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PURIFICATION OF ROCK MINERALS

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6 Claims. (Cl. 209—166)

(Granted under the act of March 3; 1883, as amended April 30, 1928; 370 O. G. 757)

The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to me of any royalty thereon in accordance with the provisions of the act of April 30, 1928 (Ch. 460, 45 Stat. L. 467).

This invention relates generally to the purification of rock minerals and particularly to the separation of silica and silicates from phosphates in the non-metallic minerals of the type found in Florida, Tennessee, Idaho and Montana.

During the early part of the 20th century the phosphate deposits, particularly those of Florida, were worked and processed, first by merely crushing the ore and later by methods in which the phosphates were extracted from the ore. As late as the last decade this method of concentrating the valuable mineral away from the residue became highly developed by processes variously referred to as froth flotation, film flotation, loose agglomeration on wet stratifying tables, certain of which are described by O'Meara, R. G., in a report of investigation No. 3139, Bureau of Mines, 1931, entitled "Added recovery by hydraulic sizing of fine material in the land-pebble district of Florida" and by O'Meara, R. G. and Pamplin, J. W., in a report of investigation No. 3195, Bureau of Mines, 1932, entitled "Selective oiling and table concentration of phosphatic sands in the land-pebble district of Florida." These processes may be briefly described as consisting of:

Wet screening the ore at about 20 mesh to recover the plus 20-mesh material, the finer material going to waste, or further separated by hydraulic classifiers. The material is agitated for a short period with 4 to 5 lbs, of previously emulsified fuel oil (21° to 22° B.) and 1½ to 2 lbs. of sodium oleate per ton, the phosphate grains alone taking up the oil and becoming agglomerated. This agglomerate is then treated by tabling to recover the high grade concentrate.

From experience it has been found that any reagent used in the process of refining phosphate ores which costs more than one tenth the market price of the concentrated phosphate mineral renders such process impracticable since at its best the market for highest grade (70–80% B. P. L.) refined phosphate ore was between $3.50 to $4.00 per ton and the prevailing price is around $2.50 per ton.

In these prior methods in which the valuable ore is floated from the gangue residue, filming of the phosphate has been accomplished by use of fatty acids, fatty acid sodium salts (soaps) and related agents in which the active constituent was the anion and for this reason have been referred to as "anionic agents". These anionic agents film or adhere to the phosphates in preference to filming or adhering to the silica and silicates of the ore. This film on the phosphates is easily augmented by and can be enhanced in thickness and water repellence by adding oils of cheaper costs if desired, such as vegetable, animal or mineral oils.

To reduce the amount of filming agents depressing salts such as water glass have been added to the ground ore pulp.

However, I have found that the presence of iron and aluminum salts minimizes the selective characteristic of these anionic agents for the reason that they activate the silica and silicate minerals and are not desired in "soap flotation or table agglomeration".

Furthermore, I have found that with the phosphate ores the phosphate is spongy and of high surficial area in comparison with smooth surfaces of low surficial area of the compact silica minerals. Accordingly a much larger amount of filming agent is required than if the silica and silicate minerals were filmed and floated.

I have also found that in agglomerate tabling there is a distinct advantage in removing the major mineral by filming and agglomeration and have discovered a process of concentrating the gangue away from the ore instead of concentrating the valuable mineral.

In this process I make use of "cationic agents" (so named because, in contrast to the soaps, the active agent is in the cation or positive ion of the compound) which film quartz, clay, silicates and alumino silicates and the other acidic minerals in preference to some of the more basic minerals such as the phosphates. These cationic agents are particularly adaptable to the separation of quartz, clay, silicates and alumino-silicates from phosphates because of the presence of iron and aluminum salts in the ores.

Although the iron and aluminum salts in the phosphate ores are in relatively non-ionized state so that their activating effect is small, I have found that because of the preponderance of the silica and silicate minerals in the Florida ores the addition of one to two pounds of these salts per ton to the ore pulp, the amount of filming reagent is appreciably reduced since the cost of these activators is practically negligible in comparison with the cost of the filming agents.

In concentrating phosphate ores as much clay as possible should be removed before attempting any filming method of concentration, because the clay is very absorbent and is a thief of filming reagents. Washing out the clay is already common practice but the washing also removes finely divided phosphate. One aspect of my invention is partial or complete removal of clay by use of a cationic reagent of low collecting power and low cost and any metal ion activators are also excluded to prevent activating quartz and feldspar during this step. Suitable reagents

for clay removal without losing finely divided phosphate are compounds of the short-chain amino type, like diamyl amine or triethanol amine, in which no substitute of over five carbon atoms is present; or reagents of the simpler nitrogenous bases like pyridine or its related homologues and derivatives like quinoline (where a pyridine ring has four extra carbon atoms in a side substituent). Cationic reagents with substituents that are too long are too strongly adsorbed on clay and will be required in greater amounts as the length of the carbon chains increases. Therefore, compounds whose substituents contain not over five carbon atoms are best adapted to clay removal by filming methods. From one-half pound to five pounds of reagent per ton solids treated is sufficient.

The resulting tailing from this clay removing operation may then be concentrated by filming methods to separate the quartz and other silicates from the phosphate. For this separation cationic reagents containing substituted ammonium ions are used, in which the substituents are groups with over twelve carbon atoms, such as mono-lauryl amine, di-lauryl amine, tri-lauryl amine, tetra-lauryl ammonium hydroxide, or the corresponding cetyl, stearyl, or oleyl bases or the simple salts of these bases. Less than two pounds of these compounds per ton of feed will suffice if the clay has been well removed by the use of the short-chain amines or ammonium salts. The poorer the colloidal clay removal of the first step, the higher the reagent consumption in this second step. Better adherence of these reagents to quartz and silicates is secured if metal ion activators like iron or aluminum ions or their anologues, to the extent of one or two pounds per ton ore, are used. To further enhance greasiness or water-repellence of the film on the mineral, any easily fluid hydrocarbon oil can also be added to the pulp during mixing. From one to ten pounds per ton solids will suffice. This addition is optional but tends to permit economy in use of cationic reagent. The reagents suitable for clay removal are not efficacious for filming quartz or feldspathic minerals. The films they produce are not sufficiently greasy in character to permit good water-repellence from the glassy quartz or silicate surfaces. Reagents with substituents intermediate between five and twelve carbon atoms are more strongly adsorbed on clay minerals, so that increasing amounts of them are needed, but not sufficiently efficient for filming the quartz and silicate minerals.

In my process of filming and separating siliceous minerals the readily available substituted ammonium compounds from the simple amines to the quaternary ammonium salts function particularly well when the configuration and magnitude of the substituents for the hydrogen of the ammonia or ammonium radical are selected with respect to the particular mineral to be filmed.

Examples of these cationic agents which I have used with success are the diethanol and triethanol amines. Diamyl-amine and the amines of longer chain substituents, especially those with eight or more carbon atoms in the chain have proven especially useful. Quaternary salts which are well adapted for use in this process are represented by tri-methyl-stearyl ammonium bromide and the corresponding cetyl-compound, lauryl-pyridinium iodide or bromide and the hydrochloride and free base of lauryl amine.

In my process as distinguished from the prior processes as applied to low grade phosphates the minor mineral is the one which remains in the riffles of the agitating table and travels along their length and over the end. The major mineral is filmed and agglomerated and immediately rafted over the side of the table through the shortest path.

Since ores from the Sangully mine in Florida consist primarily of clay, silica, and phosphate, the feldspars and mica having weathered into the clay, so that they are removed by the desliming process, the application of my process to ore from this mine will serve to illustrate my invention.

A sample of the quartz-phosphate sands of this mine containing about 29% phosphate was deslimed by the process above described and the wetted thick sand pulp filmed by the addition of 0.44 pound tri-methyl-stearyl ammonium bromide accompanied by 3.6 pounds crude oil per ton solids. This was separated on a Wilfley table, the filmed and agglomerated quartz being rafted over the side of the table and referred to hereinafter as the concentrate, with retreatment of tailing to give a scavenger concentrate which was added to the first concentrate with the following results as determined by grain count:

	Weight	Phosphate
		Percent
Combined concentrate (quartz)	127	2.2
Tailing (phosphate)	98	75.0

When the ore contains a considerable amount of clay, quartz and aluminosilicates such as micas and feldspars which will not ordinarily respond to one cationic agent, I have separated the ore first by filming the clay with a soluble type of short chain amino compound such as di-amyl-amine or tri-ethanol-amine with non-saponifiable oils and froth floated the filmed clay and then filmed the quartz and feldspar with a quaternary ammonium hydroxide or salt with at least one substituent radical of the long chain type like tri-methyl-cetyl ammonium iodide. Alternatively, I have filmed the aluminosilicates such as the micas and feldspars with salts of a single long substituent primary amine such as the hydrochloride or primary lauryl amine. While I have found that the use of non-saponifiable oil in froth flotation leads to economy in the use of the cationic agents, it is not so necessary as in the agglomerate separation process and may be omitted if desired without departing from the spirit of my invention.

From the foregoing it is apparent that detail changes may be made to adapt my process to ores of different composition without departing from the spirit of my invention as defined in the claims appended hereto and it is to be understood that the foregoing description is merely illustrative of my invention without limitation to the specific compounds mentioned therein.

Having thus described my invention, what I claim is:

1. The process of concentrating phosphate bearing minerals which consists in agitating a pulp of the ore containing the phosphate bearing mineral with two to five pounds per ton of a cationic compound of short chain amino type with substituents containing from two to five carbon atoms whereby the clay is made water

repellent, treating the pulp with an aqueous separation process to remove the filmed clay, agitating the resulting tailing with a mineral oil and a cationic substituted ammonium compound with 1 to 4 substituents carrying over 12 carbon atoms in the presence of a metal salt of the iron and aluminum whereby the quartz particles are made water repellent, and separating from the pulp a material relatively rich in silicious gangue and relatively poor in phosphate values as a concentrate and collecting the tailing as a relatively rich phosphate.

2. The process of concentrating phosphate bearing minerals which consists in agitating a pulp of the ore containing the phosphate bearing mineral with two to five pounds per ton of a cationic compound of short chain amino type with substituents containing two to five carbon atoms whereby the clay is made water repellent, treating the pulp with an aqueous separation process to remove the filmed clay, agitating the tailing resulting with a mineral oil and a cationic substituted ammonium compound with one to four substituents carrying over twelve carbon atoms in an amount less than 2 pounds per ton of ore, and separating from the pulp a material relatively rich in siliceous gangue and relatively poor in phosphate as a concentrate and collecting the tailing as a relatively rich phosphate.

3. The process of concentrating phosphate bearing minerals which consists in agitating a pulp of the ore containing the phosphate bearing mineral with a cationic compound of short chain amino type with substituents containing two to five carbon atoms and a mineral oil whereby the clay is made water repellent, treating the pulp with an aqueous separation process to remove the filmed clay, agitating the resulting tailing with a cationic substituted ammonium compound with one to four organic radicals carrying over 5 carbon atoms in an amount less than 6 pounds per ton of ore, and separating from the pulp a material relatively rich in siliceous gangue and relatively poor in phosphate values as a concentrate and collecting the tailing as a relatively rich phosphate.

4. In a process of concentrating phosphate ores the step of filming the clay in the absence of activators with two to five pounds per ton of ore of a cationic compound of the short chain amino type with substituents containing not over five carbon atoms.

5. In the process of concentrating phosphate ores the step of filming the clay with a cationic short chain nitrogeneous aromatic base with substituents containing from 2 to 5 carbon atoms in an amount less than five pounds per ton of ore.

6. The process of concentrating phosphate bearing minerals which consists in agitating the pulp of the ore containing the phosphate bearing mineral with mineral oil, a cationic substituted ammonium compound with one to four organic radicals carrying over 5 carbon atoms, and an activating agent of the iron and aluminum class causing the siliceous gangue to have a surficial affinity for the substituted ammonium compound, separating from the pulp a material relatively rich in siliceous gangue and relatively poor in phosphate values as a concentrate and collecting the tailing as a relatively rich phosphate.

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