocked polydiorganosiloxane.

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4. The composition of claim 1, further comprising a siliconate, silanolate or siloxanolate.

5. The composition of claim 1, further comprising an alkoxy silane.

20 6. The composition of claim 1, wherein the grinding aid comprises a cyclic siloxane.

7. The composition of claim 1, wherein the grinding aid comprises a hydroxyl terminated polydiorganosiloxane.

25 8. The composition of claim 1, wherein the grinding aid comprises a mixture of a cyclic siloxane and hydroxyl terminated polydiorganosiloxane.

9. The composition of claim 1, wherein the clinker was made by sintering components that include slag in an amount of from 0-80% by weight of the composition.

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10. The composition of claim 1, wherein the grinding aid has been emulsified or is in a solvent.

- 5 11. A method for improving the efficiency of clinker grinding, comprising the steps of:
treating clinker with a grinding aid selected from the group consisting of a cyclic
siloxane, a functionalized polydiorganosiloxane, or mixtures thereof; and
grinding the clinker.
- 10 12. The method of claim 11, wherein the grinding aid is present in an amount from 10
grams to 20,000 grams per metric ton of clinker.
13. The method of claim 11, further comprising the step of adding a trimethyl endblocked
polydiorganosiloxane.
- 15 14. The composition of claim 11, further comprising an alkoxy silane.
15. The method of claim 11, further comprising the step of adding a siliconate, silanolate
or siloxanolate.
- 20 16. The method of claim 11, wherein the grinding aid comprises a cyclic siloxane.
17. The method of claim 11, wherein the grinding aid comprises a hydroxyl terminated
polydiorganosiloxane.
- 25 18. The method of claim 11, wherein the grinding aid comprises a mixture of a cyclic
siloxane and hydroxyl terminated polydiorganosiloxane.
19. The method of claim 11, wherein the clinker was made by sintering components that
30 include slag in an amount of from 0-80% by weight of the composition.
20. The composition of claim 11, wherein the grinding aid has been emulsified or is in a
solvent.

- 5 · 21. The composition of claim 1, further comprising fly ash.
22. A cement made with the composition of claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/31013

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B24/42 C04B28/02 //C04B103:52

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C04B B02C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPODOC CIS TXT+ WPI PAJ CA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHEMICAL ABSTRACTS, vol. 97, no. 26, 27 December 1982 (1982-12-27) Columbus, Ohio, US; abstract no. 221776, V.S.GUMEN: "Thermally stable cement grinding intensifiers" XP002134970 abstract & KHIM. MASHINOSTR. TEKHNOL., vol. 19, 1982, pages 38-40, ---	1-3,6,7, 10-13, 16,17, 20,22
P,Y	EP 0 960 655 A (DOW CORNING) 1 December 1999 (1999-12-01) claims ---	1-3,6,7, 10-13, 16,17, 20,22
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

6 April 2000

Date of mailing of the international search report

18/04/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Theodoridou, E

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/31013

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 3 333 776 A (L.A.RAUNER ET AL) 1 August 1967 (1967-08-01)</p> <p>page 1, left-hand column, line 58 -right-hand column, line 2 page 1, right-hand column, line 57 -page 2, left-hand column, line 57</p> <p>----</p>	<p>1,3,6,7, 10,11, 13,16, 17,20,22</p>
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information on patent family members

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