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(54) Title: GRINDING AID WITH SPENT MOLASSES CONCENTRATES

(57) Abstract: The present invention involves the use of Spent Molasses Concentrates ("SMC") produced as a concentrated residue after evaporation of the raw waste water obtained from distillation of beet or cane molasses, as an extender for a poly-oxyalkene polyol grinding efficiency enhancer selected from glycol, glycerol, or a mixture thereof.



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GRINDING AID WITH SPENT MOLASSES CONCENTRATES

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Field of the Invention

5 The present invention relates to enhancing efficiency of grinding cementitious materials, and more particularly to a novel composition and method for grinding cement clinker, slag, fly ash, or mixtures thereof wherein spent molasses concentrates are used for extending a water-soluble polyol-based grinding efficiency enhancer.

Background of the Invention

As used in this section, the term “additive” refers to chemical agents that are added before or during the process whereby a cement clinker, with or without clinker substitutes, is ground to provide finished cement; while the term “admixture” refers to agents combined with cement, aggregates (e.g., sand and/or crushed gravel), and water to provide hydratable cementitious compositions such as mortar or concrete.

It is known to employ molasses and other byproducts of sugar manufacture as additives in cement manufacture as well as admixtures in mortar and concrete for modifying one or more properties.

20 In US Patent 2,311,288, Booth et al. disclosed the use of “crude fermentation residues” obtained “after fermentable carbohydrate materials have been fermented either in the production of alcohols of certain alcohol beverages,” including “fermentation of black strap molasses.” See Col. 1, ll. 26-36. An “evaporated molasses residue” is added as a dry material to
25 cement clinker during grinding for the purpose of enhancing cement plasticity. See Page 2, Col. 1, ll. 13-15).

In US Patent 2,435,594, MacPherson taught that “residuum solids of fermented sulfite liquor,” obtained by fermenting or distilling the residuum solids to remove the alcohol, could be used for hardening concrete.

5 In US Patent 3,066,031, Schifferle disclosed that sugars and “cane sugar molasses residues” could be mixed with raw materials during grinding to achieve a retarding effect in the cement. See Col. 7, ll. 41-43.

10 In US Patent 3,536,507, Klein et al. taught using liquor obtained from aerobic fermentation of liquid carbohydrates for modifying properties of cement, and confirmed that this could be done regardless of whether this altered the grinding characteristics on the cement clinker. This reference did not specify, however, what characteristic specially would be altered.

15 In US Patent 4,961,789, Barrenechea disclosed a process for manufacturing water reducing plasticizing and hardening-retarding plasticizing additives for concrete, using sugarcane derivatives that modify the structural characteristics of the concrete.

20 In US Patent 6,231,765, Barrenechea disclosed a process for obtaining a polymeric complex from a by-product effluent obtained in a process for manufacturing alcohol by distilling a fermented aqueous sugar solution containing yeast. After distilling alcohol from the effluent a chemical or biological flocculant is added to the effluent to form a homogeneous mixture, which is heated to a temperature of at least 80 degrees Celsius. Yeast is removed from the heated mixture by a first decantation, and then insoluble solids are removed by a second decantation. The mixture is concentrated by partially evaporating water to obtain a solution of polymeric complex.

25 In US Patent 6,797,050, Hoffman disclosed admixture compositions derived from fermentation still bottoms, and these admixture compositions were used for increasing flow and reducing water use in the concrete and gypsum in gypsum panel production.

30 In US Patent 7,067,003, Cooney disclosed the use of dunder, which he defined as “any residuum obtained after distillation of molasses or sugar product such as vinasse or the like.” See Col. 1, ll. 42-45. This could be used

to substitute for lignin, thereby improving flow or density of the concrete, or reducing its void content, water requirement, or set time.

Similarly, Chinese Patent No. 10333383C (ZL Patent No. 92104636.7) disclosed that molasses fermentation waste obtained from sugar refineries
5 can be used as a water reducing additive or admixture.

In view of the foregoing, the present inventors believe that various byproducts of molasses manufacturing or processing operations have been used to improve various properties of cement or concrete. However, the prior art does not disclose using molasses residues for enhancing the grinding
10 efficiency by reducing the energy required for the grinding of cement clinker to produce cement. Thus, an objective of the present invention is to provide methods and compositions for enhancing grinding efficiency by employing a molasses residue.

Summary of the Invention

The present invention provides a composition and method involving the use of Spent Molasses Concentrates ("SMC") obtained as a concentrated residue after evaporation of the raw waste water obtained from fermentation and distillation of beet or cane molasses, as an extender for an grinding efficiency enhancing additive which is a water-soluble polyol selected from glycol, glycerol, or mixtures thereof, the water-soluble polyol being used in grinding cementitious materials such as cement clinker, granulated blast furnace slag, fly ash, or mixture thereof.

The term "extender" is intended to refer to the ability of the SMC to substitute for a portion of the polyol grinding efficiency enhancer without substantial loss of grinding efficiency or compressive strength.

The present inventors surprisingly discovered that if a portion of SMC is substituted for a portion (e.g., 20%-50% by weight) of the polyalkylene polyol grinding aid, which is preferably diethylene glycol ("DIEG"), a similar grinding efficiency, compared to 100% DIEG, can be achieved at significant cost reduction.

In further embodiments, a small portion of molasses may optionally be added to compensate for any decrease in compressive strength due to the use of SMC.

A method for grinding a cementitious material, comprises: combining in the intergrinding of cementitious materials comprising cement clinker, granulated blast furnace slag, fly ash, or mixture thereof (A) water-soluble polyalkylene polyol grinding efficiency enhancing additive, the polyol being selected from glycol, a glycerol, or mixture thereof, the polyol being in the amount of 0.005%-0.1%; (B) Spent Molasses Concentrates ("SMC") obtained as a concentrated condensate after evaporation of the raw waste water obtained from fermentation and distillation of sugar beet or sugar cane molasses, the SMC being in the amount of 0.005-0.05% and effective as an extender for the polyol grinding efficiency enhancing additive; and (C) optionally, a molasses obtained from sugar beet, sugar cane, corn, wheat,

wheat gluten, wood pulp, or mixture thereof, the molasses being in the amount of 0%-0.1%, the foregoing percentages being based on total dry weight of the cementitious materials being interground.

5 The amount of SMC may, for example, be used in the range of 20%-50%, and more preferably 20%-30%, based on total weight of the polyol, and the molasses may be present in the amount of 0% to 150% based on weight of the polyol.

10 An exemplary method of the invention for grinding a cementitious material, comprises: combining in the intergrinding of cementitious materials comprising cement clinker, granulated blast furnace slag, fly ash, or mixture thereof (A) water-soluble polyalkylene polyol selected from the group of glycol, glycerol, or a mixture thereof (preferably diethylene glycol or "DIEG") in the amount of 0.005%-0.1% as a grinding efficiency enhancing additive; (B) a Spent Molasses Concentrates (SMC) obtained as a concentrated condensate
15 (remaining liquid) after evaporation of the raw waste water obtained from fermentation and distillation of sugar beet or sugar cane molasses, the SMC being in the amount of 0.005%-0.05% and being effective as an extender for the polyol grinding efficiency enhancing additive; and, (C) optionally, a molasses obtained from sugar beet, sugar cane, corn, wheat, wheat gluten,
20 wood pulp, or mixture thereof, the molasses being in the amount of 0%-0.1% (and more preferably 0.01%-0.05%), the foregoing percentages being based on total dry weight of cementitious materials being interground.

 The ratio of the SMC to the polyol is preferably between 10:90 to 90:10 and more preferably 20-30:70-80 parts by weight (SMC:polyol).

25 Other advantages and features of the invention will be described in further detail hereinafter.

Detailed Description of Exemplary Embodiments

All percentages of components described or claimed herein shall be in terms of total weight of a composition, and relative amounts or ratios shall be in terms of the weight of the components, unless otherwise indicated.

The term "cement" as used herein means and refers primarily to Portland cement, which, as used in the construction trade, means an hydratable cement produced by pulverizing or intergrinding cement clinker which consists of calcium silicates usually containing one or more of the forms of calcium sulfate as an interground addition.

"Cementitious" materials are materials that alone have hydraulic or hydratable cementing properties in that they set and harden in the presence of water. Hydratable cements may include Portland cement and also the so-called pozzolans, which are siliceous or aluminosiliceous materials that possess little or no cementitious value (i.e., as a binder) but which will, in finely divided form in the presence of water, chemically react with the calcium hydroxide released by the hydration of Portland cement to form materials with cementitious properties. See e.g., Dodson, V., Concrete Admixtures (Von Nostrand Reinhold, New York 1990), page 159. Diatomaceous earth, limestone, clay (e.g., metakaolin), shale, fly ash, silica fume, and blast furnace slag are some of the known pozzolans.

As certain ground granulated blast-furnace slags and high calcium fly ashes possess both pozzolanic and cementitious properties, the term "cementitious materials" will be used herein to refer to Portland cement as well as granulated blast furnace slag, fly ash, or mixtures thereof, as well as to gypsum which is typically incorporated in small amounts in the intergrinding of cement clinker to produce cement.

It is believed that any of the known grinding mill types may be employed, including ball mills and roll (or roller) mills. Ball mills are commonly used wherein cement clinker, along with supplemental cementitious materials (slag, fly ash, other pozzolans) are interground to produce a finished

hydratable cement (e.g., Portland cement). Mills having rolls (such as roll press mills) can be used wherein the cement clinker, slag, and/or fly ash is crushed on circular tables upon which rollers are revolved. Other types of roller mills employ two or more rollers that are nipped together, and material is then crushed by dropping materials vertically between the nipped rollers. Thus, the methods and compositions of the invention can be used in both ball mills and roller mills that are used for grinding cement, slag, and/or fly ash to produce hydratable cement particles.

An exemplary method of the invention for grinding a cementitious material, comprises: combining in the intergrinding of cementitious materials comprising cement clinker, granulated blast furnace slag, fly ash, or mixture thereof (A) water-soluble polyalkylene polyol selected from the group comprising a glycol, glycerol, or mixture thereof (preferably a glycol such as diethylene glycol or "DIEG") in the amount of 0.005%-0.1% as a grinding efficiency enhancing additive; (B) a Spent Molasses Concentrates (SMC) obtained as a concentrated condensate (remaining liquid) after evaporation of the raw waste water obtained from fermentation and distillation of sugar beet or sugar cane molasses, the SMC being in the amount of 0.005-0.05% and effective as an extender for said polyol grinding efficiency enhancing additive; and, optionally, (C) a molasses obtained from sugar beet, sugar cane, corn, wheat, wheat gluten, wood pulp, or mixture thereof, the molasses being in the amount of 0%-0.1%, and more preferably 0.01-0.05%, all percentages herein being based on total dry weight of cementitious materials.

In preferred exemplary methods, the molasses of component (C) is used in the amount of 0.0%-0.1% and more preferably 0.02%-0.05% based on dry weight of cement clinker and slag.

Exemplary water-soluble polyols used in the invention may include glycols that have been conventionally known for use as cement grinding efficiency enhancing additives. Such glycols include ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol and tripropylene glycol, combinations of these glycols, their derivatives, and reaction products formed by reacting

ethylene and propylene oxide or polyethylene glycols and polypropylene glycols with active hydrogen base compounds (polyalcohols with active hydrogen base compounds, polycarboxylic acids, polyamines, or polyphenols). Other glycols contemplated include neopentyl glycols, pentanediols, butanediols, and such unsaturated diols as butyne diols and butene diols. Diethylene glycol is a preferred grinding efficiency enhancer.

Another exemplary water-soluble polyol includes glycerols that have been conventionally known for use as cement grinding efficiency enhancing additives. Such glycerols may be selected from the group of di-, tri-, and tetraglycerol and mixtures thereof.

Further exemplary water-soluble polyols useful in the invention include blends of glycols and glycerols.

Preferably, the ratio of the water-soluble polyol component to the molasses residue of component (B) is from 20:80 parts to 50:50 parts based on weight of the components.

Most preferably, the water-soluble polyol is diethylene glycol (DIEG), and the ratio of DIEG to a molasses residue such as Spent Molasses Concentrates ("SMC") is from 70:30 to 80:20 (parts DIEG:SMC) based on weight of the components.

Spent Molasses Concentrates (SMC) is obtained from the processing of beet or cane molasses. The SMC is obtained as a waste product after the distillation (second stage) of beet or cane molasses, which is a byproduct from the sugar factory (first stage) where sugar beets or sugar cane is processed. At the first stage, the beets or cane are essentially cut up and shredded, combined with water and lime, and heated to obtain a clarified juice or syrup from which sugar crystals are obtained. After a number of stages during which sugar crystals are removed, the remaining molasses liquids are sold to distilleries (where second stage of process occurs). At this second stage, yeast and water are added to the molasses into fermentation units to convert sugars present in the molasses into alcohol (e.g., ethanol). The alcohol is removed using distillation columns. The removal of ethanol leaves

a waste bottom (solid) and a liquid condensate, which is raw waste water. This liquid condensate, which may have a concentration of about 10 Brix, is stored in a storage tank and pumped into one or more evaporators in series, from which the condensate is recycled back into production (for further
5 distillation). The liquid material remaining in the evaporator, after two or three or more distillation cycles, is the liquid concentrate referred to herein as "Spent Molasses Concentrates" ("SMC").

SMC is typically seen as dark brown-black, viscous liquid, having a specific gravity of 1.05-1.40 kg/litre, and is soluble in water. Spent Molasses
10 Concentrates are commercially available from Femprow, 102-1002, Blok A, Pusat Dagangan Phileo damansara 1, No. 9, Jalan 16/11, Off Jalan Damansara (factory located at Kawasan Perindustrian Chuping, 021450 Kangar, Perlis, Malaysia). SMC is generally believed to contain around 50% water, 20% gums, 16% wax/carbohydrate/lignin, 10% inorganic materials, 3%
15 protein, and 1% organic acid.

SMC is believed to be available in numerous countries wherein liquid molasses concentrates are obtained as a residual by-product from distillation of beet or cane molasses, and may be sold for various uses under various names (e.g., (liquid) molasses fermentation waste and others).

20 While the invention is described herein using a limited number of embodiments, these specific embodiments are not intended to limit the scope of the invention as otherwise described and claimed herein. Modification and variations from the described embodiments exist. More specifically, the following examples are given as a specific illustration of embodiments of the
25 claimed invention. It should be understood that the invention is not limited to the specific details set forth in the examples. All parts and percentages in the examples, as well as in the remainder of the specification, are by percentage weight unless otherwise specified.

Further, any range of numbers recited in the specification or claims,
30 such as that representing a particular set of properties, units of measure, conditions, physical states or percentages, is intended to literally incorporate expressly herein by reference or otherwise, any number falling within such

range, including any subset of numbers within any range so recited. For example, whenever a numerical range with a lower limit, RL, and an upper limit RU, is disclosed, any number R falling within the range is specifically disclosed. In particular, the following numbers R within the range are specifically disclosed: $R = RL + k \cdot (RU - RL)$, where k is a variable ranging from 1% to 100% with a 1% increment, e.g., k is 1%, 2%, 3%, 4%, 5% ... 50%, 51%, 52% ... 95%, 96%, 97%, 98%, 99%, or 100%. Moreover, any numerical range represented by any two values of R, as calculated above, is also specifically disclosed.

Example 1

Five grinding tests were done using the following materials: 95%YANSHAN cement clinker, 5% gypsum, and various grinding additives, including diethylene glycol (DIEG), as listed in Table 1 below. A standard laboratory mill was used, and grinding time was 40 minutes.

The amount of residue was measured using a 45 micron vacuum sieve (GB/T 1345-2005), and strength of the cement sample was measured at 3 days and 28 days after mixing with water, in accordance with GB/T 17671-1999. The cement mortar samples were shaped into cubes and prepared from cement, sand, and water in the following Cement:Sand:Water mix ratio = 450:1350:225 (g).

The sample designated as Mix 1 was a blank mix; while sample Mix 2 contained 0.03% DIEG (by weight of cement) which was used during the grinding of the cement. The sample designated as Mix 3 was same as sample Mix 2, except one quarter (0.0075%) of the DIEG by weight of cement was replaced by the same amount of SMC (by solid). The sample designated as Mix 4 was similar to sample Mix 2 except one-half (0.015%) of DIEG was replaced by the same amount of SMC (by solid). The sample designated Mix 5 was replaced with SMC (at 0.03% by weight of cement) which used during grinding.

The experiment test results are summarized in Table 1 below.

Table 1

Mix #	Additives	Dosage by weight of cement	Sieve Residue (45 micro), %	3 days Strength, MPa	% of blank	28 days Strength, MPa	% of blank
1	Blank		12.3	31.4	100	50.7	100
2	DIEG	0.03%	9.5	31.7	101	52.5	104
3	SMC+DIEG	0.0075%+ 0.0225%	9.4	30	96	49.8	98
4	SMC+DIEG	0.015% + 0.015%	10.0	28.6	91	50.2	99
5	SMC	0.03%	10.6	28.2	90	48.9	96

5 The foregoing test data supported the following conclusions: first, that SMC (solid) at dosage 0.03% by weight of cement appeared to have favorable properties on the improvement of cement fineness; second, that when SMC is used to replace 25~50% by weight of diethylene glycol (DIEG), a similar grinding efficiency (compared to 100% DIEG) could be achieved; and, third, that when 25% of DIEG was replaced using SMC (compare trial #2 and #4), the most favorable results were obtained.

The compressive strength of the mixes with SMC appeared to be slightly lower than other mixes, however.

Example 2

15 Four grinding ability tests were done using the following materials: 95%YANSHAN cement clinker, 5% gypsum, and various grinding additives (as listed in Table 2 below). A laboratory mill was used, and grinding time was 40 minutes. Test methods were similar to those used in Example 1, except that (a) 80 micro sieve was used and (b) the w/c of mortar was 0.64.

20 The sample designated as Mix-1 was a blank mix. Sample Mix 2 contained 0.03% DIEG (by weight of cement) which was used for the grinding. Sample Mix 3 was same as Mix-2 except one quarter (0.0075%) of DIEG was replaced by the same amount of SMC (by solid) and 0.0225% molasses (by solid) was added into the blend. Sample Mix 4 was similar to sample Mix-2 except one-half (0.015%) of DIEG by weight was replaced by the same amount of SMC (by solid) and 0.0225% molasses (by solid) was added into the blend.

The test results were summarized in Table 2 below.

Table 2

Mix #	SMC, %	DIEG, %	Molasses, %	Sieve Residue (80 micron), %	3 days Strength, MPa	% of blank	28 days Strength, MPa	% of blank
1	0	0	0	2.5	19.4	100	35.4	100
2	0	0.03	0	1.8	19.7	101	36.4	103
3	0.0075	0.0225	0.0225	2	19.7	102	35.6	101
4	0.015	0.015	0.0225	2.1	19.2	99	35.5	100

The foregoing results supported the following conclusions: first, that SMC replaced about 25%~50% by weight of diethylene glycol (DIEG), and a small percentage of molasses was used (0.0225% by weight), similar or slightly lower grinding efficiency (as compared to 100% DIEG) was achieved and the compressive strength was similar; and, second, that the best results were achieved when SMC replaced DIEG at 25%.

Example 3

Four grinding ability tests were done using the following materials: 95% SHUNFA cement clinker, 5% gypsum, and various grinding additives (as listed in Table 3 below). A laboratory mill was used, and grinding time was 35 minutes.

Sample Mix-1 was a blank mix. Sample Mix 2 contained 0.03% DIEG (by weight of cement) used during grinding. Sample Mix 3 was similar to sample Mix-2 except one-quarter (0.0075% by weight) of DIEG was replaced by the same amount of SMC (by solid) and 0.02% molasses (by solid) was added into the blend. Sample Mix 4 was same as Sample Mix 2 except one half (0.015%) of DIEG was replaced by the same amount of SMC (by solid) and 0.02% molasses (by solid) was added into the blend.

The test results were summarized in Table 3 below.

Table 3

Mix #	Additive dosage by weight of cement	45 micron residue, %	80 micron residue, %
1	BLANK	15.0	2.3
2	DIEG 0.03%	13.9	1.6
3	SMC 0.0075%+DIEG 0.0225%+Molasses 0.02%	13.8	1.8
4	SMC 0.015%+DIEG 0.015%+ Molasses 0.02%	15.2	1.8

The foregoing data supported the following conclusions: first, that when replacing 25%~50% of diethylene glycol (DIEG) using SMC, and adding 0.02% molasses, a similar or slightly lower grinding efficiency (as compared to 100% DIEG) could be achieved; and, second, that the most favorable results
5 were obtained when SMC was used to replace about 25% DIEG.

Based on the foregoing, the present inventors believe that the use of SMC (solid) at a dosage of 0.01%-0.05% by weight of cement demonstrated good grinding efficiency enhancement.

When replacing 25~50% of diethylene glycol (DIEG) by SMC, similar
10 grinding efficiency (as compared to 100% DIEG) can be achieved. The best results were obtained when the replacing level was close to 25% (e.g., between 20-30%).

In addition to results establishing that SMC could be used to extend the grinding efficiency enhancement provided by DIEG, the inventors
15 demonstrated that strength could be improved when the DIEG/SMC combination was augmented by the addition of 0.01~0.05% molasses (by weight of cement). Best results can be obtained when the dosage of molasses was within 0.02~0.04% by weight of cement.

The foregoing example and embodiments were present for illustrative
20 purposes only and not intended to limit the scope of the invention.

We claim:

1. A method for grinding a cementitious material, comprising:

combining, in the intergrinding of cementitious materials comprising cement clinker, granulated blast furnace slag, fly ash, or mixture thereof,

5 (A) water-soluble polyalkylene polyol grinding efficiency enhancing additive, said water-soluble polyalkylene polyol being selected from the group comprising a glycol, a glycerol, or mixture thereof, said water-soluble polyalkylene polyol being in the amount of 0.005%-0.10%;

(B) a Spent Molasses Concentrates ("SMC") obtained as a
10 concentrated condensate after evaporation of the raw waste water obtained from fermentation and distillation of sugar beet or sugar cane molasses, the SMC being in the amount of 0.005-0.05% and effective as an extender for said water-soluble polyalkylene polyol grinding efficiency enhancing additive; and

15 (C) optionally a molasses obtained from sugar beet, sugar cane, corn, wheat, wheat gluten, wood pulp, or mixture thereof, the molasses being in the amount of 0%-0.1%, the foregoing percentages being based on total dry weight of cementitious materials being interground.

2. The method of claim 1 wherein said molasses of component (C)
20 is used in the amount of at least 0.02%-0.05% based on dry weight of said cementitious materials.

3. The method of any one of the foregoing claims wherein said water-soluble polyalkylene polyol comprises a glycol, and the ratio of said SMC to said glycol is from 10:90 to 90:10 parts based on weight.

25 4. The method of claim 3 wherein said glycol is selected from diethylene glycol, polypropylene glycol, or mixture thereof.

5. The method of claim 3 wherein said glycol is diethylene glycol (DIEG) and the ratio of SMC:DIEG is 25:75 based on weight.

6. The method of claims 1 or 2 wherein said water-soluble polyalkylene polyol grinding efficiency enhancing additive comprises a glycerol selected from di-, tri-, or tetra-glycerol and mixtures thereof.

7. The method of claim 1 wherein said water-soluble polyalkylene
5 polyol grinding efficiency enhancing additive comprises a mixture of glycol and glycerol.

8. A composition comprising: (A) water-soluble polyalkylene polyol selected from glycol, glycerol, or mixture thereof, said water-soluble polyalkylene polyol grinding being operative as a grinding efficiency
10 enhancing additive for grinding a cementitious material selected from cement clinker, granulated blast furnace slag, fly ash, or mixture thereof; (B) a Spent Molasses Concentrates ("SMC") obtained as a concentrated condensate after evaporation of the raw waste water obtained from distillation of sugar beet or sugar cane molasses, the SMC being effective as an extender for said
15 polyalkylene polyol grinding efficiency enhancing additive; and (C) optionally, a molasses obtained from sugar beet, sugar cane, corn, wheat, wheat gluten, wood pulp, or mixture thereof.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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C04B 18/24 (2006.01)

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)

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 practicable, search terms used)

WPI, EPODOC, CAPLUS (keywords - glycerol, glycerin, glycerine, polyol, glycol, DIEG, molasses, beet, cane, SMC, vinasses, cement, clinker, fly ash, slag, grind, mill)

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 Plus Accession No. 2006:318807 & CN 1752046 A (ACHENG CITY KEQIANG CEMENT GRINDING AGENT CO., LTD.) 29 March 2006 See whole abstract	1-8
Y	US 3536507 A (KLEIN et al.) 27 October 1970 See abstract and columns 3 and 4	1-8
A	Derwent Abstract Accession No. 1975-63336W, SU 443008 A1 ((KAME-R) KAMENETS CEMENT WKS) 15 September 1974 See whole abstract	1-8

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Date of the actual completion of the international search
04 November 2009Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2009/060150

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 191210424 A (KEEN C. et al.) 24 April 1913 See page 1, line 11- page 2, line 11	1-8
A	CN1089245 A (CEMENT SCIENCE INST CHINESE AC) 13 July 1994 English abstract retrieved from EPODOC database See whole abstract	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2009/060150

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member
SU	443008	NONE
CN	1752046	NONE
US	3536507	NONE
GB	191210424	NONE
CN	1089245	NONE
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.		
END OF ANNEX		