Patented Apr. 12, 1949

2,466,671

UNITED STATES PATENT OFFICE

2,466,671

FROTH FLOTATION OF NONMETALLIC ORES WITH BLACK LIQUOR SOAP IN ACID CIRCUIT

Elmer William Giesecke, Old Greenwich, Conn., assignor to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application September 22, 1945, Serial No. 618,052

2 Claims. (Cl. 209—166)

1

This invention relates to the beneficiation by froth flotation of the mineral values of various ores. In particular, it relates to a novel reagent combination suitable for use in beneficiating those non-metallic ores which are amenable to flotation with anionic promoters of the fatty-acid soap type and to a method of using such reagents.

Beneficiation of various ores by froth flotation, taking advantage of the selective affinity of various materials for particular mineral constituents has come to be common practice. One of the most common procedures in that field is the use of a fatty acid, or a soap thereof, as the selective reagent. An excellent illustration of such usage is in the beneficiation of phosphate rock, particularly the treatment of rock from the Florida Pebble Phosphate District. Since most of the problems to be overcome are met in this operation, the present invention, although not necessarily so limited, will be principally illustrated with relation thereto. This is a particularly good illustration since it represents one of the best examples of large-volume, low-cost operation in which even small savings per unit become of marked commercial importance.

For many years, in this field, the practice has been standardized on a flotation agent combination comprising an alkali, such as caustic soda; a fatty acid, such as oleic acid or the like; and an unsaponifiable oil such as kerosene or fuel oil. The actual process of using these agents may be varied. For example, the reagents may be precombined before being fed to a pulp of the ore or they may be fed separately in various sequences or combinations. They may be added to the ore pulp in a preconditioning operation or during flotation. Supplementary conditioning, dispersing or depressing agents are also sometimes used. Regardless of procedure, however, the reagent combination normally is comprised of one representative of each of these three classes of materials.

A number of reasons contributed to the development of this practice. A straight oil flotation, useful in some fields, suffered from fairly high re-

2

agent cost. Also, because it gives a very poor quality of froth it does not readily lend itself to cleaning operations and when used on phosphate rock the grade of concentrate obtained is too limited. On the other hand, a fatty acid alone did not prove successful in any ordinary procedure. Saponified fatty-acids in some cases proved somewhat more effective. Even with soaps however, consumption was high and the metallurgical results were generally poor. In compromising between these factors, it came to be considered necessary to use with the fatty acid both a saponifying agent, the caustic soda; and a modifying agent, the oil. This was thought necessary in order to insure efficient distribution and lower the fatty-acid consumption.

Having come to be more or less standardized practice, the art began to seek more economical reagents. Principally this led to variations in the nature and amount of the fatty-acid used. Some appear to have greater selectivity, others give equivalent results only when used in excessive quantity. Talloel, a mixture of fatty and resin acids, was generally found the most economical of the fatty-acid reagents. In some cases, for example in phosphate flotation, it also was found to be one of the most efficient. Like other fatty-acid reagents, however, for best results it was generally considered desirable to use therewith a saponifying agent and, in phosphate flotation, a non-saponifiable oil.

Where talloel or a talloel soap can be successfully used, a natural inclination is to attempt to make use of the less expensive, crude, black-liquor soap. In addition to its general availability and low cost, such material looks particularly attractive because it is in soap form. It would appear therefrom that considerable economy in alkali consumption might be effected by its use.

Unfortunately, a direct substitution of black liquor soap for a fatty acid or the talloel of the prior art, or for soaps of these materials, does not produce satisfactory results. Such substitution, particularly in phosphate flotation, does not give results which are of sufficient utility to be com-

mercially acceptable. There remained, therefore, the desirability of using black liquor soap as a substitute for flotation reagent materials in common use, but no practical method of satisfying the demand.

It is, therefore, the principal object of the present invention to develop a process in the practice of which black liquor soap can be utilized to produce an effective and acceptable beneficiation of non-metallic ores. In particular, it is one of the principal objects of the invention to devise a process whereby black liquor soap can be effectively used to reduce the acid-insoluble content of phosphate concentrates.

Surprisingly, the desired object of the invention can be easily and simply accomplished by the exercise of a practice which is exactly contrary to that taught by the prior art. According to the present invention, it has been found that the desirable results are accomplished, not by using the black liquor soap in conjunction with an alkali, but by carrying out the operation in a circuit to which a strong acid has been added. This is particularly surprising since, as noted above, effective results in an anionic flotation of ores such as pebble phosphate were previously considered possible only on the presence of excess alkali. On the contrary, in the practice of the present invention, the optimum results in phosphate flotation are obtained when the tailing water has a pH less than 6.9.

In this respect it should be noted that an ore pulp frequently may appear to have an alkaline pH whereas the tailing water may be distinctly acid. Whether this is due to the alkaline reaction of black liquor soap or to some pulp pretreatment or to the presence of other reagents, however, may be uncertain. An instance of this may be found for example in phosphate floatation. The pulp even after being conditioned with the other reagent or reagents in the presence of the acid may have an apparent pH of 7.0 to 7.5, yet the pH of the rougher tailing water will be only 6.5–6.7. Where there is a discrepancy between the apparent pH of the ore pulp and that of the tailing water, the latter should be the chosen control since the removal of much or all of the solids content therefrom enables a more accurate reading to be taken.

It is for a similar reason that the beneficial effect of adding extra acid in the present process may not always be immediately observable. For example, a particular mill may be using process water which naturally, or because of prior use, has an inherent pH less than 6.9. In such cases addition of more acid, to a phosphate flotation for example, will not produce a particularly marked improvement in grade over that obtained when using black liquor soap without added acid. Nevertheless, the improvement over the prior practice, in which excess alkali would have been added without realizing the advantage in the acid water, is very real.

The present invention is in no way concerned with the practice of refining talloel in which crude black liquor soap is acidified to free the talloel. The amount of acid used in the process of the present invention is but a fraction of that needed to neutralize the total alkali content of the black liquor soap. In fact, the presence of free acid in the flotation circuit of the present invention is possible only because neutralization of the black liquor soap is very slow. Flotation is completed after the pH change takes place but before the acid is exhausted. In addition, if a large excess of acid, i. e., sufficient to liberate the talloel content, is used, the catalytic effect of the acid on selectivity during flotation is not obtained. The benefit of the free acid on the selectivity of the black liquor soap is not observed at a pH less than about 4.0.

The chemical nature of the acid used is not particularly critical. Any strong mineral acid, for example, sulfuric, hydrochloric or even hydrofluoric acid may be used, as well as certain of the strong organic acids. Because the advantage of the present invention is largely one of economy, the price differential favoring sulfuric acid makes it definitely preferable. However, as noted, the limitation is one of economical and not chemical considerations.

The distinguishing characteristics of the present invention therefore may be summarized as: (1) the benefication of non-metallic ores, particularly phosphate ores containing an excessive content of silica-bearing gangue; (2) by producing a froth concentrate high in mineral values; (3) in an anionic flotation; (4) using black liquor soap as the collector; (5) in the presence of sufficient acid to activate the selective tendency of the collector, but insufficient to neutralize the black liquor soap; normally enough to produce a tailing water pH of from about 4.0–6.7; and (6) completing the flotation before the acid is consumed in neutralizing the alkali content of the black liquor soap.

The present invention will be more fully illustrated in connection with the following examples which are meant to be illustrative only and not by way of limitation. All parts are by weight unless otherwise noted. In tabulating the results, the following abbreviations are used: B. P. L.—bone phosphate of lime ($Ca_3(PO_4)_2$); B. L. S. or B. L. Soap—black liquor soap; Insol—acid insoluble gangue.

Example 1

A sample of Florida pebble phosphate ore, assaying about 43.4% B. P. L. and 43.5% Insol, was prepared for flotation by reducing the size sufficiently for flotation feed; pulping with water, to about 22% solids; polishing in a Fagergren flotation machine with the air shut off for 6 minutes; and completely desliming by conventional hydraulic procedures. This sample was then divided into a number of portions which were separately conditioned at about 70% solids with various amounts of black liquor soap, diluted to about 20% solids and floated in Fagergren flotation machines under standard conditions, including a rougher float followed by 3 cleaner floats. The procedural steps and metallurgical results appear in the following table. The first test is a blank with no acid, followed by three tests in which the acid was added to the flotation cell and then by three tests in which varying amounts of acid were added during conditioning.

Table I

Procedure	Time in Minutes	% Solids
Condition	6	22.0
Do	1.0	70.0
Do	5 seconds	22.0
Rgh. Float	2	22.0
Condition	5 seconds	
1st Cl. Flot	1½	
Condition	5 seconds	
2nd Cl. Flot	1½	
Condition	5 seconds	
3rd Cl. Flot	1½	

Results

Test No.	Cleaned Concentrate					Reagents Lbs./Ton Added to Conditioning		pH R. Tail Water
	% Wt.	Assays		% Dist.		B. L. S.	H_2SO_4	
		Insol.	B. P. L.	Insol.	B. P. L.			
1	60.87	14.47	65.59	20.32	92.22	4.00	----------	6.75
2	56.27	8.42	71.17	10.90	91.66	4.00	0.167*	6.15
3	50.06	4.63	74.35	5.29	85.66	4.00	0.33*	6.2
4	34.17	2.66	75.55	2.06	59.75	4.00	0.50*	5.95
5	54.73	8.42	71.34	10.60	89.05	4.00	0.08	6.90
6	27.57	3.46	73.83	2.17	47.22	4.00	0.17	6.5
7	32.23	3.13	74.60	2.34	55.43	10.00	0.83	6.65

* Added to flotation cell.

It will be apparent that when sufficient black liquor soap alone is used, an excellent recovery is made but the grade is very inferior. However, it is also apparent that as soon as sulfuric acid is added an improvement occurs. Satisfactory grades are obtained with amounts above 1/6 lb., and recovery remains good until ½ lb. is reached, at which point the recovery begins to drop.

froth flotation using 2.0 lbs./ton of black liquor soap and varying amounts of sulfuric acid. In each case the ore was conditioned for 4 minutes prior to the rougher flotation, then given a rougher flotation of 2 minutes and a cleaner flotation of 1 minute. The amounts of acid used and the representative metallurgical results are shown in the following Table II.

Table II

Feed % Sp.	Assay—Spodumene Content						Acid (Lbs./Ton)		Tailing Water pH	
	Ro. Tail		Cl. Tail		Cl. Conc.		Ro. Float H_2SO_4	Cl. Float H_2SO_4	Ro.	Cl.
	% Sp.	% Dist.	% Sp.	% Dist.	% Sp.	% Dist.				
12.18	2	6.16	5	1.23	19	92.6	----------	----------	7.1	7.1
8.0	2	20.33	10	14.21	74	65.5	0.5	----------	6.7	6.9
9.1	1	3.63	10	5.95	69	90.4	0.25	0.25	6.8	6.2

NOTE: Sp.=Spodumene. % dist.=% Distribution.

While the present invention is primarily concerned with the use of acid and black liquor soap in the beneficiation of phosphate ores, the invention is not necessarily so limited. The mineral values of many non-metallic ores are commonly concentrated by an anionic flotation using fatty acid soap reagents. In general, these types of operations may be adapted to the substitution of black liquor soap for the more expensive reagents in common use if the acid treatment of the present invention is joined therewith. In order to demonstrate this feature, the following examples are given for purposes of illustration.

Example 2

A sample of spodumene ore was beneficiated in accordance with the following procedure. The ore was ground in a rod mill for 20 minutes at about 67% solids, the ground ore being dewatered, partially deslimed, scrubbed for 20 minutes at 50% solids with 2 lbs./ton of NaOH followed by desliming and thorough washing. Portions of this sample were then subjected to beneficiation by

Example 3

A low grade fluorspar ore was treated by grinding for 15 minutes at about 67% solids in a rod mill after which the pulp was diluted to about 22% solids and conditioned for 5 minutes with 1 lb./ton of sodium silicate and 1 lb./ton of quebracho. Where acid was used in the rougher float it was added during this conditioning operation. The conditioned pulp was transferred to a flotation machine and given a 6 minute rougher float in which the black liquor soap was stage-added. The rougher concentrate in the second and third tests was conditioned for 1 minute with the sulfuric acid and given a 2 minute cleaner flotation. The cleaner concentrate was conditioned for 1 minute with additional black liquor soap and in the second and third tests with sulfuric acid, and given a 2 minute cleaner flotation. The reagents used and representative metallurgical results are shown in the following Table III. It will be noted that the use of acid throughout the process results in an extremely high grade concentrate in a field in which grade is primarily important.

Table III

Feed Assays		Concentrate			Reagents					
		% Wt.	Assays		Ro. Float		Cl. Float		Recl. Float	
% CaF_2	% $CaCO_3$		% CaF_2	% $CaCO_3$	B. L. S.	H_2SO_4	B. L. S.	H_2SO_4	B. L. S.	H_2SO_4
71.49	1.07	58.2	97.44	0.54	0.80	----------	----------	----------	0.45	----------
72.30	1.13	35.8	99.11	0.39	0.80	----------	----------	0.50	0.45	0.50
71.88	1.52	31.4	99.17	0.18	0.80	1.00	----------	0.50	0.45	0.50

I claim:

1. In the beneficiation of non-metallic ores by froth flotation, using at least one rougher and one cleaner stage, to recover the mineral values in a high grade concentrate, the improvement which comprises subjecting an aqueous pulp of the ore to froth flotation at least the "rougher" float being carried out in the presence of an effective amount of black liquor soap as the principal collector and a sufficient amount of free strong acid to produce a pH of from not more than 6.7 or less than about 4.0 in the tailing water, but insufficient to neutralize appreciable amounts of the alkali content of the black liquor soap during the period of operation.

2. In the beneficiation of phosphate ores to recover the mineral values in a high grade concentrate, the improvement which comprises subjecting an aqueous pulp of the ore to froth flotation in the presence of an effective amount of black liquor soap as the principal collector and a sufficient amount of free strong acid to produce a pH of not more than 6.7 or less than about 4.0 in the tailing water but insufficient to neutralize appreciable amounts of the alkali content of the black liquor soap during the period of operation.

ELMER WILLIAM GIESEKE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,986,816	Hasselstrom	Jan. 8, 1935
1,986,817	Hasselstrom	Jan. 8, 1935
1,992,949	Hodges	Mar. 5, 1939
2,373,688	Keck	Apr. 17, 1945

OTHER REFERENCES

Soap Flotation by Coghill in Milling Methods, 1934, pages 452, 462, 463, 464.