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FLOTATION

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5 Claims. (Cl. 209—166)

This invention relates to improvements in flotation, reagents therefor and methods of manufacture. More particularly the invention is concerned with flotation of polar, non-metallic minerals as zircon, rutile, ilmenite and other compounds by chemical flotation. The invention has proven its worth on highly refractory ores including those of a non-metallic nature.

Flotation has heretofore been conducted largely through soaps on polar and non-polar, non-metallic minerals. However, the art has lacked selective flotation agents for polar non-metallics. I have found that non-metallics, including oxides and carbonates, can be floated as selectively as sulfides by certain chemical flotation agents and this without sulfidizing in the usual sense. The recoveries noted have in all cases been high and in addition, flotation problems, as slime, a sharp float and other factors, were all simplified.

My reagents are very stable and permit of inter-grinding with the ore so that addition and incorporation is simplified. They are generally oily liquids stable upon storage in aqueous mixtures and in the presence of alkalies and acids except under the most severe conditions. Their chemical nature is uncertain but broadly they can be classed as derived from dithiophosphates as a starting material. Thus I have made up a solution of a dithiophosphate and electrolyzed this, or otherwise oxidized it as with a chemical oxidizer as chlorine. As a starting material I can use any dithiophosphate, derivative or substitution product thereof.

While my invention is useful on metallics it shows very interesting and unusual results on non-metallics. A gold-wulfenite and vanadinite ore from Mammoth, Arizona, was ground with 2 lbs. per ton NaCN solution and with 4 lbs. per ton CaO, to pass a 100 mesh screen. The pulp was diluted 2 to 1 with 2 lbs. per ton NaCN solution and then agitated for 24 hours to extract 90.0% of the gold. The cyanide tailing was placed in a Kraut laboratory flotation machine at 20% solids. Amyl xanthate and pine oil were added in an attempt to make a differential float but only the metallic iron from the grind floated. The pulp was then activated successively with copper sulfate and sodium sulfide, flotation with amyl xanthate being attempted after each addition without success. A product of this invention (MC-2 reagent) was then added at the rate of 0.10 lbs. per ton of ore. A clean collection started immediately even though the ore had been cyanided. After five minutes a finished MoO_3 and V_2O_5 concentrate was secured without cleaning. The tailing was tabled to effect a table concentration. This concentration was floated in a small pneumatic laboratory flotation machine and a high grade lead vannate concentrate secured.

Products	Weight percent	Assays percent			Distribution percent		
		Pb	MoO_3	V_2O_5	Pb	MoO_3	V_2O_5
Calc. head	100.00	1.80	.24	.47	100.0	100.0	100.0
Flot. conc. 1	1.52	44.20	13.00	8.31	37.4	83.6	26.7
Flot. conc. 2	0.35	29.60	0.60	7.88	5.8	0.8	5.9
Tailings	93.41	0.70	0.03	0.21	36.4	11.8	41.5

Previous test with other reagents failed to give anywhere as good results, the highest combined MoO_3 and V_2O_5 concentrate secured being less than 16%. The successful flotation by the material of the present invention is indicated clearly by its successful use even after cyanidation when other collectors failed. Without cyanidation it showed excellent results and the above results are set forth to show its use under very adverse conditions.

On an ore from Malvern, Arkansas, from the Titanium Corporation, containing rutile and ilmenite and various oxidized gangue minerals, successful results were obtained although soaps, fatty acids and other reagents together with pH control and activators, failed to make even a fair grade of concentrate. A clean, slime free flotation concentrate was secured of a grade that could be magnetically separated.

The ore was ground, screened and the +200 slime free product tabled on a laboratory Deister table to make a table concentrate containing 54% of the TiO_2 of which 6.58% was originally present. The slime and this product were floated separately in a Pan-American "non-metallic" laboratory flotation machine. The slime was treated with 0.50 lb./ton HCl as a conditioner, 0.10 lb./ton sulfonated castor oil as a frother,

5.0 lb./ton of sodium sulfide as a froth control and 0.10 lb./ton of my MC–2 reagent. The table product was similarly treated except that the HCl was increased to 1.0 lb./ton. The results are as follows:—

Product	Weight percent	Assays TiO_2 percent	Distribution TiO_2 percent
Calc. head	100.00	6.58	100.0
Table concentrate	4.85	54.0	39.9
+200 mesh flot. conc	1.60	14.5	3.5
−200 mesh flot. conc	4.55	26.1	18.1
Total table and flot. conc	11.00	36.8	61.5
+200 mesh flot. midds	3.02	2.3	1.0
−200 mesh flot. midds	18.88	2.4	6.9
Total flotation midds	21.90	2.4	7.9
+200 mesh flot. tail	14.65	3.0	6.7
−200 mesh flot. tail	52.45	3.0	23.9
Total Final tailing	67.10	3.0	30.6

A black sand beach concentrate from Australia was subjected to flotation. This material had the following composition as determined by microscopic count:—

	Percent
Zircon, $ZrSiO_4$	54.6
Rutile, TiO_2	11.7
Ilmenite, $(FeTi)_2O_3$	26.8
Quartz, SiO_2	6.9

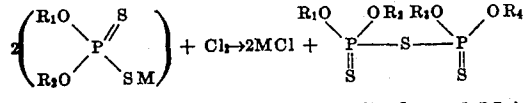
The sand was subject to flotation and the following reagents were used: HCl—0.50 lb/ton, ferric chloride —0.005 lb/ton, reagent MC-2 —.02 lb/ton, and du Pont frother B23 —0.10 lb/ton.

The flotation results are set forth in the following table:

Product	Weights percent	Analysis				Distribution			
		Zircon percent	Rutile percent	Ilmenite percent	Quartz percent	Zircon percent	Rutile percent	Ilmenite percent	Quartz percent
Calc. head	100.00	54.6	11.7	26.8	6.9	100.0	100.0	100.0	100.0
Zircon conc	47.6	87	5	8	0	75.8	20.5	14.2	0
Zircon middl	3.9	36	20	43	1	2.6	6.8	6.3	.6
R–I conc.*	41.8	28	20	50	2	21.4	71.9	78.0	11.8
Quartz tailing	6.7	1	1	6	92	.2	.8	1.5	87.6

* Rutile-Ilmenite.

The material contemplated for use in accordance with this invention can be made in a variety of ways. I have successfully manufactured the material by blowing dilute chlorine through a dilute aqueous solution of the dithiophosphate. Thus I make up a solution in water to about 10% of the dithiophosphate and blow through this solution an air chlorine mixture in which chlorine is present in about 5%. This reaction is discontinued as soon as the theoretical amount of chlorine has been passed in in accordance with the following equation:



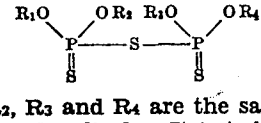
where R_1 and R_2 are organic radicals and M is a metal or H.

The products can also be prepared by electrolysis from an aqueous solution and I have successfully made the products herein disclosed by electrolyzing an aqueous solution at a substantially constant voltage between 2.5 to 2.7 volts and with a temperature of about 25° C. The solution should not be allowed to become too acid or too alkaline, the alkaline side being preferred. The current density should be kept just below the point of oxygen liberation.

The reaction between the dithiophosphates in the invention is applicable to compounds prepared from either the dithiophosphoric acid, alkyl dithiophosphates or aryl dithiophosphates. For example the compounds can be readily formed by the direct reaction of chlorine and diphenyl dithiophosphoric acid under the condition outlined above. Similarly other aryl compounds of similar constitution can be used. It will therefore be apparent that the invention is of broad scope and is not to be limited by the specific examples given above but by the scope of my invention as set forth in the claims appended hereto. The invention is applicable to polar non-metallic materials generally including oxides, silicates, vanadates, molybdates, titanates, carbonates and sulphates, phosphates, tungstates and chlorides.

It is to be understood that the structural formulae shown are employed as referring to the reaction product and that while I at present believe the materials to be thus correctly represented, it is not a matter of actual certainty. As a matter of fact the reaction product is what is employed in flotation, not a pure product, because of expense. The products made correspond to the alkyl ethyl, propyl, butyl, amyl, heptyl, hexyl dithiophosphates, including the secondary and tertiary compounds as isopropyl, secondary butyl and the three amyls (diethyl, methyl propyl and methyl isopropyl carbinols) as well as tertiary butyl and tertiary amyl.

The formula of the four sulphur atom materials is believed to be as follows:—



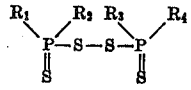
where R_1, R_2, R_3 and R_4 are the same or different alkyl or aryl radicals. It is to be understood that, while I believe the above formula to represent correctly the reaction product of an alkyl or aryl dithiophosphate or the corresponding acid, the reaction product is indicated thereby.

The MC-2 reagent heretofore mentioned is the product secured upon treating secondary butyl dithiophosphate with chlorine as detailed herein.

I claim:

1. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting a polar non-metallic ore in the form of a pulp to a froth flotation operation in the presence of a tetrathio diphospho organic compound.

2. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting a polar non-metallic ore in the form of a pulp to a froth flotation operation in the presence of a chemical compound represented by the formula



where R_1, R_2, R_3 and R_4 are any aliphatic or cyclic organic radicals or substituted derivatives thereof.

3. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting a polar non-metallic ore in the form of a pulp to a froth flotation operation in the presence of an organic sulphur phosphorous compound containing two phosphorous atoms bonded through two intervening and interlinked sulphur atoms.

4. The process as in claim 2 where R_1, R_2, R_3 and R_4 are the alkyl radical, secondary butyl.

5. The process as in claim 2 where R_1, R_2, R_3 and R_4 are the alkyl radical, ethyl.

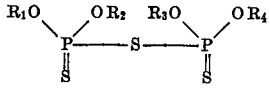
MERRILL W. MACAFEE.

Certificate of Correction

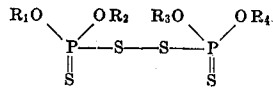
Patent No. 2,060,815. November 17, 1936.

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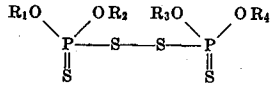
It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 17, for "vannate" read *vanadate;* page 2, first column, lines 66 to 69 inclusive, for that portion of the formula reading



read



and second column, lines 55 to 58 inclusive, and page 3, first column, lines 7 to 9 inclusive, claim 2, strike out the formula and insert instead the following:



and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 16th day of August, A. D. 1938.

[SEAL]

Leslie Frazer

Acting Commissioner of Patents.