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CONCENTRATION OF METALLIFEROUS ORES BY FROTH FLOTATION

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This application is a continuation in part of application Serial No. 146,611, filed June 5, 1937.

The present invention relates to improvements in the froth flotation concentration of metalliferous ores, especially sulphide ores.

In my United States Patent No. 1,554,216, issued September 22, 1925, a process for the concentration of ores by flotation is described, which is essentially characterized by the use of sulphur derivatives of carbonic acid, particularly alkali salts of xanthic acids, as flotation agents. I have now found that complex acid compounds formed by the combination of xanthic acids with molybdic acid are extremely effective agents in the flotation concentration of metalliferous ores, concentrates of a high degree of purity being obtained by their use. This is particularly the case with ores containing molybdenum sulphide. It is very difficult to obtain molybdenite concentrates of sufficiently high grade by the use of heretofore known flotation agents, especially when the crude molybdenite-containing ore also contains gangue minerals of the class called hydrous micas, such as sericite. However, by the use of the xanthomolybdic acid compounds of the present invention, molybdenite concentrates of a very high grade can be obtained, even in the case of ores containing the gangue minerals stated.

The invention is, of course, not limited to the treatment of molybdenum-bearing ores, but may also be employed with improved results in the concentration of other metalliferous ores, such as those of lead, copper, zinc, gold, and silver.

The xanthomolybdic acid compounds of the present invention can be prepared by acidification of an aqueous solution of xanthate and molybdate respectively present therein in proportions equivalent to two molecules of xanthic acid and one molecule of molybdic acid. As the xanthate, any one of various xanthates in the form of alkali salts may be used, such xanthates including sodium ethyl xanthate, potassium amyl xanthate, potassium octyl xanthate, potassium phenyl-ethyl xanthate, etc. The molybdate may be any soluble salt of molybdic acid, such as ammonium molybdate or sodium molybdate. Upon acidification, preferably with a mineral acid, of the stated solution of xanthate and molybdate, the desired xanthomolybdic acid compound is precipitated as a dark purplish oily liquid which, on standing, solidifies to a very dark colored amorphous mass. The formula for the xanthomolybdic acid compounds obtained in this manner appears to be $MoO_3.(RO.CSSH)_2$, wherein R is an alkyl or aralkyl group, depending on the composition of the xanthate used.

For the purpose of acidification, almost any acid can be used. Mineral acids are preferred because they are cheaper and bring about the reaction more rapidly than organic acids, but organic acids can also be used. Satisfactory results have thus been obtained not only with such common mineral acids as hydrochloric acid and sulphuric acid, but also with such organic acids as acetic acid, furoic acid, and oxalic acid. It has been found, however, that some organic acids, especially those which are substantially insoluble in water, are ineffective. Among the mineral acids, sulphurous acid and boric acid have also been found ineffective.

Purification of the xanthomolybdic acid compounds of the present invention can be effected by solution in aqueous ammonia and reprecipitation with a suitable acid. But this purification need not be carried out prior to use of the compounds as flotation agents, the crude reaction products being quite satisfactory for that purpose.

A convenient method of preparing the xanthomolybdic acid compounds of the present invention comprises the preliminary step of roasting an ore product containing molybdenite, by which roasting the molybdenum sulphide is converted into oxide, which is then leached out with a solution of caustic alkali to produce a soluble molybdate. To this liquor is then added the calculated amount of the desired xanthate and the required acid to effect the reaction. Separation of the xanthomolybdic acid compound thus precipitated, if desired, may then be effected by well-known means.

The xanthomolybdic acid compounds of the present invention are practically insoluble in water, but are soluble in many organic liquids, among which may be mentioned chloroform, acetone, and ether. Prior to use of the compounds as flotation agents, therefore, it may be convenient to dissolve them in a suitable solvent, which may be one of the three indicated, or any other. But if it is desired to use the compounds in solid form, they may be conveniently added to the ore during grinding so as to become admixed therewith.

I have found that the simplest method of employing the xanthomolybdic acid compounds of the present invention is to add them to the ore pulp directly in the form of the mixture obtained by acidification of the xanthate and molybdate solution used in their preparation, without removal of the reaction product. This method obviously can be utilized to provide the required amount of xanthomolybdic acid compound continuously in large scale operations.

The xanthomolybdic acid compounds of the present invention are very effective in the flotation of molybdenite from copper-molybdenum ores subsequent to their treatment for a removal of copper sulphides, as in the process described in United States patent to Earl H. Brown, No. 2,070,076, issued February 9, 1937. In this process copper sulphides are selectively floated away from molybdenite by adding to the ore pulp a small quantity of starch or other protective colloid, acting to depress the molybdenite and inhibit its flotation, other agents being also present in the pulp to effect flotation of the copper sulphides. It has now been found that by subsequent treatment with a xanthomolybdic acid compound of the material remaining after such a flotation of copper sulphides, a molybdenite concentrate can be obtained containing a very small proportion of gangue minerals.

When necessary, of course, the concentrates initially obtained by the use of the xanthomolybdic acid compounds of the present invention can be improved in grade by retreatment in the usual manner.

I have found that it is possible to employ the xanthomolybdic acid compounds of the present invention in acid ore pulps, as well as in pulps of a neutral or alkaline character. They are therefore very useful in the flotation of metallic values from materials that have been subjected to hydrometallurgical processes.

The xanthomolybdic acid compounds of the present invention are employed essentially as collectors. To any one skilled in the art, however, it is obvious that they can be used in conjunction with other collectors, such as xanthates or dithio phosphates. And they may be used, of course, with such additional flotation agents as frothing agents, inhibiting agents, activating agents, etc.

Examples will now be given describing certain tests which have been made in carrying the invention into effect, it being understood that the various reagent proportions indicated in each example are expressed in the usual manner as pounds per ton of dry material treated.

Example 1

A 1000 gram sample of Nevada Consolidated Copper Company ore, of a particle size to pass 10-mesh, was reground wet for four minutes in a ball mill with 12 lbs. of lime per ton of ore. The material thus initially treated was transferred to a laboratory size subaeration flotation machine where it was conditioned by agitation with 0.1 lb. of pine oil per ton and 0.02 lb. of ethyl xanthomolybdic acid per ton, the latter agent being added as a solution in acetone. Subsequently, the pulp was treated in the machine for the production of a froth, which was removed in the usual way. The results of the test are shown in the following table:

	Percent weight	Assay, percent Cu	Distribution, percent Cu
Heads	100.0	1.11	100.0
Conc.	4.48	22.24	89.68
Tail	95.52	0.12	10.32

Example 2

The procedures of Example 1 were repeated on another 1000 gram sample of the same copper ore, but with 0.1 lb. of amyl xanthomolybdic acid per ton replacing the ethyl xanthomolybdic acid of that example. Substantially the same results were obtained, as shown by the following table:

	Percent weight	Assay, percent Cu	Distribution, percent Cu
Heads	100.0	1.12	100.0
Conc.	4.59	22.00	89.82
Tail	95.41	0.12	10.18

Example 3

Here 0.10 lb. of butyl xanthomolybdic acid per ton was used instead of the ethyl xanthomolbydic acid of Example 1. All other conditions were exactly the same as before, the test being carried out on still another 1000 gram sample of the same copper ore. The following table indicates that again similar results were obtained:

	Percent weight	Assay, percent Cu	Distribution, percent Cu
Heads	100.0	1.12	100.0
Conc.	4.70	21.36	89.77
Tail	95.30	0.12	10.23

Good results were also obtained when octyl xanthomolybdic acid was substituted for ethyl xanthomolybdic acid on a similar copper ore.

Example 4

A 1500 gram sample of a similar copper ore, in the form of a pulp of 50% solids, was reground for five and one-third minutes with 5 lbs. of lime per ton. Conditioning of the reground ore was in this instance carried out with a mixture obtained by adding hydrochloric acid to admixed aqueous solutions of sodium molybdate and sodium ethyl xanthate. These two solutions were used in quantities to produce 0.04 lb. of ethyl xanthomolybdic acid per ton, agitation of the pulp being carried out with the total amount of the mixture, simultaneously with 0.067 lb. of pine oil per ton. Thereafter, frothing was carried out and the froth removed in the usual manner. The following table shows the results of the test:

	Percent weight	Assay, percent Cu	Distribution, percent Cu
Heads	100.0	1.05	100.0
Conc.	4.37	23.20	96.36
Tail	95.63	0.04	3.64

Comparative Test 1

Another 1500 gram sample of the same copper ore as in Example 4 was processed in the manner described in that example, but omitting the use of the ethyl-xanthomolybdic-acid-containing mixture. Instead, 0.04 lb. of sodium ethyl xanthate per ton of ore was added to the reground ore, the procedures being otherwise exactly the same. The results in this instance were as follows:

	Percent weight	Assay, percent Cu	Distribution, percent Cu
Heads	100.0	1.10	100.0
Conc.	4.49	22.30	91.29
Tail	95.51	0.10	8.71

Comparative Test 2

In this test, employing still another 1500 gram sample of the same copper ore, its conditioning subsequent to regrinding with lime was carried out with pine oil only. Except for this difference the conditions of the test were identical with those outlined in detail in Example 4, the lime and pine oil being employed in the same amounts. The following results were obtained:

	Percent weight	Assay, percent Cu	Distribution, percent Cu
Heads	100.0	1.05	100.0
Conc	3.38	25.12	80.71
Tail	96.62	0.21	19.29

Example 5

A 1000 gram sample of 10-mesh Desloge Lead Company ore was reground in the ball mill for fifteen minutes at about 50% solids with 1 lb. of soda ash per ton. To the reground ore, in the flotation machine, was then added a mixture obtained by adding a 0.9% solution of sodium molybdate, acidified with hydrochloric acid, to a 1% solution of sodium ethyl xanthate, the quantities of the solutions being adjusted so as to form 0.04 lb. of ethyl xanthomolybdic acid per ton. Cresol was also added at the rate of 0.1 lb. per ton. Preliminary agitation was carried out with these reagents, subsequent to which a flotation concentrate was removed in the usual manner. The following table indicates the results of the test.

	Percent weight	Assay, percent Pb	Distribution, percent Pb
Heads	100.0	4.58	100.0
Conc	8.46	52.0	96.0
Tail	91.54	0.2	4.0

COMPARATIVE TEST 3

Employing another 1000 gram sample of the same lead ore as in Example 5, the procedures of that example were repeated with the ethyl-xanthomolybdic-acid-containing mixture replaced by 0.04 lb. of sodium ethyl xanthate per ton, the results of this test being as follows:

	Percent weight	Assay, percent Pb	Distribution, percent Pb
Heads	100.0	4.44	100.0
Conc	7.48	56.2	94.78
Tail	92.52	0.25	5.22

COMPARATIVE TEST 4

Still another 1000 gram sample of the same lead ore as in Example 5 was taken, which sample subsequent to regrinding with soda ash was conditioned with cresol only. The conditions were otherwise the same as in that example, including the amounts of soda ash and cresol, the following results being obtained:

	Percent weight	Assay, percent Pb	Distribution, percent Pb
Heads	100.0	4.59	100.0
Conc	6.61	61.0	87.79
Tail	93.39	0.6	12.21

Example 6

A 1000 gram sample of 10-mesh Joplin zinc ore was reground wet in the ball mill for ten minutes and thereafter transferred to the flotation machine. There was then introduced into the pulp a mixture obtained by mixing a solution of sodium molybdate, acidified with hydrochloric acid, with a solution of potassium secondary butyl xanthate, which solutions were used in quantities to produce 0.3 lb. of butyl xanthomolybdic acid per ton. Preliminary agitation was carried out with the said mixture, together with 1 lb. of copper sulphate ($CuSO_4.5H_2O$) per ton and 0.3 lb. of pine oil per ton, subsequent to which a floating froth was produced and removed in the usual manner. The results are shown in the following table:

	Percent weight	Assay, percent Zn	Distribution, percent Zn
Heads	100.0	14.8	100.0
Conc	22.50	64.0	97.37
Tail	77.50	0.5	2.63

COMPARATIVE TEST 5

Another 1000 gram sample of the same zinc ore as in Example 6 was processed in the same manner as in that example, but with the butyl-xanthomolybdic-acid-containing mixture replaced by 0.3 lb. of potassium secondary butyl xanthate per ton, the results in this instance being as follows:

	Percent weight	Assay, percent Zn	Distribution, percent Zn
Heads	100.0	14.9	100.0
Conc	22.97	62.8	96.89
Tail	77.03	0.6	3.11

COMPARATIVE TEST 6

On still another 1000 gram sample of the same zinc ore as in Example 6, with no other agent than the copper sulphate and pine oil of that example, all other conditions remaining the same, the following results were obtained:

	Percent weight	Assay, percent Zn	Distribution, percent Zn
Heads	100.0	14.5	100.0
Conc	19.33	64.6	86.09
Tail	80.67	2.5	13.91

Example 7

A 1000 gram sample of 10-mesh Mexican Candelaria ore, containing gold and silver, was reground wet in the ball mill and thereafter transferred to the flotation machine. Conditioning in the machine was then carried out with 0.2 lb. of pine oil per ton, 0.1 lb. of cresol per ton, and a mixture obtained by mixing a solution of sodium molybdate, acidified with hydrochloric acid, with a solution of potassium amyl xanthate, the quantities of which solutions were adjusted to produce 0.2 lb. of amyl xanthomolybdic acid per ton of ore. Subsequently, frothing was carried out and a concentrate removed in the usual manner. The following table indicates the results of the test:

	Percent weight	Assay in oz/ton		Percent distribution	
		Au	Ag	Au	Ag
Heads	100.0	0.743	33.2	100.0	100.0
Conc	3.659	18.751	763.86	91.44	84.18
Tail	96.341	0.066	5.45	8.56	15.82

COMPARATIVE TEST 7

Employing another 1000 gram sample of the same gold-silver ore as in Example 7, the procedures of that example were repeated, substituting for the amyl-xanthomolybdic-acid-containing mixture 0.2 lb. of potassium amyl xanthate per ton, the following results being obtained:

	Percent weight	Assay in oz/ton		Percent distribution	
		Au	Ag	Au	Ag
Heads	100.0	0.711	33.70	100.0	100.0
Conc	3.627	17.646	785.63	89.97	84.55
Tail	96.373	0.074	5.4	10.03	15.45

COMPARATIVE TEST 8

On still another 1000 gram sample of the same gold-silver ore as in Example 7, the following results were obtained employing as agents the pine oil and cresol only of that example:

	Percent weight	Assay in oz/ton		Percent distribution	
		Au	Ag	Au	Ag
Heads	100.0	0.694	36.46	100.0	100.0
Conc	2.267	11.614	866.69	39.07	53.89
Tail	97.733	0.42	17.2	60.93	46.11

Example 8

A 1500 gram sample of Climax Molybdenum Corporation ore, of a particle size to pass 10 mesh, was reground wet in the ball mill for fifteen minutes. Preliminary agitation of the reground ore was then carried out in the flotation machine with 0.27 lb. of sodium cyanide per ton, 0.034 lb. of terpineol per ton, and a mixture obtained by adding a solution of sodium molybdate, acidified with hydrochloric acid, to a solution of sodium ethyl xanthate, which solutions were used in quantities to form 0.2 lb. of ethyl xanthomolybdic acid per ton of ore. Thereafter, the pulp was subjected to froth flotation in the usual manner, the results being shown in the following table:

	Percent weight	Assay, percent MoS_2	Distribution, percent MoS_2
Heads	100.0	0.844	100.0
Conc	0.954	63.6	71.84
Tail	99.046	0.24	28.16

COMPARATIVE TEST 9

Another 1500 gram sample of the same molybdenum ore as in Example 8 was processed in identical manner, except that the use of the ethyl-xanthomolybdic-acid-containing mixture was omitted, the sodium cyanide and terpineol only of that example being used. The results in this instance were as follows:

	Percent weight	Assay, percent MoS_2	Distribution, percent MoS_2
Heads	100.0	0.79	100.0
Conc	0.887	60.0	67.37
Tail	99.113	0.26	32.63

Example 9

A sample of 10-mesh Miami Copper Company ore, containing both sulphide and oxidized copper minerals, was reground wet in the ball mill for ten minutes and thereafter transferred to the flotation machine. Preliminary agitation of the material in the machine was then carried out with 0.1 lb. of pine oil per ton, and a mixture obtained by mixing a solution of sodium molybdate, acidified with hydrochloric acid, with a solution of sodium ethyl xanthate, the quantities of which solutions were adjusted to yield 0.04 lb. of ethyl xanthomolybdic acid per ton of ore. Frothing was then carried out in the machine, yielding a concentrate of sulphides. The remaining pulp was then removed from the machine, thickened, and leached with sulphuric acid to dissolve oxidized copper, the dissolved copper being then precipitated in the pulp in the form of metallic copper by addition of metallic iron. Thereafter, upon return to the machine, the pulp was reconditioned with 0.1 lb. of pine oil, 0.1 lb. of Barrett No. 4 flotation oil, and 0.26 lb. of ethyl xanthomolybdic acid as a mixture prepared in the same manner as above indicated in this example, all per ton of dry ore. Frothing was then resumed and a cement copper concentrate separated. The results obtained are shown in the following table, wherein the tailing refers to the material remaining after the second flotation operation:

	Percent weight	Assay, percent Cu	Distribution, percent Cu
Heads	100.0	2.41	100.0
Cu sulphide conc	2.087	42.12	36.43
Cement Cu conc	4.541	29.76	56.02
Tail	93.372	0.195	7.55

The pH value of the liquid from the tailing was 4.8.

Example 10

A 1000 gram sample of the same copper ore as in Example 9 was reground wet for ten minutes and thereafter leached, at about 35% solids, with 36 grams of sulphuric acid to dissolve the oxidized copper, the resultant pulp being then filtered and washed once with water. The solids thus obtained were made up into a freely flowing pulp, which was agitated in the flotation machine with 0.1 lb. of General Naval Stores No. 5 pine oil per ton and 0.08 lb. of ethyl xanthomolybdic acid per ton, the latter agent being added as a mixture obtained by adding a solution of sodium molybdate, acidified with hydrochloric acid, to a solution of sodium ethyl xanthate. Subsequently, a flotation concentrate was removed in the usual way. The following table indicates the results of the test:

	Percent weight	Assay, percent Cu	Distribution, percent Cu
Heads	100.0	2.27	100.0
Leached Cu	1.167	100.0	51.32
Flot. Conc	3.614	26.8	42.60
Tail	95.219	0.145	6.08

The pH value of the liquid from the tailing was 6.0.

Example 11

A 1000 gram sample of the same copper ore as in Example 9 was reground wet for ten minutes and thereafter leached with 36 grams of sulphuric acid to dissolve the oxidized copper. The dissolved copper was precipitated in the form of metallic copper by agitation with 20 grams of metallic iron, whereupon the pulp was subjected to flotation in the usual way, employing as reagents 0.1 lb. of General Naval Stores No. 5 pine oil, 0.1 lb. of Barrett No. 4 flotation oil, and 0.26 lb. of ethyl xanthomolybdic acid, all per ton of ore, the last-mentioned agent being added as a mixture obtained by admixing a solution of sodium molybdate, acidified with hydrochloric acid, with a solution of sodium ethyl xanthate. Both sulphides and cement copper were simultaneously removed in this test, the results of which are shown in the following table:

	Percent weight	Assay, percent Cu	Distribution, percent Cu
Heads	100.0	2.376	100.0
Conc	5.82	38.08	93.26
Tail	94.18	0.17	6.74

The pH value of the water from the tailing was 4.9.

Example 12

A 1000 gram sample of 10-mesh Arizona Molybdenum Corporation ore, containing both copper sulphides and molybdenite, was reground wet in the ball mill for fifteen minutes. Thereafter, the pulp was transferred to the flotation machine where it was treated for the production of a copper concentrate by employing as reagents 1 lb. of starch, 0.1 lb. of sodium ethyl xanthate, and 0.25 lb. of cresol, all per ton of ore, the usual conditioning period with these reagents preceding the frothing of the pulp. With the material remaining was then admixed 0.5 lb. of amyl xanthomolybdic acid per ton, added as a mixture obtained in the manner described below, together with 0.25 lb. of pine oil per ton, a rougher molybdenum concentrate being subsequently separated. Upon removal of the tailing, this rougher concentrate was conditioned in the machine with 0.5 lb. of sodium cyanide per ton and 0.1 lb. of pine oil per ton, whereupon a final molybdenum concentrate was obtained, the tailing of this cleaning operation constituting a molybdenum middling.

The aforementioned mixture used in floating the rougher molybdenum concentrate was obtained by first preparing a sodium molybdate solution from a molybdenite middling obtained in concentrating a copper-molybdenum ore, this middling being roasted and thereafter leached with sodium hydroxide solution. To the sodium molybdate solution thus obtained was added a potassium amyl xanthate solution in relative proportion of two molecules of xanthate to one molecule of molybdate, hydrochloric acid being then added to the resultant solution to effect the reaction. In thus preparing the mixture, the mixed solutions of xanthate and molybdate were employed in quantities sufficient to form the aforestated 0.5 lb. of amyl xanthomolybdic acid per ton of ore. The results obtained in the above test are shown in the following table:

	Percent weight	Assay percent		Percent distribution	
		Cu	MoS_2	Cu	MoS_2
Heads	100.0	0.626	1.50	100.0	100.0
Cu Conc	4.91	10.30	1.95	80.75	6.37
Mo Conc	1.22	0.38	91.50	0.73	74.34
Mo Midd	3.61	1.84	6.10	10.60	14.66
Tail	90.26	0.055	0.077	7.92	4.63

Example 13

A rougher molybdenite concentrate containing about 2.9% MoS_2 and obtained by froth flotation of a sample of ore from Utah Copper Company, from which sample a copper concentrate had already been removed, was retreated eight times employing as reagents sodium cyanide and butyl xanthomolybdic acid. This last-mentioned agent was produced from secondary butyl xanthate and ammonium hepta molybdate. The amount of sodium cyanide, 2.98 lbs. per ton of material retreated, was added during the first five retreatments. The xanthomolybdic acid was added in equal amounts in the last three retreatments, the total amount being 0.04 lb. per ton of material retreated. The final concentrate contained 94.2% molybdenite and 0.12% copper.

COMPARATIVE TEST 10

Starting with a rougher molybdenum concentrate of the same character as in Example 13, the procedures of that example, with the butyl xanthomolybdic acid omitted and with the cyanide used in the last eight of nine retreatments, gave a final concentrate of only 75.2% molybdenite, the copper content therein being 0.26%.

Example 14

A 1500 gram sample of Nevada Consolidated Copper Company ore, of a particle size to pass a 10-mesh screen and in the form of a pulp of 50% solids, was reground for five and one-third minutes with 5 lbs. of lime per ton of ore. The reground pulp was transferred to the flotation machine, diluted to about 23% solids, and conditioned by agitation with a mixture obtained by adding a hydrochloric-acid-acidified aqueous solution of sodium molybdate to an aqueous solution of potassium phenyl-ethyl xanthate in such quantities as to produce .04 lb. of beta phenyl-ethyl xanthomolybdic acid per ton of ore, agitation of the pulp being carried out simultaneously with 0.067 lb. of pine oil per ton of ore. Thereafter, frothing was carried out and the froth removed in the usual manner. The following table shows the results of the test:

	Percent weight	Assay, per cent Cu	Distribution, percent Cu
Heads	100.0	1.07	100.0
Concs	4.43	22.32	92.40
Tails	95.57	0.085	7.60

Example 15

The procedures of Example 14 were repeated on another 1500 gram sample of the same copper ore, but increasing the amounts of acidified sodium molybdate and beta phenyl-ethyl xanthate so as to produce 0.08 lb. of phenyl-ethyl xanthomolybdic acid per ton of ore, eliminating the lime during grinding, and carrying out the conditioning of the pulp and subsequent frothing in a circuit made acid with 6.1 lbs. of sulphuric acid per ton of ore. The results of this test were as follows:

	Percent, weight	Assay, percent Cu	Distribution, percent Cu
Heads	100.0	1.073	100.0
Concs	5.39	18.16	91.18
Tails	94.61	.10	8.82

In each of the following three examples, the same xanthomolybdic acid compound was used, but was prepared with the use of a different organic acid as a solution-acidifying agent.

Example 16

A 1500 gram sample of 10-mesh Nevada Consolidated Copper Company ore was reground in the ball mill for five and one-half minutes with 1.5 liters of water and 7.5 grams of lime (equivalent to 10 lbs. per ton of ore). The material thus treated was transferred to the flotation machine where it was conditioned by agitation with 0.067 lb. of pine oil per ton and 0.04 lb. of ethyl xanthomolybdic acid per ton, the latter agent being prepared by acidifying a solution containing the required amounts of sodium molybdate and sodium ethyl xanthate by means of acetic acid. Frothing was then carried out and the froth removed in the usual manner. The heads assayed 1.119% Cu, the concentrate 22.0% Cu, and the tailing 0.071% Cu, which represented a recovery of 93.95% of the total copper contained in the heads.

Example 17

The procedures of Example 16 were repeated on another 1500 gram sample of the same copper ore, but in this instance the ethyl xanthomolybdic acid was prepared with the use of furoic acid for acidifying the solution of sodium molybdate and sodium ethyl xanthate. The heads assayed 1.128% Cu, the concentrate 22.48% Cu, and the tailing 0.07% Cu, which represented a recovery of 94.08% of the total copper contained in the heads.

Example 18

Here the xanthomolybdic acid of Example 16 was prepared by adding oxalic acid to the solution of sodium molybdate and sodium ethyl xanthate. All other conditions were exactly the same as in that example, the test being carried out on still another 1500 gram sample of the same copper ore. The heads assayed 1.123% Cu, the concentrate 24.38% Cu, and the tailing 0.076% Cu, which represented a recovery of 93.52% of the total copper contained in the heads.

COMPARATIVE TEST 11

Repeating the procedures of the last three examples on a further 1500 gram sample of the same copper ore, but omitting the use of the xanthomolybdic acid, a concentrate was obtained weighing 25.3 grams and assaying 20.66% Cu, accounting for only 46.78% of the total copper contained in the heads, the assay of which was 1.117% Cu.

None of the procedures herein described in detail should be interpreted as limiting the invention, which procedures may be modified in many ways without departing from its spirit.

What is claimed is:

1. In the concentration of metalliferous ores by froth flotation, the step which consists in carrying out the froth flotation operation with the aid of a xanthomolybdic acid compound.

2. In the concentration of metalliferous ores by froth flotation, the step which consists in subjecting an acid pulp of the ore to froth flotation in the presence of a xanthomolybdic acid.

3. In the concentration of metalliferous ores by froth flotation, the step which consists in effecting the froth flotation operation with the aid of a xanthomolybdic acid obtained from a soluble xanthate and a soluble molybdate by the action of an acid.

4. In the concentration of metalliferous ores by froth flotation, the step which consists in effecting the froth flotation operation with the aid of a compound of the general formula

$$MoO_3.(RO.CSSH)_2,$$

wherein R is an alkyl or aralkyl group.

5. In the concentration of metalliferous ores by froth flotation, the step which consists in effecting the froth flotation operation with the aid of a compound of the general formula

$$MoO_3.(C_nH_{2n+1}O.CSSH)_2$$

wherein n is a whole number.

6. In the concentration of metalliferous ores by froth flotation, the step which consists in subjecting to froth flotation an aqueous pulp of the metalliferous ore admixed with a xanthomolybdic acid added thereto in the state of solution in a suitable solvent.

7. In the concentration of metalliferous ores by froth flotation, the step which consists in subjecting to froth flotation an aqueous pulp of the metalliferous ore admixed with a xanthomolybdic acid added thereto in the state of solution in acetone.

8. In the concentration of metalliferous ores by froth flotation, the step which consists in carrying out the froth flotation operation with the aid of the reaction product obtained by admixing in an aqueous medium a soluble xanthate, a soluble molybdate, and an acid.

9. In the concentration of metalliferous ores by froth flotation, the step which consists in carrying out the froth flotation operation with the aid of the material obtained by the action of an acid on admixed solutions of a salt of a xanthic acid and a salt of molybdic acid.

10. In the concentration of metalliferous ores by froth flotation, the step which consists in carrying out the froth flotation operation with the aid of the material obtained by the reaction in an aqueous medium of a soluble xanthate, a soluble molybdate, and a mineral acid, the said xanthate and molybdate being employed in relative proportions equivalent to two molecules of xanthic acid and one molecule of molybdic acid.

11. In the concentration of metalliferous ores by froth flotation, the step which consists in carrying out the froth flotation operation with the aid of the material obtained by roasting a molybdenite ore, leaching the roasted ore with a solution of caustic alkali, and reacting the resultant liquor with a soluble xanthate and an acid.

12. In the froth flotation concentration of molybdenum ores, the step which consists in effecting the froth flotation operation on the molybdenum ore by the aid of a xanthomolybdic acid compound.

13. The process of concentrating ores containing molybdenite by froth flotation, which comprises admixing a pulp of the molybdenite-containing ore with a compound of the general formula $MoO_3.(C_nH_{2n+1}O.CSSH)_2$ where n is a whole number, treating the pulp by froth flotation so as to produce a concentrate rich in molybdenite, and separating the concentrate.

14. The process of concentrating ores containing copper and molybdenum sulphides, which comprises subjecting a pulp of such an ore to a treatment resulting in a removal of copper sulphide, treating by froth flotation the remaining pulp admixed with a xanthomolybdic acid compound so as to produce a concentrate rich in molybdenite, and separating the concentrate.

15. The process of concentrating ores containing copper and molybdenum sulphides, which comprises treating a pulp of such an ore in the presence of a flotation inhibitor of molybdenite so as to separate a concentrate rich in copper sulphide; and treating the remaining pulp, after the addition of a xanthomolybdic acid compound thereto, so as to remove a froth flotation concentrate rich in molybdenite.

16. The process of concentrating ores containing copper and molybdenum sulphides, which comprises treating a pulp of such an ore in the presence of a protective colloid so as to remove a floating concentrate rich in copper sulphide, adding to the remaining pulp a xanthomolybdic acid compound, and thereafter treating the said remaining pulp by froth flotation so as to remove a concentrate rich in molybdenite.

17. The process of concentrating ores containing copper and molybdenum sulphides, which comprises treating a pulp of such an ore in the presence of a flotation inhibitor of molybdenite so as to remove a floating concentrate rich in copper sulphide; and separating from the remaining pulp by froth flotation a molybdenite concentrate with the aid of the material obtained by the reaction in an aqueous medium of a soluble xanthate, a soluble molybdate, and an acid.

18. In the process of concentrating metallic copper by froth flotation, the step which consists in subjecting a pulp containing metallic copper to a froth flotation operation with the aid of a xanthomolybdic acid compound.

19. The process of concentrating ores containing sulphide and oxidized copper minerals, which comprises subjecting a pulp of such an ore to a treatment resulting in the separation by flotation of a concentrate rich in copper sulphide, leaching the remaining pulp with an acid to dissolve the oxidized copper, precipitating the dissolved copper in the form of metallic copper, and treating the resulting material in the presence of a xanthomolybdic acid compound so as to separate by froth flotation a concentrate rich in metallic copper.

20. The process of concentrating ores containing sulphide and oxidized copper minerals, which comprises treating a pulp of such an ore with the aid of a xanthomolybdic acid compound so as to separate by froth flotation a concentrate rich in copper sulphide, leaching the remaining pulp with an acid to dissolve the oxidized copper, precipitating the dissolved copper in the form of metallic copper, and treating the resulting material in the presence of a xanthomolybdic acid compound so as to separate by froth flotation a concentrate rich in metallic copper.

21. The process of concentrating ores containing sulphide and oxidized copper minerals, which comprises leaching such an ore with an acid to dissolve the oxidized copper, removing the solids from the dissolved copper, and treating a pulp of said solids in the presence of a xanthomolybdic acid compound so as to separate by froth flotation a concentrate rich in copper sulphide.

22. The process of concentrating ores containing sulphide and oxidized copper minerals, which comprises leaching such an ore with an acid to dissolve the oxidized copper, precipitating the dissolved copper in the form of metallic copper, subjecting the resulting material to froth flotation in the presence of a xanthomolybdic acid compound so as to produce a concentrate rich in copper sulphide and metallic copper, and separating the concentrate.

23. In the concentration of metalliferous ores by froth flotation, the step which consists in carrying out the froth flotation operation with the aid of ethyl xanthomolybdic acid.

24. In the concentration of metalliferous ores by froth flotation, the step which consists in carrying out the froth flotation operation with the aid of amyl xanthomolybdic acid.

25. In the concentration of metalliferous ores by froth flotation, the step which consists in carrying out the froth flotation operation with the aid of butyl xanthomolybdic acid.

CORNELIUS H. KELLER.

CERTIFICATE OF CORRECTION.

Patent No. 2,148,475. February 28, 1939.

CORNELIUS H. KELLER.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 70, in the table, third column thereof, for the numeral "18.751" read 18.571; 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 4th day of April, A. D. 1939.

Henry Van Arsdale

(Seal) Acting Commissioner of Patents.