Oct. 29, 1957 C. M. NOKES 2,811,255

PROCESS FOR RECOVERY OF MOLYBDENITE FROM COPPER SULFIDE - MOLYBDENITE FLOTATION CONCENTRATES

Filed April 21, 1954 2 Sheets-Sheet 1

FIG. 1.

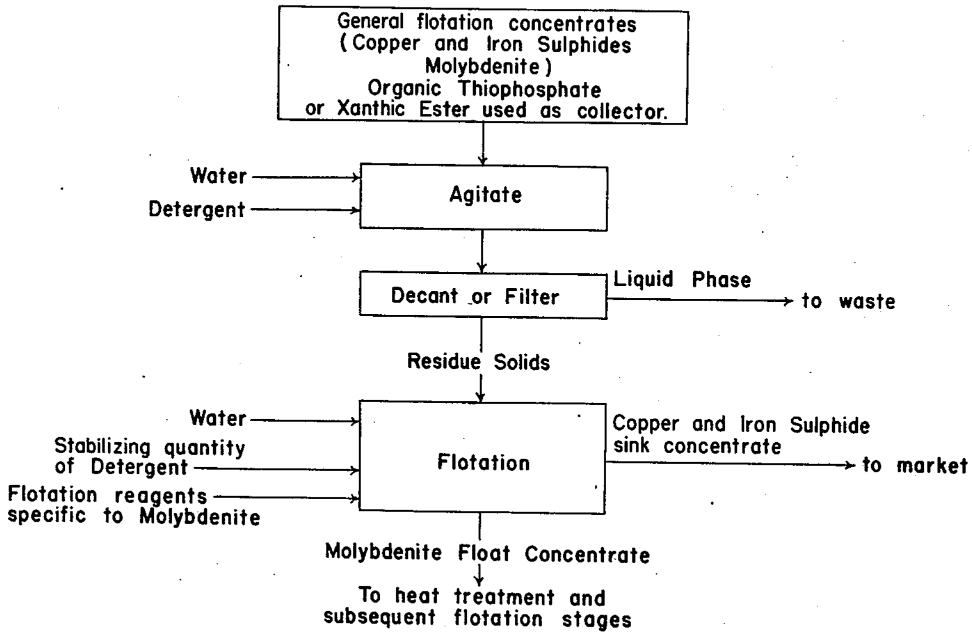

FIG. 2.

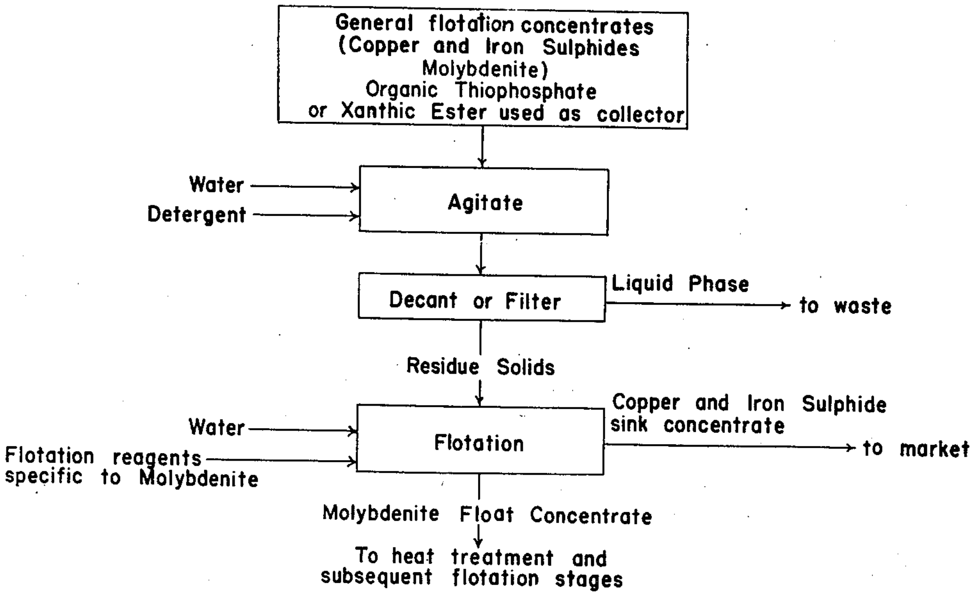

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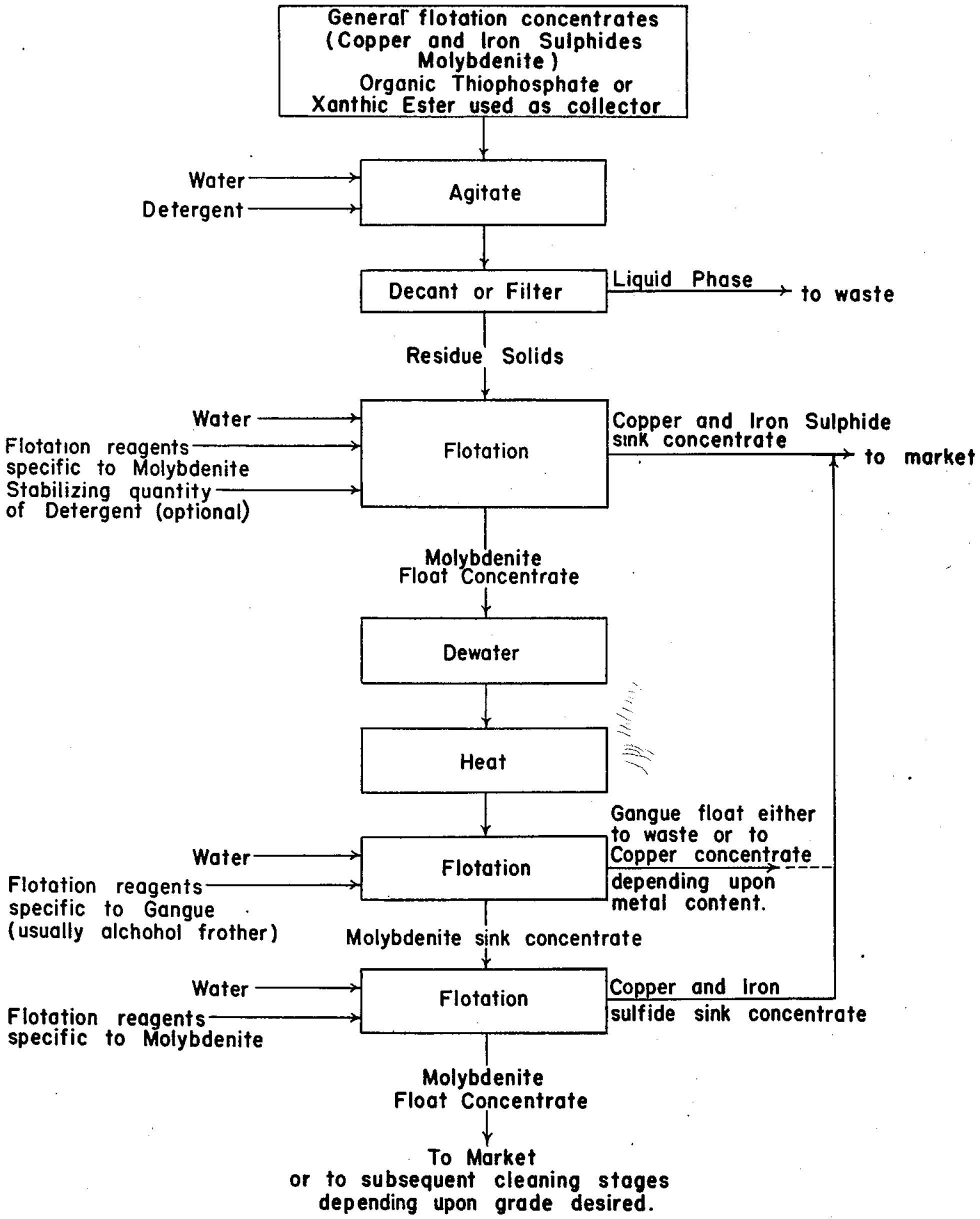
FIG. 3.



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PROCESS FOR RECOVERY OF MOLYBDENITE FROM COPPER SULFIDE-MOLYBDENITE FLOTATION CONCENTRATES

Charles M. Nokes, Salt Lake City, Utah

Application April 21, 1954, Serial No. 424,621

4 Claims. (Cl. 209—167)

This invention relates to processes of differential froth flotation, and has particular reference to the treatment of certain metal sulfide flotation concentrates for the recovery of values which represent relatively minor components of the original ore pulp.

Low grade copper sulfide ores containing relatively minor quantities of molybdenite are mined and milled commercially at various locations in the western part of the United States. Since the copper content is often less than one percent of the ore, it can be readily seen that the molybdenum content is exceedingly small.

Original methods employed in the processing of these ores ignored the molybdenum content, and permitted it to go to waste. At the present time, however, the molybdenum is regarded as constituting a substantial portion of the total values contained by the ore, and, consequently, its clean separation from the copper content has become a matter of economic importance.

It is customary practice to beneficiate these low grade copper sulfide ores by an initial froth flotation procedure, which produces an initial or general flotation concentrate containing major proportions of both the copper sulfide and the molybdenite values, and to thereafter treat this general flotation concentrate to effect a separation between the molybdenite, on the one hand, and the copper sulfides together with accompanying iron sulfide, on the other. A typical range of the pertinent metal values in the general concentrate is from approximately 25 to 38% copper, as sulfides, and from approximately 1 to 2½% molybdenite.

A fair degree of success has been achieved heretofore in the separation of the copper sulfides from the molybdenite by specialized flotation processes.

One of the more widely used of these involves a selective flotation of the copper sulfides by subjecting the general flotation concentrate to a re-flotation procedure in the presence of an organic colloid, such as starch or dextrin, which apparently acts as a depressant for the molybdenite.

Another involves, in the commercial application, heating the general flotation concentrate, either wet or dry, to alter the surface characteristics of the copper sulfides, and, thereafter, subjecting such treated concentrate to a re-flotation procedure, for selectively floating the molybdenite from the copper sulfides, which latter are depressed by reason of their surface alteration. This forms the subject of U. S. Reissue Patent No. Re. 22,117, granted jointly to me, Thomas A. Janney, and Alpha G. Johnson under date of June 16, 1942.

Thus, in the first of these processes the molybdenite is depressed and the copper sulfides floated, while in the second the copper sulfides are depressed and the molybdenite floated. In actual practice, it is customary to grade up the tailings or what might appropriately be referred to as a "sink product" (primary molybdenum concentrates) of the first process by application thereto of the second process.

A process which is, under certain conditions, superior to either of the above from the standpoint of recoveries and economy of application is set forth in U. S. Patent No. 2,492,936 granted jointly to me, Charles G. Quigley, and Robert T. Pring under date of December 27, 1949, and involves the selective floating of the molybdenite relative to the copper sulfides by subjecting the general flotation concentrate to a reflotation procedure in the presence of an inorganic compound of phosphorus, arsenic or antimony containing sulfur in the bivalent state and an inorganic cation, such inorganic compound acting to depress the copper and iron sulfides. Typical of these inorganic depressants is a compound consisting of or largely including an inorganic thiophosphate, which compound is formed as a reaction product of sodium hydroxide and phosphorus pentasulphide in an aqueous medium. This compound will be hereinafter referred to as "sodium thiophosphate."

While this last process results in a concentrate relatively high in molybdenite and requires only moderate grading up by the heating process referred to above, it has been found in commercial practice utilizing an organic thiophosphate, e. g. sodium dicresyldithiophosphate, or one of the xanthic esters (known commercially as "Minerecs") as the collector in the production of the general flotation concentrate, which is customary with certain types of the particular ores concerned, notably those of the Utah Copper Division, Kennecott Copper Corporation, that difficulty is encountered by reason of the accompanying production of a voluminous and unmanageable froth, which seriously interferes with the flotation operation.

I have now found, however, that these so-called inorganic depressants may be employed in a somewhat different role, to overcome the difficulty mentioned above, and that various other chemical compounds may be similarly employed in accordance with the procedures herein set forth to accomplish generally similar results.

Thus, I have found that if the general flotation concentrate is prepared as an aqueous pulp, and is vigorously agitated in the presence of one of the aforementioned inorganic depressants, particularly an inorganic thiophosphate, and if, thereafter, the aqueous phase is removed, as by decanting or filtering, and the residue repulped with fresh water, i. e. water free from flotation agents, and subjected to a flotation operation utilizing reagents specific to molybdenite, that not only is the froth produced by the latter operation of normal value and completely manageable, but an unusually satisfactory molybdenite froth concentrate is obtained. Furthermore, I have found that the aforesaid heat treatment process of Reissue Patent No. Re. 22,117 is applicable to this molybdenite concentrate, and accomplishes a peculiarly effective grading up thereof, due, at least in part, to the greater control possible by reason of the unique character of the concentrate, it being noted in this connection that there are less iron sulfides present in given quantities of the concentrate.

It now appears that the step, in the above procedure, of vigorously agitating the general concentrate as a wet pulp in the presence of what has heretofore been regarded only as an inorganic depressant, actually constitutes a washing or cleansing of the general flotation concentrate, and that these so-called inorganic depressants of the afore-referred-to Patent No. 2,492,936 serve in the capacity of detergents with respect to the particle-surface residuum of the initial flotation operation, that is to say, as cleansing agents with respect to the reagents carried over from the general flotation operation in the form of surface coatings on the mineral particles.

This follows logically from the fact that I have also found that other chemical agents known to have detergent action may be satisfactorily employed in this first step of the process of the present invention in place of the inorganic depressants mentioned above. Thus, such substances as alkali metal sulfides, hydroxides, and hypochlorites, as well as alkali cyanides have been found to produce excellent results. The important thing is that at least enough of the liquid phase of the resulting pump be removed as will prevent excessive frothing, and that the pulp residue be thereafter re-pulped with fresh water prior to flotation with reagents specific to molybdenite.

In practice, it is desirable that as much of the liquid phase of the cleansed pulp be removed as is reasonably possible, filtering being a preferred way of accomplishing this. Nevertheless, reasonably satisfactory results have been obtained by settling the solids and decanting.

While results which are far superior to those achieved by prior processes may be obtained by merely subjecting the cleansed and re-pulped general concentrate to a flotation operation using reagents specific to molybdenite, for example, ordinary burner oil as a collector and methyl amyl alcohol as a frother, I have found that even better results can ordinarily be obtained if a moderate quantity of the detergent be added to the repulped solids before subjecting them to flotation. The action involved is apparently one of stabilization of the flotation circuit for best separation of the molybdenite and copper sulfides.

A variety of tests have been made utilizing the process of the invention in comparison with prior art processes. Of these tests, those conforming to the process of this invention were performed in accordance with one or another of the procedures outlined in the respective flow sheets of the accompanying drawing, wherein Fig. 1 represents the procedure utilizing the step of stabilization of the flotation stage of the process, while Fig. 2 represents the alternative but less preferred procedure of carrying out this flotation stage without stabilization. Fig. 3 represents the complete process employed in practice to derive the maximum separation between the molybdenite and the copper and iron sulfides.

EXAMPLE NO. 1

Comparative tests were carried out on general copper sulfide-molybdenite flotation concentrate produced by Utah Copper Division, Kennecott Copper Corporation, as part of its ordinary and regular commercial operations.

Each of the tests employed a charge of wet pulp containing 500 grams of the solid concentrate, which latter assayed 31.850% copper, 21.70% iron, 15.80% insolubles, and 1.44% molybdenite, and was produced in accordance with normal practice, utilizing sodium dicresyldithiophosphate as the collector and a mixture of cresylic acid and methyl amyl alcohol as the frother.

The test employing the detergent process of the invention followed the procedure indicated by the flow sheet of Fig. 1. The charge of wet pulp was introduced into a Fagergren laboratory flotation cell together with 4 milliliters of sodium thiophosphate, as a detergent, and was vigorously agitated for a period of three minutes in what might be regarded as a preliminary conditioning operation. (The sodium thiophosphate was prepared on the basis of 13 grams $NaOH$, in aqueous solution, reacted with 10 grams P_2S_5, the reaction product made up with water to 100 milliliters.)

Following this step of agitation of the charge of general flotation concentrate in the presence of the detergent, and in accordance with the invention, the so-processed pulp was filtered, producing a liquid filtrate and a solid residue.

The liquid filtrate was passed to waste, and the residue solids were repulped with fresh water.

The resulting pulp was introduced into the same flotation cell, together with 2 milliliters of the aforesaid detergent reagent, one gram of lime, two drops of burner oil from a serological pipette, and sufficient methyl amyl alcohol to produce and maintain desired frothing conditions.

Agitation of this repulped charge for a period of two minutes in a flotation operation of normal character, produced a normal and manageable volume of steel-grey froth relatively rich in molybdenite and relatively poor in copper.

In comparison with this procedure of the present invention, a similar charge of the same wet pulp concentrate was subjected to a differential froth flotation operation in accordance with the depressant process of the aforementioned U. S. Patent No. 2,492,936, for depressing the copper and iron sulfides while flotating the molybdenite.

Pursuant to such prior art procedure, the charge of pulp was agitated for a period of three minutes with 6 milliliters of the sodium thiophosphate reagent. Thereafter, one gram of lime was added, and the pulp was agitated for a period of two minutes, whereupon two drops of burner oil were added and the pulp agitated for an additional period of one minute.

After this conditioning treatment, the pulp was subjected to flotation without first eliminating the liquid phase and repulping, resulting in a voluminous froth of unmanageable proportions.

Comparative recoveries of the two procedures are shown by the following table:

	Test No. 1 Detergent Process of this invention (flotation stage stabilized)	Test No. 2 Depression Process of Patent No. 2,492,936
Copper Concentrate (sink):		
Percent wt	93.88	75.74
Percent Cu	33.300	33.750
Percent distr. Cu	96.62	79.72
Percent Fe	21.80	21.80
Percent distr. Fe	96.06	78.73
Percent Insol	14.10	13.80
Percent distr. Insol	92.02	69.48
Percent MoS_2	.07	.04
Percent distr. MoS_2	4.11	1.94
MoS_2 Concentrate (float):		
Percent wt	6.12	24.26
Percent Cu	17.900	26.800
Percent distr. Cu	3.38	20.28
Percent Fe	13.80	18.40
Percent distr. Fe	3.94	21.27
Percent Insol	18.80	18.90
Percent distr. Insol	7.99	30.52
Percent MoS_2	25.05	6.30
Percent distr. MoS_2	95.89	98.06

EXAMPLE NO. 2

A series of comparative tests corresponding procedurally to the tests of Example No. 1, above, but utilizing several different detergent reagents to indicate the scope of the present invention, were carried out on respective wet pulp charges of a general flotation concentrate obtained at a different time from Utah Copper Division, Kennecott Copper Corporation. This concentrate assayed 20.850% copper and 2.77% molybdenite, and represented a mixture of the normal general flotation concentrate with a scavenger concentrate resulting from the further flotation of such normal concentrate for additional mineral recovery, as is often commercially practiced in the plant concerned.

In the first group of tests of the series (tests Nos. 1 and 2) sodium thiophosphate was utilized both as a detergent reagent, in connection with the process of the invention, and as a depressant reagent, in connection with the comparative prior art process.

In the second group of tests (tests Nos. 3 and 4), sodium sulfide was utilized in both instances.

In the third group of tests (tests Nos. 5 and 6), "Aero Brand" cyanide was utilized for both (crude calcium cyanide).

It should be noted that, in each of these groups of comparative tests, that test which employed the process of the invention was characterized by a normal and manageable froth and relatively high recoveries, while that which conformed to the prior art was characterized by excessively voluminous and practically unmanageable froth and by somewhat poorer recoveries.

The comparative recoveries are shown by the following tables:

Sodium thiophosphate

	Test No. 1 Detergent Process of this invention (flotation stage stabilized)	Test No. 2 Depression Process of Patent No. 2,492,936
Cu Concentrate (Sink):		
Percent wt	95.71	88.74
Percent Cu	21.050	21.950
Percent distr. Cu	98.51	92.89
Percent MoS_2	.06	.06
Percent distr. MoS_2	2.03	1.78
MoS_2 Concentrate (Float):		
Percent wt	4.29	11.26
Percent Cu	7.100	13.250
Percent Cu	7.100	13.250
Percent distr. Cu	1.49	7.11
Percent MoS_2	64.70	26.10
Percent distr. MoS_2	97.97	98.22

Sodium sulfide

	Test No. 3	Test No. 4
Cu Concentrate (Sink):		
Percent wt	94.19	83.80
Percent Cu	22.000	22.200
Percent distr. Cu	98.37	88.55
Percent MoS_2	.10	.08
Percent distr. MoS_2	3.40	2.54
MoS_2 Concentrate (Float):		
Percent wt	5.81	16.20
Percent Cu	5.900	14.850
Percent distr. Cu	1.63	11.45
Percent MoS_2	46.70	15.90
Percent distr. MoS_2	96.60	97.46

"Aero Brand" cyanide

	Test No. 5	Test No. 6
Cu Concentrate (Sink):		
Percent wt	90.47	55.82
Percent Cu	21.350	17.200
Percent distr. Cu	91.39	45.77
Percent MoS_2	.08	.09
Percent distr. MoS_2	2.59	3.27
MoS_2 Concentrate (Float):		
Percent wt	9.53	44.18
Percent Cu	19.00	25.750
Percent distr. Cu	8.61	54.23
Percent MoS_2	28.60	3.00
Percent distr. MoS_2	97.41	96.73

EXAMPLE NO. 3

Comparative tests were made between, first, that aspect of the invention shown by the flow sheet of Fig. 1 (involving stabilization of the flotation stage, following the detergent conditioning stage, by the addition of a relatively small amount of the detergent reagent to the repulped charge); second, the less preferred practice of the invention as shown by the flow sheet of Fig. 2 (without stabilization of the flotation stage); and, third, the prior art copper depression process of Patent No. 2,492,936.

These three tests were carried out on similar quantities of wet pulp made up from general copper-molybdenite concentrates of Utah Copper Division, Kennecott Copper Corporation, assaying 30.600% copper, 14.40% insolubles, and 1.84% molybdenite.

In the first test, the wet pulp charge was vigorously agitated with 4 ml. of sodium thiophosphate for a period of one minute, and was then filtered. The residue solids from this filtration operation were repulped with fresh water, and subjected to flotation for a period of seven minutes with 4 drops of burner oil, 2 drops of reagent

B-22 (a proprietary alcohol frother manufactured by DuPont) and 2 ml. of the sodium thiophosphate detergent reagent.

In the second test, the charge of wet pulp was filtered following vigorous agitation for a period of two minutes with 6 ml. of sodium thiophosphate, the residue solids being thereafter repulped and subjected to flotation for a period of seven minutes with 4 drops of burner oil and 2 drops of reagent B-22. None of the sodium thiophosphate detergent reagent was used during this flotation stage.

The third test was carried out in conformity with the prior art copper depressant process of Patent No. 2,492,936. In this instance, the pulp was agitated for a period of one minute with 6 ml. of sodium thiophosphate, after which 4 drops of burner oil were added, and the remaining pulp subjected to flotation for a period of seven minutes.

In both of those tests which conformed to the present invention, the froth was normal and completely manageable, but it will be noted from the following tables of results that superior recoveries were obtained in test No. 1, where stabilization of the flotation stage was carried out. This was due chiefly to better copper rejection and to an overall better grade of concentrate. In test No. 3, where filtration of the conditioned pulp and repulping of the residue solids were not practiced, the froth was excessive in quantity, and practically unmanageable.

	Test No. 1 Detergent Process of present invention with stabilization	Test No. 2 Detergent Process of present invention without stabilization	Test No. 3 Depression Process of Patent Number 2,492,936
Copper Concentrate (Sink):			
Percent wt	94.17	93.20	82.14
Percent Cu	31.050	31.100	30.900
Percent distr. Cu	97.46	96.47	84.18
Percent Insol	14.70	14.60	14.40
Percent distr. Insol	94.34	94.98	81.93
Percent MoS_2	.02	.02	.02
Percent distr. MoS_2	9.45	10.65	8.75
Moly. Concentrate (Float):			
Percent wt	5.83	6.80	17.86
Percent Cu	16.050	21.500	26.700
Percent distr. Cu	2.54	3.53	15.82
Percent Insol	15.50	10.60	14.60
Percent distr. Insol	5.66	5.02	18.07
Percent MoS_2	36.70	25.40	10.40
Percent distr. MoS_2	90.55	89.35	91.25

EXAMPLE NO. 4

Here, a series of tests were run comparing the use of different quantities of the detergent reagent in the process of the invention, both with respect to that aspect thereof utilizing stabilization of the flotation stage and that not so doing. In addition, comparative tests were run reversing the relative quantities of the detergent reagent employed as between the conditioning and the flotation stages of the process, to show the differences in effect of the reagent with respect to these distinct stages of the process.

The general flotation concentrate utilized for each of the tests corresponded with that used for the tests of Examples Nos. 1 and 3. Here, however, the assay was 33.650% copper, 10.10% insolubles, and 1.10% molybdenite. The procedures employed corresponded with those of Example No. 3. In tests Nos. 1, 2 and 5, where stabilization of the flotation stage was carried out, quantities of 6 ml., 5 ml., and 4 ml., respectively, of the sodium thiophosphate reagent were used for the initial conditioning, while stabilization quantities of 2 ml., 3 ml., and 2 ml., respectively, were used for the subsequent flotation.

In tests Nos. 3 and 4, quantities of 8 ml. and 6 ml., respectively, of the sodium thiophosphate detergent reagent were used for the initial conditioning, while none was employed for the subsequent flotation.

Test No. 6 reversed the quantities of sodium thiophosphate detergent reagent used in test No. 5 for the initial conditioning and for the subsequent flotation stages.

The results obtained from these several tests are shown in the following tables:

	Test No. 1 Detergent Stabilized (6+2 ml.)	Test No. 2 Detergent Stabilized (5+3 ml.)	Test No. 3 Detergent not stabilized (8 ml.)
Copper Concentrate (Sink):			
Percent wt	91.39	91.27	71.20
Percent Cu	34.300	35.150	33.100
Percent distr. Cu	95.69	95.26	71.48
Percent Insol	9.80	7.90	13.40
Percent distr. Insol	77.37	74.48	79.04
Percent MoS_2	.02	.02	.02
Percent distr. MoS_2	1.33	1.43	1.40
MoS_2 Concentrate (Float):			
Percent wt	8.61	8.73	28.80
Percent Cu	16.400	18.300	32.650
Percent distr. Cu	4.31	4.74	28.52
Percent Insol	30.40	28.30	8.80
Percent distr. Insol	22.63	25.52	20.96
Percent MoS_2	15.80	14.40	3.48
Percent distr. MoS_2	98.67	98.57	98.60
Character of froth	Manageable	Manageable	Manageable
Frothing agent added	B–22	B–22	B–22

	Test No. 4 Detergent not stabilized (6 ml.)	Test No. 5 Detergent stabilized (4+2 ml.)	Test No. 6 Same as No. 5 but quantities reversed (2+4 ml.)
Copper Concentrate (Sink):			
Percent wt	77.66	90.28	86.60
Percent Cu	33.300	34.900	34.350
Percent distr. Cu	78.53	94.49	91.06
Percent Insol	10.40	8.70	9.30
Percent distr. Insol	72.79	76.36	71.81
Percent MoS_2	.02	.02	.02
Percent distr. MoS_2	1.46	1.35	1.91
MoS_2 Concentrate (Float):			
Percent wt	22.34	9.72	13.40
Percent Cu	31.650	18.900	21.800
Percent distr. Cu	21.47	5.51	8.94
Percent Insol	13.50	25.00	23.60
Percent distr. Insol	27.21	23.64	28.19
Percent MoS_2	4.68	13.60	6.64
Percent distr. MoS_2	98.54	98.65	98.09
Character of froth	Manageable.	Manageable.	Unmanageable.
Frothing agent added	B–22	B–22	None

Comparing the results of tests Nos. 1, 2 and 5, it can be seen that the increased quantities of the detergent reagent used in the conditioning stages of tests Nos. 1 and 2 over that of test No. 5 were of substantially no benefit, and that the increase for this stabilization stage of test No. 2 was of little significance.

On the other hand, comparing the results of tests Nos. 5 and 6, it can be seen that an insufficient quantity of the detergent reagent was employed in the initial conditioning stage of test No. 6 to accomplish the purposes of the invention. In that latter test, not only were the metallurgical recoveries somewhat lower than in test No. 5, but the froth was excessively voluminous and practically unmanageable.

With respect to tests Nos. 3 and 4, where stabilization of the flotation was not carried out, it can be seen that, just as in those tests where stabilization was carried out, the greater quantity of detergent reagent utilized in the initial conditioning of the pulped concentrates was of substantially no benefit.

Accordingly, it can be logically concluded that only so much of the detergent reagent is necessary in any given instance as will cleanse, from the surfaces of the concentrated mineral particles, residual reagents carried over from the previous flotation treatment. No depression phenomena is involved in the present process.

If the results of tests Nos. 4 and 5 be compared, the advantages of the preferred stabilization aspect of the invention as against non-stabilization, are further demonstrated.

EXAMPLE NO. 5

The several tests made for this example were designed to compare results as between the stabilization and non-stabilization aspects of the invention, utilizing the same quantity of detergent reagent in the initial conditioning stages of the respective tests, and, furthermore, to compare these results with the use of corresponding quantities of that reagent in the prior art copper depression process of Patent No. 2,492,936.

The Utah Copper Division, Kennecott Copper Corporation, general flotation concentrates employed for these tests assayed 38.200% copper, 9.50% insolubles, and 1.63% molybdenite. The respective procedures corresponded with those of test No. 3, one drop of frothing agent B–22 being utilized here, however, instead of two.

In test No. 1, a quantity of 6 ml. of sodium thiophosphate was utilized in the initial detergent stage, while an additional quantity of 3 ml. was added in the subsequent flotation stage.

In test No. 2, a quantity of 6 ml. of sodium thiophosphate was utilized for the initial detergent stage, while none was added in the subsequent flotation stage.

Test No. 3 corresponded to test No. 1 in the total quantity of sodium thiophosphate utilized, but employed the prior art copper depressant process.

Test No. 4 corresponded to test No. 2 in the total quantity of sodium thiophosphate utilized, but also employed the prior art copper depressant process.

The results obtained appear in the following table:

	Test No. 1	Test No. 2	Test No. 3	Test No. 4
Copper Concentrate (Sink):				
Percent wt	92.36	88.83	83.35	82.07
Percent Cu	39.500	39.400	39.600	39.450
Percent distr. Cu	96.16	92.46	87.66	86.60
Percent Insol	8.70	9.10	8.10	7.80
Percent distr. Insol	85.08	86.88	73.13	71.51
Percent MoS_2	.04	.02	.08	.11
Percent distr. MoS_2	1.82	.99	3.48	5.36
MoS_2 Concentrate (Float):				
Percent wt	7.64	11.17	16.65	17.93
Percent Cu	19.050	25.550	27.900	28.300
Percent distr. Cu	3.84	7.54	12.34	13.40
Percent Insol	18.50	10.90	14.90	14.20
Percent distr. Insol	14.92	13.12	26.87	28.49
Percent MoS_2	26.10	15.90	11.10	8.90
Percent distr. MoS_2	98.18	99.01	96.52	94.64
Character of froth	Manageable.	Manageable.	Unmanageable.	Unmanageable.
Frothing agent added	B–22	B–22	None	None

It can be seen that these tests also indicate superiority of the process of the present invention over that of Patent No. 2,492,936, as well as superiority of the stabilization aspect of the invention over that of non-stabilization.

EXAMPLE No. 6

Inasmuch as a depression process extensively practiced by the Utah Copper Division, Kennecott Copper Corporation, in the commercial treatment of its copper sulfide-molybdenite general flotation concentrates is that set forth in U. S. Patent No. 2,070,076, granted February 9, 1937 to Earl H. Brown, entitled "Separation of Molybdenite from Copper Sulphides," and involving use of dextrine as a depressant for the molybdenite, along with an alkali xanthate for floating the copper sulfides from the depressed molybdenite, two series of comparative tests were made between that prior art molybdenite depression process, the prior art copper depression process of the afore-referred-to Patent No. 2,492,936, and the copper detergent process of the present invention.

The general flotation concentrate employed in the first series of tests assayed 31.350% copper, 17.90% insolubles, and 1.11% molybdenite.

Test No. 1 followed the preferred practice of the present invention, employing stabilization of the flotation stage. A quantity of 4 ml. of sodium thiophosphate was used as the detergent reagent in the initial conditioning stage, and a stabilization quantity of 2 ml. in the subsequent flotation stage.

In test No. 2, a quantity of 6 ml. of sodium thiophosphate was used as a depressant reagent in accordance with the process of Patent No. 2,492,936 as detailed hereinbefore.

In test No. 3, the charge of wet pulp was conditioned for a period of one minute with 4 ml. of dextrine solution (1.6 lbs. per ton), and was thereafter subjected to flotation for five minutes in the presence of 2 ml. sodium ethyl xanthate solution (0.2 lbs. per ton) and 2 drops of methyl amyl alcohol, in accordance with the molybdenite depressant process of Patent No. 2,070,076.

The comparative results obtained in this series of tests appear in the following table:

First series

	Test No. 1 Copper Detergent Process	Test No. 2 Copper Depressant Process	Test No. 3 Dextrine-Xanthate Process
Copper concentrate:	(sink)	(sink)	(float)
Percent wt	89.86	74.66	68.88
Percent Cu	28.050	27.750	33.250
Percent distr. Cu	92.85	77.38	85.09
Percent Insol	17.50	17.40	4.30
Percent distr. Insol	84.21	69.69	16.23
Percent MoS_2	.09	.08	.11
Percent distr. MoS_2	6.71	4.73	6.02
Molybdenite concentrate:	(float)	(float)	(sink)
Percent wt	10.14	25.34	31.12
Percent Cu	19.150	23.900	12.90
Percent distr. Cu	7.15	22.62	14.91
Percent Insol	29.10	22.30	49.10
Percent distr. Insol	15.79	30.31	83.77
Percent MoS_2	11.10	4.75	3.80
Percent distr. MoS_2	93.29	95.27	93.98

It will be noted that the total molybdenite recovered by the respective processes is about the same, but that the grade of the molybdenite was superior for test No. 1 where the present invention was practiced. Furthermore, because more of the copper sulfides and insolubles were rejected from the molybdenite concentrate in test No. 1, there was considerable less bulk to encumber subsequent processing of such molybdenite concentrate, a factor whose importance will become apparent in the consideration of tests conforming to the flow sheet of Fig. 3.

For the second series of tests under this example, a similar Kennecott general flotation concentrate, assaying 24.350% copper, 19.80% insolubles, and 1.34% molybdenite, was used.

The tests of this series, namely, Nos. 4, 5 and 6, corresponded procedurally with tests Nos. 1, 2 and 3, respectively, of the first series.

The results set forth below show the same trend as those for the first series:

Second series

	Test No. 4 Copper Detergent Process	Test No. 5 Copper Depressant Process	Test No. 6 Dextrine-Xanthate Process
Copper concentrate:	(sink)	(sink)	(float)
Percent wt	94.51	84.73	38.58
Percent cu	25.150	25.950	31.650
Percent distr. cu	95.92	86.36	49.73
Percent Insol	18.10	17.40	2.80
Percent distr. Insol	93.80	80.24	5.24
Percent MoS_2	.04	.10	.10
Percent distr. MoS_2	2.71	5.99	2.79
Molybdenite concentrate:	(float)	(float)	(sink)
Percent wt	5.49	15.27	61.42
Percent cu	18.400	22.750	20.100
Percent distr. cu	4.08	13.64	50.27
Percent Insol	20.50	23.80	31.80
Percent distr. Insol	6.20	19.76	94.76
Percent MoS_2	24.70	8.70	2.34
Percent distr. MoS_2	97.29	94.01	97.21

Considering the further processing of the molybdenite concentrates from these two series of tests in accordance with the flow sheet of Fig. 3, it is significant to note that the ratios of the weight thereof as between the three different tests are, for the tests of the first series:

Test No. 1 (copper detergent)	1.0
Test No. 2 (copper depressant)	2.5
Test No. 3 (Dextrine-xanthate)	3.1

and, for the tests of the second series:

Test No. 4 (copper detergent)	1.0
Test No. 5 (copper depressant)	2.8
Test No. 6 (Dextrine-xanthate)	11.2

It can be seen that, in terms of tons, these differences are very substantial.

EXAMPLE NO. 7

For this example, comparative tests were made to demonstrate the advantages of that aspect of the present invention which is represented by the flow sheet of Fig. 3, as against generally corresponding standard procedures.

As mentioned hereinbefore, the present commercial practice at the mills of the Utah Copper Division, Kennecott Copper Corporation, is to produce a molybdenite sink concentrate by the use of a dextrin depressant, together with a xanthate collector, in the processing of the initial or general flotation concentrate, and, thereafter, to further treat such molybdenite sink concentrate by the use of heat for altering the surfaces of the copper and iron sulfide particles so that they will be depressed during a differential flotation operation for the recovery of a molybdenite float final concentrate.

Over a period of years in the use of the above procedure, optimum temperature range and time range for the heating stage have been established. In the comparative tests of this example, the test conforming to such prior practices employs the temperature and time period for the heating stage which is indicated by these established optimum ranges of temperature and time of application. It will be seen from the tables appearing herebelow, that the over-all process of the present invention contrasts with such established commercial procedures in employing a substantially lower temperature range to produce superior metallurgical results. While the time of heat application is extended in this instance, it can be appreciated that the total B. t. u.'s involved is considerably less in the instance of the invention. Furthermore, there is considerably less danger of the body of concentrate igniting, to the detriment of the final results. In this connection, it should be noted that not only is the bulk of the intermediate concentrates going to the heating processing stage greatly reduced in the instance of the process of the invention as against the standard practices, but the amount of sulfides present in the intermediate concentrate is also considerably reduced.

In the first test of this example, which conformed to the invention, an intermediate molybdenite concentrate was obtained by a procedure conforming to the first portion of the flow sheet of Fig. 3, sodium thiophosphate having been utilized as the detergent reagent and a stabilizing quantity of same having been used in the flotation stage in accordance with the preferred procedure of the invention.

Such intermediate molybdenite concentrate assayed 6.500% copper, 50.60% insolubles, and 27.70% molybdenite. The moist concentrate was first dried, and then subjected to heat treatment in a laboratory roaster for a period of sixty minutes at from 480 degrees to 510 degrees F., this procedure corresponding generally to mill practice of passing the moist concentrate through a conventional hearth roaster. After cooling and repulping, the heat-treated concentrate was subjected to lime conditioning for a period of approximately two minutes on the basis of the addition of 0.32 pound of lime per ton of concentrate, and was then subjected to flotation for a period of approximately five minutes in the presence of the aforementioned B–22 frother reagent, added on the basis of 0.36 pound of the reagent per ton of the concentrate.

A gangue float concentrate was produced from this flotation operation. The sink concentrate, containing the values, was subjected to further conditioning and flotation to produce a final molybdenite float concentrate, ready for market, and a copper sink concentrate. The conditioning stage in this operation employed four pounds of lime and two pounds of sodium silicate per ton of concentrate, and extended over a period of approximately one minute. Burner oil and B–22 frother were added to the so-conditioned pulp, on the basis of two pounds and 0.12 pound, respectively, per ton of pulp, for the flotation operation, which extended over a period of seven minutes.

The results obtained are set forth herebelow under the heading "Test No. 1."

In contrast to this procedure of the invention, an intermediate concentrate obtained from the standard dextrin-xanthate process ordinarily employed in commercial operations of the Utah Copper Division, Kennecott Copper Corporation, was subjected to a heat treatment and flotation procedure identical with that detailed above, except for the temperatures applied and the duration of application thereof in the heat treatment stage and for the quantity of lime utilized in the initial conditioning treatment of the subsequent flotation operation.

In this instance, the intermediate molybdenite concentrate (dextrin-xanthate) assayed 6.500% copper, 63.20% insolubles, and 11.00% molybdenite, and the moist concentrate was subjected to the aforespecified heat treatment for a period of 30 minutes at temperatures of from 530 degrees to 560 degrees F. A quantity of 4.8 pounds of lime per ton of solids in the cooled and repulped concentrate was employed for the conditioning stage of the initial flotation operation in order to obtain substantially the same pH (7.3) for the initial sink concentrate as in the previous instance of the invention.

The molybdenite float concentrate and copper sink concentrate obtained from the final flotation of such initial sink concentrate were as set forth in the below table of results under the heading "Test No. 2."

	Test No. 1 Process of Invention Detergent Process	Test No. 2 Dextrin-Xanthate Process
	(float)	(float)
Gangue Concentrate:		
Percent wt	45.88	9.38
Percent Cu	1.300	3.800
Percent distr. Cu	9.47	5.61
Percent Insol	91.40	24.30
Percent distr. Insol	82.75	3.60
Percent MoS_2	.66	57.30
Percent distr. MoS_2	1.11	49.97
	(sink)	(sink)
Copper Concentrate:		
Percent wt	19.61	82.42
Percent Cu	23.550	7.200
Percent distr. Cu	73.41	93.55
Percent Insol	25.40	70.90
Percent distr. Insol	9.83	92.28
Percent MoS_2	2.44	.31
Percent distr. MoS_2	1.75	2.38
	(float)	(float)
Molybdenite Concentrate:		
Percent wt	34.51	8.20
Percent Cu	3.120	.65
Percent distr. Cu	17.12	.84
Percent Insol	10.90	31.80
Percent distr. Insol	7.42	4.12
Percent MoS_2	76.80	62.50
Percent distr. MoS_2	97.14	47.65

EXAMPLE NO. 8

Here, tests were run to demonstrate the effectiveness of a hypochlorite as a detergent compared with sodium thiophosphate. The hypochlorite selected was a 5.25% solution of sodium hypochlorite, known commercially as "Clorox."

Concentrates from Utah Copper Division, Kennecott Copper Corporation, assayed 29.300 percent copper, 13.30 percent insolubles, and 2.00 percent molybdenite. Procedures corresponded to those of Examples Nos. 1 and 2 which followed the invention as set forth in the flow sheet of Fig. 2.

For test No. 1, sodium thiophosphate was utilized as both detergent and stabilization reagent, while, for test No. 2, sodium hypochlorite (as "Clorox") was used as the detergent reagent, and sodium thiophosphate as the stabilization reagent.

The comparative results appear in the following table:

	Test No. 1 Sodium Thiophosphate as Detergent	Test No. 2 Sodium Hypochlorite as Detergent
Cu Conc. (Sink):		
Percent wt	93.31	92.32
Percent Cu	30.750	30.600
Percent distr. Cu	98.29	97.50
Percent Insol	11.90	11.30
Percent distr. Insol	79.29	72.28
Percent MoS_2	.09	.17
Percent distr. MoS_2	3.94	6.87
MoS_2 Conc. (Float):		
Percent wt	6.69	7.68
Percent Cu	7.450	9.450
Percent distr. Cu	1.71	2.50
Percent Insol	43.40	52.10
Percent distr. Insol	20.71	27.72
Percent MoS_2	30.60	27.70
Percent distr. MoS_2	96.06	93.13

From the above, it is apparent that, while the sodium thiophosphate detergent is more efficient in its action, excellent results are also obtained by the use of the hypochlorite as a detergent.

Experimental work with the process of this invention over an extended period of time indicates that, in instances where general flotation concentrates of mixed molybdenite and copper sulfides, as produced from a copper sulfide ore pulp by the use of either an organic thiophosphate or a xanthic ester collector, are subjected to the detergent process of the invention utilizing an inorganic thiophosphate or any one of the cleansing compounds specified herein as the detergent reagent, a reaction product is obtained from the interaction of such detergent reagent and the particle surface residuum of the general flotation operation, which has prodigious frothing characteristics. The elimination of such reaction product from the pulp in accordance with the process of this invention, enables the subsequent differential flotation procedure for the separation of the molybdenite from the accompanying copper and iron sulfides to be accomplished to best advantage from the standpoint of both ease of handling and clean metallurgical separation.

Such experimental work indicates, further, that the differential flotation of any general flotation concentrate is benefited by cleansing of the particle surface residua of the initial flotation operation, followed by elimination from the pulp of the liquid phase carrying such residua as cleansed from the surface of the particles of at least one of the minerals to be separated by a subsequent differential flotation operation.

It should be understood that any flotation process is subject, in its detailed application, to variations in grade, type, and other characteristics of ore passing through a mill from time to time. The process of this invention is no exception, and numerous variations in detail may be found necessary on the basis of knowledge gained as to particular ores from routine laboratory procedures incidental to any commercial operation. In this connection, it must be realized that advantages will show up in the use of one or another of the detergent reagents coming within the purview of the invention, as respects any given mineral or bulk concentrate concerned. Thus, the test results of the various examples set forth herein should be regarded as merely indicative of what it is possible to achieve in practice by the use of the invention. Likewise, the specific procedures employed for these tests, apart from the basic steps disclosed and claimed, should be regarded as merely indicative of what detailed approaches may be found advisable in the instance of particular ores and particular runs of ore from the same ore body.

The outstanding results achieved in the use of the particular detergent reagents employed in the several tests set forth herein on the specific ore concentrates concerned indicate that useful and worthwhile results may be achieved by a general application of the cleansing concepts dealt with herein and comprehended within the scope of the claims which here follow.

I claim:

1. A process for the recovery of molybdenite from a general flotation concentrate of mixed molybdenite and copper sulfides produced from a copper sulfide ore pulp by the use of a collector selected from the group consisting of organic thiophosphates and xanthic esters, comprising conditioning an aqueous pulp of the concentrate in the presence of a reagent selected from the class consisting of soluble inorganic alkaline, alkali metal, and alkali earth metal compounds of:

1. Sulfur and an element selected from the group consisting of phosphorus, arsenic, and antimony
2. Sulfides
3. Cyanides
4. Hypochlorites;

removing the liquid phase of the so-conditioned concentrate; repulping the residue solids of said conditioned concentrate with fresh water; and subjecting the said repulped residue solids to a flotation operation in the presence of a collector specific to molybdenite, for the recovery of a molybdenite float concentrate.

2. A process for the recovery of molybdenite from a general flotation concentrate of mixed molybdenite and copper sulfides produced from a copper sulfide ore pulp by the use of a collector selected from the group consisting of organic thiophosphates and xanthic esters, comprising conditioning an aqueous pulp of the concentrate in the presence of a reagent selected from the group consisting of alkali metal thiophosphates, alkali metal sulfides, alkali cyanides, and hypochlorites; removing the liquid phase of the so-conditioned concentrate; repulping the residue solids of said conditioned concentrate with fresh water; and subjecting the said repulped residue solids to a flotation operation in the presence of a collector specific to molybdenite, for the recovery of a molybdenite float concentrate.

3. A process for the recovery of molybdenite from a general flotation concentrate of mixed molybdenite and copper sulfides produced from a copper sulfide ore pulp by the use of a collector selected from the group consisting of organic thiophosphates and xanthic esters, comprising conditioning an aqueous pulp of the concentrate in the presence of a reagent selected from the class consisting of soluble inorganic alkaline, alkali metal, and alkali earth metal compounds of:

1. Sulfur and an element selected from the group consisting of phosphorus, arsenic, and antimony
2. Sulfides
3. Cyanides
4. Hypochlorites;

removing the liquid phase of the so-conditioned concentrate; repulping the residue solids of said conditioned concentrate with fresh water; and subjecting the said repulped residue solids to a flotation operation in the presence of a collector specific to molybdenite and of a stabilizing quantity of the said reagent, for the recovery of a molybdenite float concentrate.

4. A process for the recovery of molybdenite from a general flotation concentrate produced from an ore containing molybdenite by the use of a collector selected from the group consisting of organic thiophosphates and xanthic esters, comprising conditioning an aqueous pulp of the concentrate in the presence of a reagent selected from the group consisting of alkali metal thiophosphates, alkali metal sulfides, alkali cyanides, and hypochlorites; removing the liquid phase of the so-conditioned concentrate; repulping the residue solids of said conditioned concentrate with fresh water; and subjecting the said repulped residue solids to a flotation operation in the presence of a collector specific to molybdenite, for the recovery of a molybdenite float concentrate.

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