MINERAL GRINDING AIDS

ABSTRACT: Solid inorganic compounds such as naturally occurring inorganic mineral compounds and Portland cement are interground with certain amine salts of aryl hydroxy compounds (e.g., triethanolamine phenoxide) to enhance the efficiency of the grinding operation.
MINERAL GRINDING AIDS

This application is a continuation-in-part of application Ser. No. 556,589, filed June 10, 1966 and now abandoned. This invention relates to grinding minerals and more particularly to the use of an additive for improving the grinding efficiency and pack set characteristics of minerals.

In the processing of minerals, a grinding operation is generally employed either in the unprocessed or semiprocessed state to reduce the particular mineral 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 particular size at a relatively rapid rate.

A grinding aid is frequently employed in such a grinding operation to assist the grinding of the minerals 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 any of the properties of the ground product.

Cleavage of the particles during grinding of the minerals exposes fresh or nacent surfaces which have high energy. The surface forces of the ground particles persist for some time after grinding to lead to compaction or pack set and/or fluidity if they are not reduced. Mineral particles when compacted by vibration, e.g., when transported in a hopper car often become semiglued and will not flow until considerable mechanical effort has been applied to break up the compaction. Therefore, it is desirable that a material be employed to reduce the above-described adhesion of the particles.

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 minerals. "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 the untreated sample compared to the treated sample. This ratio is used to permit comparison between different samples of the mineral.

A novel additive has now been found which will function as a grinding aid and a pack set inhibitor for minerals. The novel additive of the present invention is an amine salt of an aryl hydroxy compound. Such additives are the reaction product of an aryl hydroxy compound, e.g., phenol, with an amine. In preparing the novel additives of the present invention, one or more aryl hydroxy compounds are mixed with one or more amines. The starting materials may be pure materials or materials containing impurities. The methods of preparing the additives are known to the art. Preferably, equimolar parts of the amine and aryl hydroxy compound are employed.

The term "aryl" as used herein is intended to refer to phenyl or naphthyl radical. It should be understood that one or more of the hydrogen atoms on the aryl radical may be replaced by a nitro; halogen, preferably chlorine; alkyl, preferably to a 1- to 5-carbon group, more preferably methyl; aryl, preferably of one to three aromatic rings, amino and alkoxyl preferably a one to five carbon alkyl group.

The amines employed in the present invention include mono-; di- and trialkanol amines and morpholine. The alkanol group or groups in the mono-, di- and trialkanol amines each contain about one to five carbon atoms. Illustrative of such alkanolamines are monethanolamine, diethanolamine, dipropanolamine, dibutanolamine, triethanolamine, tripropionalamine, etc., as well as mixtures thereof. Obviously the aforementioned amines employed in the invention 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 minerals mentioned herein. Exemplary of such nondeleterious substituted amines are N-methyl-morpholine and 4-(2-aminoethoxy) ethylmorpholine. Trialkanolamines, for example, triethanolamine, are especially preferred for use in forming the additive of the invention.

The additive is interground with the mineral in the grinding mill to provide increased grinding efficiency as well as other advantageous results, e.g., inhibiting pack set of bulk stored materials. It has also been found that the novel additive of the present invention serves to provide fluidity to the ground minerals when they are being transported by conveying systems, particularly to pneumatic air systems.

The term "mineral" as used herein is intended to refer to solid inorganic compounds including naturally occurring inorganic mineral compounds such as phosphate rock; iron ore, for example, taconite; bauxite; clay; gypsum; amorphous silica and limestone; as well as such materials derived from naturally occurring mineral compounds as Portland cement clinker; beryllium oxide and magnesia. The naturally occurring mineral compounds can be more efficiently ground according to the invention either as recovered in their natural state or at some point in their processing.

The grinding aids of the present invention are particularly preferred for use with cement, particularly Portland cement. Portland cement represents a class of hydraulic cement and is 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 clinker. The clinker is ground with the addition of about 2 percent gypsum, or some other form of calcium sulfate, to obtain the desired setting qualities in the finished cement. It is to the clinker that the novel additive of this invention is preferably added to increase grinding efficiency and to inhibit subsequent pack set in the finished cement. The additive of the invention was also found to ideally enhance the compressive strength of concrete made from Portland cement interground therewith.

The additives of the present invention 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 a suitable wetting agent, for example, sodium dodecyl benzene sulfonate. The addition is accomplished either prior to the grinding or the additive is introduced into the grinding mill simultaneously with the mineral. If the additive is employed merely for the reduction of pack set or for fluidizing purposes, it is added at any convenient point in the processing.

The additive is employed effectively over a relatively wide range. The preferred range is about 0.001 to 1 percent based on the weight of the mineral, i.e., the weight of additive solids based on the weight of the mineral 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 Portland cement clinker high surface area and the amount of additive is limited solely by the desired surface area and the degree of fluidity desired.

EXAMPLE I

In the following table, the efficiency of triethanolammonium phenoxide, prepared by mixing equimolar parts of triethanolamine and phenol, as a grinding aid is reported. The data was collected on Type I Portland cement ground in a laboratory steel ball mill for 3403 revolutions at 210 °F.
A novel grinding aid was prepared by mixing 34 parts by weight of a 50–50 mixture of phenol and cresol with 65.9 parts by weight of a 50–50 mixture of morpholine and triethanolamine. The grinding efficiency was determined on Type I Portland cement ground in a laboratory mill for 4941 revolutions at 230°F. At a level of 0.012 percent based on the weight of the cement, an increase in Blaine Surface Area of 6.75 percent over a blank was found.

**EXAMPLE II**

A sample of magnesia was interground with 0.010 percent by weight of triethanolammonium phenoxide in a laboratory steel ball mill. For comparison, a blank sample containing no additive was also ground. Each sample was ground for 4125 revolutions at 230°F, using a steel to magnesia ratio of 6.5 to 1. The results were as follows.

<table>
<thead>
<tr>
<th>Amount of Additive</th>
<th>Blaine Surface Area, Cm²/g.</th>
<th>% Increase over blank</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>5217</td>
<td></td>
</tr>
<tr>
<td>Triethanol-</td>
<td>5644</td>
<td>8.11</td>
</tr>
<tr>
<td>ammonium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenoxide</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**EXAMPLE III**

A sample of amorphous silica was interground with 0.04 percent by weight of triethanolammonium phenoxide in a laboratory steel ball mill. For comparison, a blank sample containing no additive was also ground. Each sample was ground for 8855 revolutions at 190°F, using a steel to silica ratio of 6.5 to 1. The results are as follows.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Amount of additive (wt.% additive solids on wt. of silica)</th>
<th>Blaine Surface Area, Cm²/g.</th>
<th>Percent Increase over blank</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.000</td>
<td>10.480</td>
<td>11.91</td>
</tr>
<tr>
<td>Triethanolammonium phenoxide</td>
<td>0.040</td>
<td>11.01</td>
<td>14.1</td>
</tr>
</tbody>
</table>

1 Weight percent additive solids on weight of silica.

**EXAMPLE IV**

A sample of taconite was interground with 0.050 percent by weight of triethanolammonium phenoxide in a laboratory steel ball mill. For comparison, a blank sample containing no additive was also ground. Each sample was ground for 14,880 revolutions at 220°F, using a steel to taconite ratio of 6.5 to 1. The results were as follows.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Amount of Additive (wt.% additive solids on wt. of taconite)</th>
<th>Blaine Surface Area (Cm²/g.)</th>
<th>% Increase over blank</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>5702</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triethanolammonium Phenoxide</td>
<td>0.050</td>
<td>6806</td>
<td>19.4</td>
</tr>
</tbody>
</table>

The additive of the present invention is employed preferably as the sole grinding aid but it should be understood that it can also be employed with a mixture of one or more grinding aids or in admixture with other additives.

1. A composition consisting essentially of a solid, inorganic compound selected from the group consisting of naturally occurring mineral compounds, Portland cement clinker, magnesium and beryllium oxide, and intimately admixed therewith, about 0.001 to 1% weight, based on the weight of said solid compound, of an additive, consisting of a salt of an amine selected from the group consisting of morpholine and an alkanolamine wherein the alkanol group contains about 1–5 carbon atoms and an aryl hydroxy compound wherein the aryl radical is selected from the group consisting of phenyl, naphthyl and substituted phenyl and naphthyl wherein the substituent is selected from the group consisting of nitro, halo, alkyl of 1–5 carbon atoms, aryl, amino and alkoxy of 1–5 carbon atoms.

2. The composition as defined in claim 1 wherein said additive is triethanolammonium phenoxide.

3. The composition of claim 1 wherein said inorganic compound is selected from the group consisting of phosphate rock, iron ore, bauxite, clay, gypsum, limestone, silica, Portland cement clinker, magnesium and beryllium oxide.

4. The composition of claim 1 wherein said solid material is magnesia.

5. The composition of claim 1 wherein said solid material is amorphous silica.

6. The composition of claim 1 wherein said solid material is taconite.

7. The method which comprises intergrinding a solid, inorganic compound selected from the group consisting of naturally occurring mineral compounds, Portland cement clinker, magnesium and beryllium oxide, an amount of an additive consisting of a salt of an amine selected from the group consisting of morpholine and an alkanolamine wherein the alkanol group contains about one to five carbon atoms and an aryl hydroxy compound wherein the aryl radical is selected from the group consisting of phenyl, naphthyl and substituted phenyl and naphthyl wherein the substituent is selected from the group consisting of nitro, halo, alkyl of 1–5 carbon atoms, aryl, amino and alkoxy of 1–5 carbon atoms, the amount of said additive being sufficient to enhance the efficiency of the grinding operation.

8. The method of claim 7 wherein said amount is about 0.001 to 1 percent by weight, based on the weight of the solid compound.

9. The method of claim 7 wherein the solid inorganic compound is Portland cement and said additive is triethanolammonium phenoxide.

10. A composition consisting essentially of Portland cement, and, intimately admixed therewith, about 0.001 to 1 percent by weight, based on the weight of said Portland cement, of an additive consisting of a salt of an amine selected from the group consisting of morpholine and triethanolamine and an aryl hydroxy compound wherein the aryl radical is selected from the group consisting of phenyl, naphthyl and substituted phenyl and naphthyl wherein the substituent is selected from the group consisting of nitro, halo, alkyl of 1–5 carbon atoms, aryl, amino and alkoxy of 1–5 carbon atoms.

11. The composition as defined in claim 10 wherein said amine comprises a mixture of morpholine and triethanolamine and said aryl hydroxy compound is phenol.

12. The composition as defined in claim 10 wherein said additive is triethanolammonium phenoxide.

13. The composition as defined in claim 10 wherein the amount of additive employed is about 0.004 to 0.04 percent by weight, based on the weight of said Portland cement.

14. The method which comprises intergrinding Portland cement with about 0.001 to 1 percent by weight, based on the weight of said Portland cement, of an additive consisting of a salt of an amine selected from the group consisting of morpholine and triethanolamine and an aryl hydroxy com-
5. The method as defined in claim 14 wherein said additive is triethanolammonium phenoxide.
16. The method as defined in claim 14 wherein the amount of the additive is about 0.004 to 0.04% by weight, based on the weight of said Portland cement.