

SPECIFICATION

Grinding aid for granular blast furnace slag

- 5 This invention relates to grinding blast furnace slag and more particularly to the use of an additive for improving the efficiency of the grinding operation as well as improving characteristics of the ground slag product. 5

Granular blast furnace slag is produced by air and water quenching of the molten, non-metallic residue remaining after the treatment of metallic core in a blast furnace in the production of iron and steel. Grinding 10 of such slag, followed by exposure to the proper catalyst such as lime, produces a product which acts as a cementitious material, but only behaves well as such when ground to a very fine particle size. 10

The grinding of any solid material to obtain a desired finer particle size often involves the consumption of a considerable amount of energy by the grinding equipment. It is desirable in this grinding therefore to have as efficient an operation as possible.

- 15 It has become customary in grinding products which are used in relatively large volume such as Portland cement to employ chemical "grinding aids". Such grinding aids are added before or during the grinding operation to assist in the grinding operation either by increasing the rate of production, or by increasing the fineness of the cement particles at the same rate of production, without having adverse effects on any of the properties of the ground product. In some instances, the presence of the grinding aid in the finished, ground 20 product causes the ground product to exhibit a reduced tendency to compact or to "pack set". The tendency of ground solids to compact or "pack set" is thought to be brought about by cleavage of the particles during grinding, which exposes fresh or nascent surfaces which have high energy. Reduction of this tendency to "pack set" or compact is desirable since it facilitates the transportation of the ground product. 20

- Many chemicals and combinations thereof have been suggested for use as grinding aids in the reduction 25 of the particle size of Portland cement clinker and hydraulic cements, as well as other minerals materials. Some examples of grinding aids which have been successfully utilized on a commercial scale in the grinding of Portland cement clinker are phenol, acetic acid, amines and salts thereof, glycols, and combinations of the foregoing. U.S. Patent 3,607,326 to Serafin discloses a grinding aid and pack set inhibitor for Portland cement and other "minerals" which is an amine salt of an aryl hydroxy compound, for example, 30 triethanolammonium phenoxide. This patent also states that the same grinding aids are useful in the grinding of phosphate rock, iron ore, bauxite, clay, gypsum, amorphous silica, limestone, beryllium oxide and magnesia. 30

- It has now been discovered that chemical additives of the type disclosed in the aforementioned U.S. Patent 3,607,326 to Serafin are particularly effective as grinding aids in the grinding of granular blast furnace slag. 35

- The presence of the additives also appears to reduce the tendency of the ground slag product to "pack set". 35

- The amine salt additives which have been found particularly effective as grinding aids and pack set inhibitors for granular blast furnace slag according to the invention, are, as already mentioned, described in U.S. Patent 3,607,326. As disclosed in that patent, the salts are produced by the reaction of an aryl hydroxy compound such as phenol, with an amine such as triethanolamine. In preparing the additives one or more 40 aryl hydroxy compounds are mixed with one or more amines. The starting materials may be pure chemicals or mixtures containing differing chemicals or impurities. The method of preparing the additives are known to the art. Preferably, equimolar parts of the amine and the aryl hydroxy compounds are employed. The amine salt additives can be used alone or in combination with other chemical additives such as other grinding aids to obtain the desired results. 40

- 45 The term "aryl" as used herein in describing the aryl hydroxy reactant includes more particularly phenyl or naphthyl radicals. Such radicals may be substituted by replacing one or more of the hydrogen atoms on the aryl radical by nitro; halogen, preferably chlorine; alkyl, preferably of 1 to 5 carbons, more preferably methyl; aryl, preferably of one to three aromatic rings; amino; and alkoxy, preferably of one to five carbons. 45

- The amines employed in the present invention include mono-, di- and trialkanol amines, or mixtures 50 thereof and morpholine. The alkanol group or groups in the mono-, di- and trialkanol amines may each contain 1 to 5 carbon atoms. Illustrative of such alkanolamines are monoethanolamine, diethanolamine, dipropanolamine, dibutanolamine, triethanolamine, tripropanolamine, etc. and mixtures thereof. The aforementioned amines can contain substituent groups which do not deleteriously affect the reaction of the amine with the aryl hydroxy compound or the desired effects of the additive of the invention on blast furnace 55 slag. Exemplary of such nondeleterious substituted amines are N-methylmorpholine and 4-(2-aminoethoxy) ethylmorpholine. Trialkanolamines, for example triethanolamine, are especially preferred for use in forming the additive used in the invention. 55

- The term "granular blast furnace slag" as used herein is intended to refer to the solidified and preliminarily crushed (preferably -20 mesh, U.S. Sieve System i.e. to a particle size not greater than 0.84 mm,) mixture of 60 iron ore impurities and fluxing materials resulting from the manufacture of iron and steel in a blast furnace. The chemical composition of typical blast furnace slags from various parts of the world is given in Kirk Othmer's Encyclopedia of Chemical Technology, Second Edition, Supplement Volume, page 877 (1971, John Wiley & Sons, Inc.). 60

- Generally speaking, slags that can be ground in the process of this invention comprise the ingredients 65 shown in Table 1. 65

TABLE I

	Ingredients	Weight Percent	Preferred	
5	CaO	35-45	about 40	5
	SiO ₂	30-40	about 35	
	Al ₂ O ₃	5-20	about 12	
10	MgO	3-15	about 5	10
	Others	balance	balance	
15	On the same page in the above encyclopedic reference, there is a phase diagram for the CaO-Al ₂ O ₃ -SiO ₂ -MgO system (at least 5% MgO) showing the distinction between blast furnace slag and other materials of the same general system.			15
20	The grinding aids are employed in either dry or liquid form. For convenience, the additive is in water solution to permit accurate metering into the mill stream. In instances where the additive is not very soluble in water, it can be utilized in liquid form by emulsifying with suitable wetting agent, for example, sodium dodecyl benzene sulfonate. The additive may also contain a chelating agent (such as trisodium N-hydroxyethylethylene diamine triacetate hydrate (hereinafter "NEDTA")) in order to chelate the cations commonly found in hard water and thereby prevent precipitation of the product. The addition of the additive of the invention to the slag is accomplished either prior to the grinding operation, or the additive is introduced into the grinding mill during the grinding of the slag. If the additive is employed merely for the reduction of pack set or for fluidizing purposes, it can be added at any convenient point in the processing.			20
25	The additive is effectively employed over a relatively wide range. The preferred range is about 0.001 to 1 per cent based on the weight of the slag, i.e. the weight of additive solids based on the weight of the slag 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 per cent. Higher levels are employed if grinding to a relatively high surface area is desired, and the amount of additive is limited solely by the desired surface area and the degree of fluidity desired.			25
30	The term "pack set" as used herein 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 slag. "Pack set index" is a relative term which indicates numerically how prone a particular material is to start flowing after it is stored or transported in bulk. "Pack set index ratio" is the relative pack set index of an untreated sample compared to a sample treated with additives. This ratio is used to permit comparisons to be made between different samples.			30
35	Pack set index is determined in the following manner:			35
40	One hundred grams of the slag is placed in a 250 milliliter Erhienmeyer flash set on top of a variable vibrator. The flask containing the slag 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 slag which is compacted in the bottom of the flask collapses. Such rotation is accomplished by twisting the flask at 180° angles at approximately 100 twists per minute. The number of 180° twists required for the slag sample to collapse establishes the pack set index. Thus the greater the energy required to break up the bed, the higher will be the pack set index.			40
45	The invention is illustrated further by the following non-limiting Examples.			45
	<i>Example I</i>			
50	An additive composition according to the invention is prepared containing the following components:			50
	Components	Percent by Weight		
55	Phenol	31		55
	Triethanolamine	49		
	Water	19.5		
60	Chelating agent ("NEDTA")	0.25		60
	Dye	0.25		

The composition shown above is prepared using the following steps:

Steps

1. Combine phenol and 38% of the total triethanolamine; mix.
2. Add remainder of triethanolamine to step 1 material; mix
3. Mix water, chelating agent and dye in a separate container.
- 5 4. Combine step 2 material with step 3 material.

5

Example II

Several chemical products were tested for usefulness as grinding aids in the grinding of blast furnace slag. The chemical products were products previously sold and used commercially as grinding aids and pack set inhibitors in the grinding of Portland cement clinker. In one study, the results of which are reported in Table I below, replicate grinds were performed using 3500 grams of granular blast furnace slag (-20 mesh) in a laboratory batch mill. The grinds were performed for approximately 20,000 revolutions at 220° Fahrenheit (about 105°C) using as grinding aids (i) an additive composition produced as in Example I; (ii) a glycol based product; and (iii) combinations of (i) and (ii). Grinds were also made using no grinding aid at all, the latter serving as a control blank. The results are shown in Table I.

15

TABLE I

20 Grinding Aid	Addition Rate	Blaine Surface Area Per Mill Revolution (cm ² /gm/rev)		Average	%Improvement Over Blank	20
		Run 1	Run 2			
25 None	-	0.2359	0.2395	0.2377	-	25
Commercial (glycol ¹)	0.02	0.2451	0.2469	0.2460	3.5	
Example I	0.02	0.2557	0.2528	0.2542	7.0	
30 Commercial (glycol ¹) + Example, 1:1	0.02	0.2479	0.2489	0.2484	4.5	30
Example I	0.04	0.2719	0.2692	0.2705	13.8	
35 Commercial (glycol ¹) + Example, 1:1	0.04	0.2660	0.2644	0.2652	11.6	35

(1) A proprietary mixture containing approximately 90 per cent diethylene glycol by weight of total solids.

40

Example III

In another grinding study, replicate grinds of blast furnace slag were made as in Example II except that the test samples were ground for approximately 11,000 revolutions of the batch mill. The products tested for effectiveness as grinding aids included a composition of the invention (made as in Example I) the glycol-based commercial grinding aid of Example II, and another commercial product based on an acetate salt, also used previously as a grinding aid for Portland cement. The results are shown in Table II.

45

45

TABLE II

Grinding Aid	Addition Rate (% solids on solids)	Blaine Surface Area Per Mill Revolution (cm ² /gm/rev)	% Improvement Over Blank	
None	-	0.3087	-	5
Commercial (acetate ¹)	0.02	0.3172	2.7	10
Commercial (glycol)	0.02	0.3183	3.1	
Example I	0.02	0.3246	5.1	
Commercial (acetate ¹)	0.04	0.3302	7.0	15
Commercial (glycol)	0.04	0.3294	6.7	
Example I	0.04	0.3388	9.8	20

(1) A proprietary commercial product containing about 60 per cent by weight of an acetate salt based on the total solids present.

Example IV

A test was conducted to determine the effectiveness of the grinding aid of the invention (Example I) as a pack set inhibitor for ground blast furnace slag. The test was conducted in the manner described above. The results shown in Table III below indicate that the slag grinding aid of the invention also acts to reduce the tendency of the ground slag to "pack set".

TABLE III

Effect of additive of the invention on pack set index:

Pack Set Inhibitor	Addition Rate (%solids on solids)	Pack Set Index	
None	-	6	35
Example I	0.02	2	40
Example I	0.04	0	

As shown by the above Examples, a highly effective grinding aid for ground blast furnace slag has been found. The additive also acts as a pack-set inhibitor of the ground product. The grinding aid of the invention was unexpectedly shown to be more effective as a grinding aid for the slag than products based upon glycols and acetate salts, which like the additive of the invention have been previously utilized as grinding aids for Portland cement.

CLAIMS

1. A method for producing ground granular blast furnace slag which comprises grinding granular blast furnace slag in the presence of enough of an additive comprising a salt formed by reacting an amine and an aryl hydroxy compound to enhance the efficiency of the grinding operation.
2. A method according to claim 1, wherein the said additive comprises a salt formed by reacting an amine selected from morpholine and alkanolamines wherein each alkanol group contains 1 to 5 carbon atoms, with an arylhydroxy compound wherein the aryl radical is selected from phenyl, naphthyl and substituted phenyl and naphthyl wherein each substituent is nitro, halo, alkyl of 1 to 5 carbon atoms, aryl, amino or alkoxy of 1 to 5 carbon atoms.
3. A method according to claim 2, wherein the additive comprises a salt of triethanolamine.
4. A method according to claim 2, wherein the additive comprises a salt of phenol.
5. A method according to claim 2, wherein the said additive is triethanolammonium phenoxide.
6. A method according to any of claims 1 to 5, wherein the additive is used in an amount of 0.001 to 1 percent by weight, based on the weight of the slag.
7. A method according to claim 6, wherein the amount of additive is 0.004 to 0.04 percent by weight,



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5. A method according to claim 2, wherein the said additive is triethanolammonium phenoxide.
6. A method according to any of claims 1 to 5, wherein the additive is used in an amount of 0.001 to 1 percent by weight, based on the weight of the slag.
7. A method according to claim 6, wherein the amount of additive is 0.004 to 0.04 percent by weight,



based on the weight of the said slag.

8. A method according to claim 1 substantially as described in Example 1.
9. A composition comprising solid particulate blast furnace slag, and, intimately admixed therewith, about 0.001 to 1 percent by weight, based on the weight of said slag, of an additive comprising a salt formed by reacting an amine with an aryl hydroxy compound, as defined in any one of claims 1 to 5.
10. A composition as claimed in claim 9, further including a small amount of a chelating agent.
11. A composition as claimed in claim 9 or 10 comprising 0.004 to 0.04 percent by weight, based on the weight of the said slag, of the additive.
12. A composition as claimed in claim 9 when produced by the method of any of claims 1 to 8.

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