United States Patent Office 3,814,789
Patented June 4, 1974

3,814,789

PROCESS FOR COMPACTING FLUORSPAR FOR METALLURGICAL USE

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No Drawing. Filed Feb. 25, 1972, Ser. No. 229,451
Int. Cl. B01j 2/10
U.S. Cl. 269—117 3 Claims

ABSTRACT OF THE DISCLOSURE

An improved process for compacting finely divided fluorspar for use as a metallurgical flux is provided in which tall oil pitch is added to finely divided wet fluorspar which is then mixed and heated until a uniform coating of the pitch on the fluorspar particles is obtained. The fluospar particles coated with tall oil pitch are then dried to a low moisture content while cooling to produce agglomerates which are then compacted in a suitable manner such as by briquetting. The process provides improved continuity in compacting operations to produce compacted fluorspar with improved physical qualities while permitting the use of tall-oil pitch, an inexpensive binder.

This invention is directed to processes for compacting finely divided fluorspar particles for use as a flux in steel manufacture and other metallurgical operations. Fluorspar may be briquetted, extruded, molded, pelletized or tableted for this purpose in order to overcome the furnace drafts which sweep fluorspar fines out of the furnace.

Various binding additives, both organic and inorganic have been incorporated with fluorspar to assist in compacting. These various additives have been shown in the following U.S. Patents; 2,220,383; 2,220,384; 2,220,385; 2,232,242; 2,459,203; 2,465,955; 2,620,267; 3,027,227 and 3,044,140.

The purpose of the binder additives is to provide a mixture in which fine fluorspar particles are bonded together by the binder when the mass is compacted. The tacky nature of most binders causes considerable difficulty in clogging of the compacting machine and many compacts are broken because of the tendency of the compacts of adhere to the surfaces of the compacting sections and not discharge freely. Briquetting is the preferred type of compacting for finely divided fluorspar. I have discovered a process for compacting finely divided fluorspar which uses tall oil pitch in an improved manner as a superior binding agent. Theh invention produces a fluorspar compact while eliminating blockage of the compacting machine, excessive breakage and dusting. The invention also increases the density of the compact. Moisture penetration is reduced with its resulting disintegration and loss as dust or solid particles in stack gases during steel manufacture.

Sufficient tall oil pitch is added to the fluorspar particles to act as a binding agent. Because of the tacky nature of the mixture, I prefer a continuous operation as distinguished from batch processing. A small amount of water in the fluorspar, and heating of the liquid tall oil pitch and fluorspar while mixing, facilitates thorough mixing and coating of the solid fluorspar particles with pitch. The heating and mixing is continued until a uniform coating of tall oil pitch is obtained on the fluorspar particles. Thereafter, the coated particles are dried and cooled to produce small relatively dry and free flowing, agglomerates which can be compacted in various manners with high efficiency.

Tall oil pitch in the amonut of 2 to 6% of the finely divided fluorspar on a dry basis is added to the fluorspar in a mixing or blending apparatus. A preferred amount of pitch binder is 3 to 4%. Slightly higher amounts than 6% can be used but, generally no additional improvement is obtained. Excessive amounts of tall oil pitch will prevent

free flowing properties in the agglomerated product and prevent satisfactory compacting.

Tall oil pitch is obtained from refining tall oil. Crude tall oil is vaporized and fed into a stripping tower where tall oil pitch is removed from the bottom of the tower. Rosin, fatty acids and other organics pass overhead in the vapor. A typical tall oil pitch which I have used had the following analysis:

Acid number	50
Rosin acid, percent	22
Fatty acids, percent	43
Unsaponifiable, percent	30
Approximate viscosity, centipoises, 100° C.	400
Softening point, ° C.	37

The source of finely divided fluorspar particles for compacting is fluorspar concentrate, fluorspar ore fines and mixtures thereof. The concentrate may be mixed with other finely divided fluorspar-bearing materials or if the fluorspar concentrate is to be diluted to produce compacts of a specified lower calcium flouride concentration finely ground limestone or other non-objectionable inert material is added in required proportions. Calcium fluoride produced as a by-product in procesing fluorapatite rock may be combined with the fluorspar. The metallurgical market requires compacts of various calcium fluoride concentrations ranging from 60 to 94%.

Fines resulting from mining and classifying fluorspar ore are also used. These fines may be used alone or mixed with fluorspar concentrate.

The finely divided fluorspar ore particles range from all passing 8 mesh to virtually all retained on 325 mesh. Fluorspar concentrate particles usually range from 100 to 250 mesh, but some producers furnish product as fine as 50% passing 250 mesh. Fluorspar ore fines are ground or classified to substantially all passing 8 mesh with 60 to 70% passing 16 mesh. The finer solids provide the best compacts since high surface area per unit of weight is required for satisfactory bindering.

The finely divided fluorspar may be wet with water from a previous processing operation and, in this case, additional water may not be required to facilitate mixing. On the other hand, if dry concentrate of ore fines are used, water is added in any convenient manner to aid in the heat distribution and dispersion of the tall oil pitch in the fluorspar.

Generally at least 2% water by weight of the fluorspar particles on a dry basis facilitates mixing. Amounts of water up to 10% are useful. Water in exces of 10% merely unnecessarily burdens the subsequent drying operation. A moisture content of 5 to 10% is preferred.

A thoroughly mixed mass of heated pitch and fluorspar particles containing 2 to 10% moisture is much more plastic and fluid than a mixture of dry fluorspar at the same temperature and the same weight ratio of pitch to dry fluorspar. Since pitch is in a liqud state when heated, the total fluid, pitch and moisture increases fluidity and therefore increases the plasticity and ease of pitch distribution. Thorough mixing and heating of pitch and moist fluorspar is required to provide satisfactory bindering of fluorspar and to obtain the best physical qualities of hardness, resistance to fracture and abrasion and resistance to distintegration from atmospheric moisture when the finished briquette is stored outdoors. Mixing is accomplished in conventional mixing equipment for solids. Mixing is continued until the fluorspar particles are completely coated with liquid pitch.

The temperature of the mixing mass of fluorspar and tall oil pitch is raised by applying heat in any conventional manner such as by mixing in steam jacketed vessels.

The higher the temperature the easier it is to thoroughly mix the pitch with the fluorspar to obtain a coating of

liquid pitch on all solid particles, and thereby provide a condition for complete adhesion of the solid particles when the mixture is subsequently compacted. Temperatures in the range of 145° F. to 180° F. are preferred while a mixture temperature as high as 220° F. can be used. At temperatures lower than 120° F. mixing is not satisfactory since the solid particles are not uniformly and completely coated and blotches of unmixed pitch may be observed in the finished compacts. Temperatures higher than 200° F. further improve ease of mixing but are too costly to justify unless the moisture content of the solids is so high that additional heating is required to dry the mixture.

The next of the two most important steps in my process is to reduce the moisture content of the thoroughly mixed fluorspar-tall oil pitch. Cooling of the mixture to about atmospheric temperature in order to congeal the dispersed tall oil pitch is of equal importance. Drying and cooling may be conveniently done in a single operation.

I have found that reducing the moisture content and cooling of the pitch coated fluorspar particles, preparatory to briquetting or other compacting processes causes the particles to develop into a relatively dry free-flowing mass of granular to pebble size agglomerates which do not adhere to the feeder and the molding pockets of the briquetting machine. Briquettes and tablets formed under these conditions discharge freely from the pockets and are so firm that they do not disintegrate or break in mechanical handling prior to curing.

If the heated mixture of fluorspar and pitch is not sufficiently reduced in moisture content and cooled to congeal the pitch preparatory to briquetting, the feeding device of the briquettes will plug, the briquettes will not discharge freely from the briquetter and intolerable damage of the briquettes occurs in mechanical handling. Furthermore, the broken surfaces of the damaged briquettes abrade easily even after curing. This causes excessive dusting when handled. Such broken surfaces permit moisture to readily penetrate the briquettes causing their further disintegration.

The pitch coated fluorspar particles should be dried until the residual water does not exceed 4%, to insure good quality briquettes. Generally, the dried agglomerates will be within the range of 1 to 4% water. A slightly harder briquette is obtained when the moisture is within the range of 2.5 to 3% and this water content is preferred.

The coated fluorspar particles are conveniently and inexpensively dried by passing chilled air through them while they are simultaneously cooled. Chilled air may be used to increase the rate of drying and cooling. The hot pitch coated particles may be fed to a steel rotary cooler-drier equipped with lifting flights to lift and distribute the pitch coated particles in a stream of chilled air which flows counter-current to the flow of solids. During hot weather the atmospheric air may be chilled to approximately 40° F. In cool weather when the humidity of the atmosphere is relatively low there is no need to chill the air. The drying and cooling of the fluorspar particles is only dependent on sufficiently low humidity and/or low temperature of the air.

Transfer of heat from the fluorspar and pitch to the air increases the temperature of the air and resultingly decreases the relative humidity of the air thereby causing vaporization of moisture from the fluorspar and particles. The combined effect of the air being heated by the fluorspar and vaporization of water from the fluorspar and pitch causes the coated particles to dry and cool, to reduce fluidity through loss of moisture and to change the pitch from liquid phase to a firm plastic state. Cooling is continued until the pitch coated fluorspar particles are at about atmospheric temperature, i.e., within the range of 40 to 90° F. Temperatures of 50 to 70° F. are preferred for compacting purposes.

Over the range of moisture and temperature cited we find an optimum relationship between moisture and temperature for compacting. For example, if the moisture is 1.5%, an 80° F. temperature is satisfactory for feeding the briquetter and forming briquettes efficiently and of good physical quality. Conversely, 4% moisture and 50° F. temperature will provide about the same effect in feeding and briquetting quality.

The use of a rotary cooler-drier unit using air to cool and dry the pitch coated fluorspar particles is particularly useful but not specifically required. Such equipment is adaptable as a unit operation to simultaneously cool and dry and eliminate sticking of the mixture to the interior surface. When using other types of equipment for the cooling and drying operation, such as water cooled surfaces of a mechanical mixer, a thermo-screw conveyor or metal cooling belt conveyor, the particles stick to the surfaces which transfer heat from the particles. The time required for mixing, drying and cooling is not critical in my process.

Drying and cooling the pitch coated fluorspar particles as described above produces a relatively dry-free-flowing mass of granular to pebble size fluorspar agglomerates. The agglomerates are then fed into a compacting machine such as a briquetting, molding, pelletizing or other type compacting machine. Pelletizing fluorspar materials is described in U.S. 2,220,383.

Fluorspar compacts made in the above manner are generally satisfactory for metallurgical furnace use. However, these compacts are not as resistant to moisture and fracture as may be obtained by an added curing operation. When fluorspar compacts made from moist fluorspar as described above are then heat cured at an elevated temperature they have a much higher degree of hardness, resistance to moisture penetration, abrasion and fracture. Heat cured fluorspar compacts are satisfactory for outdoor storage even during below freezing temperatures.

The fluorspar compacts are cured by heating them to a temperature within the range of 200° F. to 500° F. for at least 30 minutes. A curing time of 60 minutes is also satisfactory while longer heating times do not generally lead to any significant improvement in physical properties.

Curing of the fluorspar compacts is conveniently done by subjecting them to circulating hot air in a hot air dryer, with air temperatures in the range of 270° F. to 500° F.

The fluorspar compacts will reach a temperature within the range of 200° F. to 500° F. during the curing operation. Following the curing operation, the fluorspar compacts are cooled to atmospheric temperature. This may be accomplished by forced-air cooling or by allowing them to cool through natural loss of heat by radiation and convection.

The best mode of practicing my invention will be apparent from a consideration of the following example:

Tall oil pitch having a softening point of 37° C. and finely divided fluorspar particles were continuously added to a steam jacketed paddle mixer. The fluorspar was composed of 70% by weight of filter cake concentrate containing 97% calcium fluoride by weight on a dry basis and 30% by weight of fluorspar ore fines containing 55% calcium fluoride by weight. The moisture content of the mixed concentrate and ore fines was 7.88% by weight. The tall oil pitch was added at a rate to produce a concentrate of 4% by weight of the combined concentrate and fines on a dry basis.

Saturated steam at 100 p.s.i.g. was fed to the jacket. Average retention time of the mixture in the mixer was about five minutes. The average temperature of the coated particles discharging from the mixer was 142° F.

An open trough with heat applied to the exterior was used to transfer the pitch coated particles to the cooler-drier unit. The average temperature of the particles being continuously fed to the cooler-drier was 146° F. and moisture content was 4.1%. The feed rate averaged 16.16 lb. per minute, dry weight. The fluorspar agglomerates discharged from the cooler-drier averaged 16.59 lb. per minute (16.16 lb. per minute, dry weight), containing 2.63%

moisture and averaged 50° F. temperature. The cooled dried material discharged from the cooler totaled 1244 lb. over a period of 75 minutes.

Atmospheric temperature during the run was about 91° F. Chilled air flowing counter-current to the mixture in the cooler was 306 c.f.m. at 40° F. and saturated with water vapor. Air leaving the cooler averaged 82° F. and 81° F. wet bulb.

The cooled dried particles consisted of granular to pebble size agglomerates and was not at all tacky but slightly dusty. The 1224 lbs. collected was fed to a commercial briquetting machine equipped with an auger type feeder. The material did not stick to the auger nor the molding pockets of the briquetter. All briquettes were uniformly formed, dense, hard and did not fracture when being transferred from the briquetter to the perforated steel conveying belt of the cuing oven.

Some of the briquettes were withdrawn for testing but the remainder were cured in the oven for forty minutes at progressively increasing air temperatures from 350° F. to 420° F. and then cooled to room temperature. After two days in dry storage some of the uncured and cured briquettes were dropped twenty feet to a concrete surface for fracture testing. Some cured fluorspar-pitch briquettes, mixed at approximately 100° F., and from fluorspar initially containing 3% moisture, were also drop-tested. Some competitive briquettes with an undetermined organic binder were also drop-tested.

TABLE I.—DROP TESTING

	Fractured, percent
Hot mixed, cured	30
Hot mixed, not cured	50
Cold mixed, cured	30
Competitive	33

In none of these cases did fracture cause complete disintegration.

Other samplings of these same lots were weighed and then immersed in water for 16 hours. They were then surface dried with paper towels. Then they were exposed for one hour in the laboratory at room temperature and weighed to determine moisture penetration. Six and one half hours after removal from the water soaking bath they were subjected to hand-twisting and drop-testing. The drop test in this case consisted of individually dropping each briquette six feet to a concrete surface.

Hand twisting consisted of holding the briquette between the thumb and index finger of each hand with hands in fist position and thumbs up, adjacent and parallel to each other and the longitudinal axis of the briquette at right angles to the sides of the thumbs. When held in this way and then twisting with the maximum hand force of an average man, a briquette will not break if bindering is satisfactory. The hand-twisting and drop tests are not well based scientifically but do give a good indication of resistance to fracture in the case of drop-testing and resistance to forces which develop in stock-piling, shipping, and handling commercial quantities.

TABLE II.—HAND TWISTING AND DROP TESTING

	Percent		
Sample	Water absorption	Hand-twist breakage	Drop-test fracture
Hot mixed, cured	1.59	10	29
Hot mixed, not cured	2.78	50	None
Cold mixed, cured	3.75	100	33
Competitive	3.46	20	29

More chipping than complete fracturing occurred in the 29% shown as fracturing in drop-testing the hot mixed, cured briquettes.

Having thus described my invention, I claim:

1. The process for producing fluorspar compacts from fluorspar particles comprising:
   - adding while mechanically mixing, from 2 to 6% by weight of tall oil pitch to finely divided fluorspar particles whose water content has been adjusted within the range of 2 to 10% by weight by adding water if necessary;
   - heating and mechanically mixing the said wet fluorspar and tall oil pitch at a temperature within the range of 120 to 220° F. until the fluorspar particles are uniformly coated with tall oil pitch;
   - continuing mechanically mixing the said uniformly coated fluorspar particles in a manner to form agglomerates while cooling to atmospheric temperature to congeal the dispersed tall oil pitch while
   - simultaneously drying the pitch coated fluorspar particles to a residual water content not exceeding 4% by weight until dry free-flowing pitch coated fluorspar agglomerates are obtained; and finally
   - introducing the cooled and dried pitch coated fluorspar agglomerates to a compacting machine to produce fluorspar compacts.

2. The process of claim 1 in which the pitch coated fluorspar agglomerates are compacted in a briquetting machine.

3. The process of claim 1 in which the fluorspar compacts are heat cured by raising their temperature to within the range of 200° F. to 500° F. for a period of 30 to 60 minutes and thereafter cooling them to atmospheric temperature.

References Cited

UNITED STATES PATENTS

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