

GRINDING AIDS FOR HYDRAULIC CEMENTS

This invention relates to the grinding of hydraulic cements to reduce the particle size thereof, and more particularly to the addition of certain chemical additives to such cements during the grinding thereof to improve the efficiency of the grinding operation and also the "pack-set" characteristics of the ground cement.

In the processing of Portland cement for example, a grinding operation is generally employed either in the unprocessed or semiprocessed state to reduce the cement to relatively small particle size. It is desirable in this grinding step to have as efficient an operation as possible, that is, to reduce the particular mineral to the desired size using as little energy as possible. Toward this end, it is customary to add chemicals known as "grinding aids" during the grinding operation which facilitate the operation either by increasing the rate of production, or by increasing the fineness of the particles at the same rate of production, without having adverse effects on the properties of the ground product.

Cleavage of the cement particles during grinding exposes fresh or nascent surfaces which have high energy. The surface forces of the ground particles persist for some time after grinding and can lead to compaction or "pack-set" and/or poor fluidity if they are not reduced. Cement particles when compacted by vibration, e.g. when transported in a hopper car often become semirigid and will not flow until considerable mechanical effort has been applied to break up the compaction. It is desirable

therefore if the "grinding aid" also acts to reduce this tendency to compact or "pack-set".

Many chemicals and chemical mixtures have been suggested for use as grinding aids and pack-set inhibitors for hydraulic cements such as Portland cement. Examples of such chemicals which have been successfully commercially applied include triethanolamine salts of acetic acid (U.S. Patent 3,329,517 to Serafin) and triethanolamine salts of phenol (U.S. Patent 3,607,326 to Serafin). Also, the use of amine salts of alkyl benzene sulphonic acid and the diethanolamine salt of dodecyl benzene sulphonic acid in particular have been suggested as grinding aids for cements (Japanese Patent Nos 7421408 and 7421410 to H. Miyairi and M. Nakano).

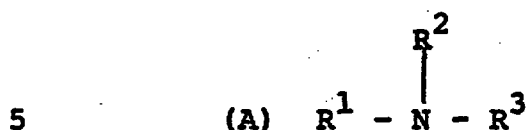
The present invention is based upon the discovery that amine salts formed by reacting aromatic group-containing carboxylic acids with amines are excellent grinding aids in the grinding of hydraulic cements such as Portland cement. The presence of such salts in the ground cement also acts to inhibit the tendency of ground cement to compact or "pack-set". Such salts moreover offer the advantage that the carboxylic acid reactant is obtainable commercially in many instances from starting materials (benzene, toluene, xylenes, etc.) produced in the distillation of coal, and therefore avoid the price fluctuations and shortages currently characteristic of chemicals derived solely from petroleum.

A particular advantage of the invention is that either or both reactants, and especially the acid reactant, can be an impure by-product of another commercial process.

The grinding aids of the invention are prepared by mixing the aromatic group-containing carboxylic acid component and the amine to obtain an essentially neutral amine salt. The starting materials may be pure chemicals but preferably are chemical mixtures. Preferred amine salts are described and claimed in our divisional application No. 84,24501.

The amines employed in the present invention include primary, secondary and tertiary aliphatic or aromatic amines and preferably alkanolamines, as well as mixtures

of such. Useful amines may be represented by the formulae:



and



wherein R^1 is hydrogen, an alkyl, alkanol, alkaryl or aryl radical; R^2 is hydrogen, alkyl or alkanol radical;
 10 R^3 is hydrogen, hydroxyl, alkyl, alkanol or aryl radical;
 R^4N is pyrrolidinyl, pyrrolinyl, pyrrolyl, morpholinyl, piperdiny, or piperazinyl radical and R^5 is hydrogen, alkyl, or alkanol radical. The term "aryl" as used herein is intended to refer to a phenyl or naphthyl radical.
 15 One or more of the hydrogen atoms on the aryl radical may be replaced by a substituent group such as a nitro; halogen, preferably chlorine, alkyl, preferably a 1 to 5 carbon group, more preferably methyl; aryl, amino and alkoxy, preferably a 1 to 5 carbon alkoxy group. In addition,
 20 pyridazine, pyrimidine and pyridine and such compounds wherein one or more hydrogen atoms are replaced with hydrogen, hydroxy or alkyl radicals are also useful in preparing additives within the scope of the present invention. The heterocyclic groups mentioned above,
 25 for instance in the definition of R^4 are intended to include the substituted radicals which are known to the art, e.g. N-methylmorpholine, and 4-(2-aminoethoxy)ethylmorpholine.

A particularly preferred amine component for reacting with the aromatic group-containing carboxylic acid
 30 to produce the additives of the invention is a residue product derived from commercial processes to produce alkanolamines such as that described in U.S. Patent No. 3,329,517 to Dodson. The additive is derived from the residue obtained in preparing ethanolamines. The residue
 35 product may be derived from a number of well known methods which are employed to synthesise ethanolamines. It may be obtained from such reactions as the ammonolysis or amination of ethylene oxide, the reduction of nitro

alcohols, the reduction of amino aldehydes, ketones and esters, and the reaction of halohydrins with ammonia or amines. The exact composition of the residue product varies within certain limits and includes one or more
 5 mono-, di-, or triethanolamines, preferably between 40 to 85% by volume triethanolamine. In general the residue product is predominantly triethanolamine and is referred to below as a triethanolamine mixture. A specific residue product which is employed in a particularly
 10 preferred embodiment of this invention is a mixture of mono-, di-, and triethanolamine which is available commercially and has the following chemical and physical properties:

Triethanolamine45 to 55% by volume
 15 Equivalent weight.....129 to 139
 Tertiary amine6.2 to 7.0 meq/gm
 Water.....0.5% by wgt. maximum
 Density.....9.49 lbs./gal (949 g/l)

The aromatic group-containing carboxylic acids
 20 reacted with the amines herein include mono- and polycarboxylic acids having one or more aromatic groups in their molecular structure. The terms "aromatic" and "aryl" as employed herein include the unsaturated cyclic hydrocarbon radicals principally, as exemplified by the phenyl,
 25 benzyl, naphthyl, etc., radicals. Such carboxylic acids could have groups (e.g. alkyl-, halo-, nitro-, hydroxy, etc., groups) in addition to, for example located upon, such aromatic or aryl groups so long as such do not deleteriously affect the intended use of the additive compound
 30 according to the invention. Illustrative of the aromatic group-containing carboxylic acids useable herein are aromatic carboxylic acids such as benzoic acid, phthalic acid and the alkyl benzene carboxylic acids. Also, aryl-substituted aliphatic acids such as naphthaleneacetic
 35 acid and mandelic acid (α -hydroxyphenylacetic acid). Mixtures of such acids may also be used. Moreover, anhydrides for such acids may be used herein but it may be necessary to first convert the anhydride to the acid prior

to reaction with the amine component.

A particularly preferred carboxylic acid component for reaction with the amines to produce the additives according to the invention is that obtained from a by-product in commercial processes to produce phthalic anhydride by the oxidation of naphthalene, typically in the presence of catalyst, to phthalic anhydride. In the final stages of such processes, the oxidation product is subjected to a distillation step towards recovery of the highly pure anhydride product. A by-product produced from such distillation, sometimes referred to in the industry as "phthalic lites", comprises a mixture of benzoic acid and phthalic anhydride. This by-product because of its impurity has limited usage. Also, its toxicity makes its disposal complicated. It has been found that such by-product, after treatment to convert the phthalic anhydride to the acid, is an ideal material to react with amine to produce the grinding acid additive of the invention. The by-product is economically available, and its use in hydraulic cement wherein it is ultimately encased (in concretes, etc), is an environmentally desirable disposal. Moreover, the by-product is obtained from a feedstock, naphthalene, obtainable from coal tar, and thus many of the problems associated with chemicals solely dependent upon petroleum for their availability are avoided.

The "phthalic lites" by-product mixture as aforescribed is principally comprised of a mixture of benzoic acid and phthalic anhydride. The exact proportions of each of such ingredients in the mixture can vary widely, say from 99:1 to 1:99 benzoic acid to anhydride. It has been found desirable to convert the anhydride in the by-product to the acid prior to reaction with the amine to produce the grinding aid of the invention. If the product is not so converted, esters are produced in the reaction with the amine, which leads to products which are less effective as grinding aids.

The preferred method for conversion of the "phthalic

lites" by-product mixture is hydrolysis, hereinafter termed "hydrolyzed phthalic lites". In the preferred procedure, the by-product mixture is heated to a molten condition (e.g. 110°C) which renders it easily transportable, pumpable, etc., and added to hot water (e.g. about 80°C) to effect the conversion of the anhydride to phthalic acid. After cooling, the amine reactant is added to produce essentially a mixture of amine salt of benzoic acid and amine salt of phthalic acid.

10 The amine salt additive of the invention is interground with the cement in the grinding mill to provide increased grinding efficiency as well as other advantageous results, e.g. inhibiting pack-set of bulk stored cement. The additives of the invention are particularly preferred for use with Portland cement, 15 a class of hydraulic cement comprised essentially of two calcium silicates and a lesser amount of calcium aluminate. These cements are produced by heating an intimate mixture of finely divided calcareous material (limestone) and argillaceous material (clay) to form a 20 clinker. The clinker is ground with the addition of about 2 percent gypsum, or some other form of calcium sulphate, to obtain the desired setting qualities in the finished cement. It is to the clinker that the additive 25 of the invention is preferably added to increase grinding efficiency and to inhibit subsequent pack-set in the finished cement.

The additives of the present invention may be employed in either dry or liquid form. For convenience, 30 the additive is in water solution to permit accurate metering into the mill stream. The addition is accomplished either prior to the grinding or the additive is introduced into the grinding mill simultaneously with the cement. If the additive is employed merely for the reduction 35 of pack-set or for fluidising purposes, it is added at any convenient point in the processing.

The additive of the invention is employed effectively over a relatively wide range. The preferred range is

about 0.001 to 1 percent based on the weight of the cement, i.e. the weight of additive solids based on the weight of the cement solids (herein referred to as "solids on solids"). In a particularly preferred embodiment, the amount of additive employed is about 0.004 to 0.04 percent. Higher levels are employed if grinding to a relatively high surface area, and the amount of additive is limited solely by the desired surface area and the degree of fluidity desired.

As used herein, the term "pack-set" is intended to refer to the agglomeration or adhesion of particles by, for example, storing or transporting in bulk. Adhesion results from surface forces, the majority of which are believed to be created during the grinding of the cement.

Pack-set is determined in the following manner:

One hundred grams of the cement is placed in a 250 milliliter Erhlenmeyer flask set on top of a variable vibrator. The flask containing the cement is vibrated 15 seconds after which it is removed from the vibrator and set into a jig with the axis of the flask lying horizontally. The flask is then rotated around its axis until the cement which is compacted in the bottom of the flask collapses. The flask is twisted at 180° angles at approximately 100 twists per minute. The number of 180° twists required for the sample to collapse establishes the pack-set. Thus, the greater the energy required to break up the bed, the higher will be the pack-set.

The following examples will serve to further illustrate the invention.

Example 1

In experiments testing the effectiveness of chemicals as grinding aids for Portland cement, several aromatic acid components were first reacted with a triethanolamine mixture to form a salt thereof, and test grinds made in a laboratory batch mill. The triethanolamine mixture was a product obtained as a residue product

of ethanolamine synthesis previously described. Several clinkers ("A" through "D" in Table I), each from a different manufacturing source, were used in the tests. In the tests, 3325 grams of clinker (-20 US mesh size) were
5 ground along with 175 grams of gypsum (the latter is used in commercial production of "Portland cement"). The amine salts were added in various proportions (salt solids on cement solids) to the clinker-gypsum mixture before grinding. For comparison, a "blank" control
10 grind, that is, a grind of each of the clinkers "A" through "D" with gypsum and no grinding aid was also performed. Each grind with respect to a single clinker was identical, that is, the mill was operated the same number of revolutions at 220°F (104°C), and the surface area ("Blaine Surface
15 Area") of the resulting ground product measured in centimeters square per gram. The exact number of revolutions varied between 5000 and 10,000 depending upon the particular clinker. The increase in fineness (the increase in "Blaine Surface Area") evidenced by the ground test
20 samples containing grinding aid was calculated as a percent of the surface area measured for the "blank" control. This percentage is recorded as "Percent Improvement Over Blank" in Table I. Duplicate, and in some cases triplicate, grinds were made of the grinding
25 aids tested and the "Percent Improvement Over Blank" shown in Table I is an average value thereof. In Table I the "Hydrolysed Phthalic Lites" product was obtained as previously generally described, using in particular the "Procedure No. 1" of Example II. For further comparison,
30 additional test grinds were made using a commercial grinding aid. The results are reported in Table I.

TABLE IPercent Improvement Over Blank

Clinker	Grinding Aid	Addition Rate (% sos)	Run No.1	Run No.2	Run No.3	Average
A	Triethanolamine Salt of Phthalic Acid	0.025	6.7	8.6	7.3	7.5
A	Triethanolamine Salt of Phthalic Acid	0.014	3.5	1.8	-	2.7
A	Commercial Product	0.025	9.8	7.8	9.3	9.0
A	Commercial Product	0.013	2.2	2.3	-	2.3
A	Triethanolamine Salt of Naphthal- eneacetic Acid	0.025	5.7	7.3	-	6.5
A	Triethanolamine Salt Benzoic Acid	0.025	6.9	8.5	-	7.7
A	Triethanolamine Salt of Hydrolysed Phthalic Lites	0.015	3.1	6.0	6.5	5.2
A	Commercial Product	0.015	6.3	6.3	8.1	6.9
B	Triethanolamine Salt of Hydrolysed Phthalic Lites	0.015	8.9	9.3	8.9	9.0
B	Commercial Product	0.015	5.8	8.3	10.7	8.3
C	Triethanolamine Salt of Hydrolysed Phthalic Lites	0.015	6.1	5.0	8.7	6.6
C	Commercial Product	0.015	7.8	5.9	7.0	6.9
D	Triethanolamine Salt of Hydrolysed Phthalic Lites	0.015	8.2	8.5	7.1	7.9
D	Commercial Product	0.015	6.4	7.7	8.6	7.6
A	Triethanolamine Salt of Naphtha- lene Sulphonic Acid	0.025	4.9	6.4	-	5.7

Example II

Two procedures may be used in the preparation of the triethanolamine salt from "hydrolysed phthalic lites", the method of choice being dictated primarily by the type of processing equipment available. The figures given in this example are based upon a 1000 gram batch although in practice batches as large as 500 lbs. (227 kg) have been prepared using both procedures.

Procedure No. 1

- 10 Step 1: Melt 929 grams of phthalic lites and heat molten material to between 110° and 115°C.
- Step 2: Add 20 grams of hot water (93°-100°C) to the molten phthalic lites with vigorous stirring.
- Step 3: Monitor the temperature of the reaction mixture. Initially it will climb as the exothermic hydrolysis reaction takes place, then become constant as thermal equilibrium is reached and finally fall after the hydrolysis step reaches completion.
- 20 Step 4: Upon completion of the hydrolysis (as indicated by the decrease in reaction mixture temperature) add 448 grams of triethanolamine with moderate stirring.
- Step 5: When the reaction mixture temperature falls to below 90°C. add 240 grams of water.
- 25

Procedure No. 2

- Step 1: Heat 260 grams of water to between 75° and 100°C.
- Step 2: Add 929 grams of molten phthalic lites to the hot water with vigorous stirring. The temperature of the molten material should be between 110° and 115°C.
- 30 Step 3: Monitor the temperature of the reaction mixture as in Step 3 of Procedure No. 1.
- Step 4: When the temperature of the reaction mixture falls to 70°C begin a slow addition of 448 grams of triethanolamine with moderate agitation. The rate of triethanolamine addition should be adjusted so that the temperature of the reaction
- 35

mixture does not exceed 100°C.

Example III

The ability of the grinding aid of the invention to also act as inhibitors of the "pack-set" of the ground product was tested. Table II shows the results of tests as described previously for ability to inhibit the "pack-set" tendencies of Portland cement clinker mixtures "A", "B" and "D". The lower the "Pack-Set" number, the more effective the grinding aid is as an inhibitor of "pack-set".

TABLE II

Cement Clinker	Grinding Aid	Addition Rate (% sos)	Pack-Set
A	None (blank)	-	30
A	Triethanolamine Salt of Naphthaleneacetic Acid	0.025	5
A	Triethanolamine Salt of Benzoic Acid	0.025	2
A	Triethanolamine Salt of Phthalic Acid	0.025	3
A	Commercial Product	0.025	5
A	Commercial Product	0.015	9
A	Triethanolamine Salt of "Hydrolysed Phthalic Lites"	0.015	7
B	None (blank)	-	14
B	Triethanolamine Salt of "Hydrolysed Phthalic Lites"	0.015	9
B	Commercial Product	0.015	14
D	None (blank)	-	29
D	Triethanolamine Salt of "Hydrolysed Phthalic Lites"	0.015	11
D	Commercial Product	0.015	8

CLAIMS

1. A hydraulic cement composition comprising hydraulic cement and an amine salt of a carboxylic acid containing an aromatic group.
2. A composition according to claim 1 in which the cement is Portland cement.
3. A composition according to claim 1 or claim 2 in which the amine salt is a salt of an alkanolamine or mixture of alkanolamine.
4. A composition according to claim 3 in which the amine comprises triethanolamine.
5. A composition according to claim 4 in which the amine is a residue product of an ethanolamine synthesis and comprises one or more ethanolamines.
6. A composition according to any preceding claim in which the acid of the amine salt comprises an aromatic mono- or di-carboxylic acid containing a benzene or naphthalene nucleus or an aryl-substituted aliphatic acid.
7. A composition according to claim 6 in which the acid comprises benzoic acid, phthalic acid or naphthalene-acetic acid.
8. A composition according to claim 7 in which the acid comprises a mixture of aromatic carboxylic acids obtained as a by-product in a process for the synthesis of phthalic anhydride.
9. A composition according to claim 7 in which the acid comprises a mixture of aromatic carboxylic acids obtained by hydrolysing a mixture that comprises benzoic



acid and phthalic anhydride and that is obtained as a by-product in the synthesis of phthalic anhydride from naphthalene.

10. A composition according to claim 8 or claim 9 in which the amine is a residue product of an ethanolamine synthesis and comprises one or more ethanolamines.

11. A composition according to any preceding claim in which the amount of the amine salt is 0.001 to 1% by weight.

12. A method of grinding hydraulic cement in which there is used, as grinding aid, an amine salt as defined in any of claims 1 or 3 to 10.

13. A method according to claim 12 in which the cement is Portland cement.
