United States Patent

Sanders et al.

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[54] MINERALS SEPARATION PROCESS

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[52] **U.S. Cl.** **209/166**

[51] **Int. Cl.** **B03d 1/02**

[58] **Field of Search** 209/166, 167

[56] **References Cited**

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[57] **ABSTRACT**

Titanium oxide containing concentrates are recovered from sand composed in the particle size range of 100 mesh and smaller of titanium oxides, heavy metal silicates, and silica. A plural stage flotation process is used. In the first stage the sand in the above size range is subjected to flotation using air and an anionic collector to yield a heavy mineral concentrate. The second stage flotation involves treating this heavy mineral concentrate with nitrogen and an anionic collector to float off the heavy metal silicates, the titanium oxide concentrate remaining in the tailings.

6 Claims, No Drawings

MINERALS SEPARATION PROCESS

This invention relates to beneficiation of heavy mineral sands and more particularly to the recovery of titanium oxide concentrates from sands whose heavy mineral contents are of small particle size (100 mesh or below).

Within the interior of the United States, particularly in areas along the Cretaceous coast lines there are potentially valuable heavy mineral placer deposits. A feature of these sands is that the heavy minerals are of small particle size—i.e., most of the heavy minerals exist in the form of particles of 100 mesh size or smaller. In composition the small particle fractions of these sands are made up principally of titanium oxides, heavy metal silicates, and of course silica or quartz. The titanium oxides usually involve mixtures of ilmenite, leucoxene and rutile. The heavy metal silicates present invariably include zircon and frequently include monazite or staurolite or both. Other silicates such as kyanite or sillimanite or both are also present in these small particle size fractions.

So far as is known no commercially feasible method for recovering a titanium oxide concentrate from sands of the foregoing character has been reported in the art.

In accordance with this invention titanium oxide containing concentrates are efficiently and economically recovered from the small particle size fractions of such sands by means of a plural stage flotation process. The first stage of the process involves subjecting the sand within the size range of 100 mesh and smaller (e.g., within the range of 100/400 mesh and preferably within the range of 100/200 mesh) to one or more flotations using air and an anionic collector such as a carboxylic acid collector to obtain a heavy mineral concentrate enriched in titanium oxides and heavy metal silicates. In this first stage the tailings are composed predominantly of silica.

In the second stage of the process the heavy mineral concentrate from the first stage is subjected to one or more flotations using nitrogen and an anionic collector (e.g., a carboxylic acid collector) to float off heavy metal silicates and leave as tailings a concentrate enriched in titanium oxides.

It will be seen that the process is a paragon of simplicity. The use of expensive chemicals and condition operations or the like is kept to a minimum. Moreover, titanium oxide containing concentrates of good quality are readily recovered as the tailings from the second stage flotation(s).

With most sands of the type with which this invention is concerned it is desirable to initially screen or otherwise classify the ore. As noted, the invention is particularly adapted for use with sands whose heavy mineral content is concentrated within the fractions between 100 and 400 mesh size. For example efficacious results have been achieved on subjecting a 140/200 mesh size fraction of heavy mineral alluvial sand to the plural stage process.

In both of the flotation stages any suitable anionic collector may be used. For example use may be made of such common reagents as oleic acid, coconut oil fatty acid, talloel, saponified fatty acids, saponified talloel, and others of a similar nature. Long chain mono- and poly- unsaturated monocarboxylic acids similar to oleic acid and the corresponding saturated fatty acids are generally suitable.

In the first stage it is particularly desirable to use a carboxylic acid collector while keeping the pH of the aqueous pulp at from about 2.5 to about 7. In most cases the best results are achieved when the pH of the pulp is in the range of from about 3.5 to about 5 and accordingly this range is preferred. The inclusion within the pulp of a dispersing agent such as sodium fluoride has also been found advantageous.

The amount of the collector used will of course be governed to some extent by the character of the sand being treated, the flotation conditions being used, and the identity of the particular collector selected for use. Generally speaking, however, the amount used in the first stage will range from about 0.1 to about 5 pounds per ton of solids treated. Amounts ranging from about 2 to about 4 pounds per ton are generally preferred.

For the second stage flotation operations the use of oleic acid as the collector has been found to be of advantage especially when the aqueous pulp also includes sodium carbonate. However, other carboxylic acid collectors may be used, e.g., long chain mono- or poly- unsaturated monocarboxylic acids. As in the case of the first stage flotation(s) the amount of the collector employed will vary depending upon its identity, the make-up of the solids being processed, and the flotation conditions being utilized. However, generally speaking the amount of the collector for the second stage will be in the range of from about 0.1 to about 5 pounds per ton of solids treated. Good results are achieved when the second stage pulp has a pH of in the range of from about 7 to about 11, preferably 8 to 10.

In the first stage air or air enriched with oxygen is used as the gas phase. On the other hand in the second stage use is made of either nitrogen or air from which the oxygen has been largely if not entirely removed.

The pulp loadings in both stages of the process will vary from about 5 to about 40 percent depending upon the properties of the solids being processed. The flotations will normally be conducted at temperatures within the range of from about 20° to about 60° C., temperatures in the range of from about 30° to about 50° C. being generally preferred. Flotation times are generally up to about 5–10 minutes. The optimum flotation conditions for use with any given ore can readily be ascertained by means of a few preliminary experimental trial runs.

The remaining conditions of the flotation steps are along conventional lines. For example common modifiers, frothers, dispersing agents (e.g., sodium silicate), or like reagents may be used if desired.

In order to still further appreciate the practice and advantages of this invention reference should be had to the following illustrative example.

EXAMPLE

A heavy mineral alluvial sand from Tennessee was used in these operations. Petrographic mounting showed that the sand contained ilmenite, leucoxene, rutile, kyanite, zircon and quartz. Over-all the sand contained titanium minerals in amount equivalent to about 7.4 percent TiO_2, iron minerals equivalent to about 1.9 percent of Fe, and aluminum minerals equivalent to about 5.6 percent Al_2O_3. The balance was chiefly silica and zirconium species.

The sand was dried and screened. The relative amounts of each fraction and its analysis for aluminum, iron and titanium are given in Table I.

TABLE I

Classification and Partial Analysis of a Heavy Mineral Alluvial Sand

Size Range	Percent	Analysis, Wt. % Al_2O_3	Fe	TiO_2
/50	3	*	*	*
50/100	6	19.7	1.9	3.2
100/140	65	6.4	0.8	1.5
140/200	12	5.7	3.3	13.6
200/	14	14.1	6.4	30.4

Using a Denver Equipment Company laboratory flotation machine, model D, multiple flotation runs were made on the 140/200 mesh fraction of Table I. In each of the nine runs the pulp had a pH of 3.5 and contained sodium fluoride equivalent to 3.3 pounds per ton of sand and a commercially available tall oil fatty acid collector in amount equivalent to 2.5 pounds per ton of sand. The flotations were conducted at 38° C. The collectives from these nine runs (12.7 percent of the 140/200 mesh fraction) were combined, as were the tailings.

The combined collectives from the initial flotations were subjected to a second series of flotations using the same reagents under the same conditions with the exception that the tall oil fatty acid collector was employed in amount equivalent

to 5 pounds per ton of collective concentrate fed. In these flotations 60.7 percent of the total floated while 39.3 percent did not float.

The flotation cell was then modified to use nitrogen gas rather than air and the total, combined collective concentrate from the second series of flotations was again floated but in this instance using sodium carbonate and oleic acid, each at the one pound per ton level. The pH of the pulp was approximately **8**. In this nitrogen-induced flotation operation, 48 percent of the material floated, the tailings amounting to 52 percent.

The analyses for aluminum, iron and titanium on each of the above collective concentrates and corresponding tailings are presented in Table II.

TABLE II.

Partial Analysis of Flotation Concentrates, Wt. %

Sample	Al_2O_3	Fe	TiO_2
Initial Collective Concentrate	4.4	5.1	40.9
Initial Tailings	1.8	1.5	8.5
Intermediate Collective Concentrate	3.1	5.9	47.9
Intermediate Tailings	2.6	4.3	32.5
Final Collective Concentrate	5.1	4.3	45.4
Final Tailings	1.7	5.9	70.3

We claim:

1. A process for the recovery of a titanium oxide containing concentrate from a sand composed in the particle size range of 100 mesh and smaller of titanium oxides, heavy metal silicates, and silica which comprises:

a. subjecting the sand within said size range to flotation at a pH of from about 2.5 to about 5 using air and a carboxylic acid collector to obtain a heavy mineral concentrate enriched in titanium oxides and heavy metal silicates;

b. subjecting the heavy mineral concentrate to flotation using nitrogen and an anionic collector to float off heavy metal silicates and leave as tailings a concentrate enriched in titanium oxides; and

c. recovering said tailings.

2. The process of claim **1** wherein the sand is within the 140/200 mesh range.

3. The process of claim **1** wherein in Step (a) the collector is a carboxylic acid collector and the pH of the pulp is from about 3.5 to about 5.

4. The process of claim **1** wherein in Step (b) the collector is a carboxylic acid collector and the pH of the pulp is from about 7 to about 11.

5. The process of claim **1** wherein in Step (a) the collector is a carboxylic acid collector and the pH of the pulp is from about 2.5 to about 5 and wherein in Step (b) the collector is a carboxylic acid collector and the pH of the pulp is from about 7 to about 11.

6. The process of claim **1** wherein the sand is within the 140/200 mesh size range; wherein in Step (a) the collector is a tall oil fatty acid collector, the pulp contains sodium fluoride dispersing agent, and the pH of the pulp is about 3.5; and wherein in Step (b) the collector is oleic acid, the pulp contains sodium carbonate and the pH of the pulp is about 8.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,669,266 Dated June 13, 1972

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 21, reads "a carboxylic acid collector", should read -- a tall oil fatty acid collector -- . Column 4, claim 3 should read as follows:

3. The process of Claim 1 wherein in Step (a) carboxylic acid collector and the pH of the pulp is from about 3.5 to about 5.

Signed and sealed this 27th day of February 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents