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## DIFFERENTIAL FROTH FLOTATION OF SULFIDE ORES

Charles M. Nokes, Salt Lake City, Charles G. Quigley, Garfield, and Robert T. Pring, Magna, Utah

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This invention relates to a process of froth flotation in which certain metalliferous sulfides are depressed by means of novel inorganic chemical agents or compounds exhibiting a selective depressing action for the sulfides.

In the flotation of sulfides and certain precious metals such as gold and silver which behave toward sulfide collectors in the same manner as sulfides, it is sometimes desirable to remove certain materials which have the property of floating with oily collectors or frothers which are hydrocarbons or water-insoluble alcohols or mixtures thereof. The most important minerals of this class are molybdenite, graphite and carbons. Another group of minerals comprises some of the hydrous magnesium or aluminum-containing silicates which exhibit strongly hydrophobic surfaces. The principal minerals of this class are the various talcs, sericite, the micas and pyrophyllite. Chlorites for the most part are only weakly hydrophobic and are unsuitable for the processes of the present invention although there are occasional chlorites which exhibit a greater water-repellency and are about on the borderline of utility. These minerals, although chemically quite different, behave identically in froth flotation and are characterized by ready floatability with hydrocarbon collectors or alcohol collectors or frothers.

Unfortunately, when molybdenite, carbon, and strongly hydrophobic hydrous silicates containing magnesium or aluminum, are associated with sulfide minerals, or in the case of carbon, with free precious metals, a differential flotation is difficult because the oily hydrocarbon and alcohol collectors and frothers also show some collecting activity for the sulfide minerals and prevent a sharp separation. An even more serious problem is presented by the fact that, chemically, molybdenite, graphite and carbons and strongly hydrophobic hydrous silicates containing magnesium or aluminum may have to be removed from bulk sulfide or precious metal concentrates. This is due to the fact that molybdenite and carbons are often present in comparatively small amounts which makes a preliminary bulk sulfide float necessary. Talc and mica also are often present in sulfide concentrates and a high degree of removal is economically desirable. However, the problem of separation by flotation is greatly complicated in the case of such concentrates because they usually contain the residue of the sulfide flotation collectors used in floating concentrates. For example, they may contain xanthates, dithiophos-

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phates or the like. The presence of small amounts of the original sulfide collector enhances the tendency of the sulfides to float and makes the separation of molybdenite, carbon or strongly hydrophobic hydrous silicates containing magnesium or aluminum from such concentrates even more difficult than in the case of original ores.

The present invention is based on our discovery that inorganic compounds of phosphorus, arsenic and antimony containing oxygen and sulfur in the bivalent state exert a strong depressant action on sulfide minerals other than molybdenite in the presence of hydrocarbon and alcohol collectors and depress these minerals so vigorously that even in the presence of sulfide promoters it is possible to float molybdenite, carbons and strongly hydrophobic hydrous silicates containing magnesium or aluminum away from the sulfides without serious contamination of the concentrate by the sulfides and with a high degree of removal of the molybdenite, carbons and strongly hydrophobic hydrous silicates containing magnesium or aluminum.

The exact chemical composition of the novel depressants has not been fully determined and it is possible that in some instances at least they are not a single pure compound but are mixtures. They are, however, characterized, in addition to phosphorus, arsenic or antimony respectively, by the presence of bivalent sulfur, oxygen and a cation. In the initial preparation of the depressants, the cation is ammonium or an alkali-forming metal. The depressants may be used as such or they may be transformed into their corresponding heavy metal compounds by reaction with a heavy metal salt. For example, they may be transformed into copper compounds by reaction with copper sulfate or into simple compounds of iron, lead, chromium, aluminum or molybdenum by reacting with ferrous sulfate, lead nitrate, chromium nitrite, aluminum sulfate and ammonium molybdenite. The frothers and collectors for the molybdenite, carbons and strongly hydrophobic hydrous silicates containing magnesium or aluminum are the usual collectors and frothers used in floating these metals, that is to say, hydrocarbons, such as for example, fuel oils and various alcohols such as alcohols of from 5 to 10 carbon atoms, terpene alcohols and the like, also combined oily and synthetic frothers, such as mixtures of higher paraffin alcohols and hydrocarbons.

It should be noted that the depression effected

by the novel agents of the present invention may be temporary or permanent depending on the specific requirements in any individual case. Thus, for example, if the original ore is treated which contains sulfides and either molybdenite, carbons, or strongly hydrophobic hydrous silicates containing magnesium or aluminum, the first float will be effected in the presence of a hydrocarbon and/or alcohol frother or collector with the sulfides temporarily depressed by the novel reagents of the present invention. Thereafter, the sulfides in the tailing may be activated by suitable reagents which are well-known in the art, for example, copper sulfate, and a sulfide concentrate obtained. Where bulk sulfide concentrates are treated to remove molybdenite, carbon or strongly hydrophobic hydrous silicates containing magnesium or aluminum, it is not necessary that the depression be temporary as the flotation in the presence of the novel depressants of the present invention is then the final flotation step.

A number of methods of preparing the depressants are possible. Typical reactions are the following:

Thiophosphoryl chloride and sodium hydroxide  
 Thiophosphoryl chloride and calcium hydroxide  
 Thiophosphoryl chloride and sodium silicate  
 Thiophosphoryl chloride and sodium carbonate  
 Thiophosphoryl chloride and ammonium hydroxide  
 Thiophosphoryl chloride and ammonium phosphate  
 Thiophosphoryl chloride and sodium phosphate  
 Thiophosphoryl chloride and sodium borate  
 Phosphorus sulfides and sodium hydroxide  
 Phosphorus sulfides and calcium hydroxide  
 Phosphorus sulfides and sodium silicate  
 Phosphorus sulfides and sodium carbonate  
 Phosphorus sulfides and ammonium hydroxide  
 Phosphorus sulfides and ammonium carbonate  
 Phosphorus sulfides and ammonium phosphate  
 Phosphorus sulfides and sodium phosphate  
 Phosphorus sulfides and sodium borate  
 Phosphorus sulfides and calcium cyanide  
 Phosphorus sulfides and sodium cyanide  
 Arsenic sulfide and sodium hydroxide  
 Arsenic sulfide and potassium hydroxide  
 Arsenic sulfide and calcium hydroxide  
 Arsenic oxide, sulfur and sodium hydroxide  
 Arsenic oxide, sulfur and potassium hydroxide  
 Antimony oxide, sulfur and sodium hydroxide  
 Antimony oxide, sulfur and potassium hydroxide

It is an advantage of the present invention that the depressants may be prepared with widely varying quantities of reagents. This simplifies manufacture and eliminates the necessity for extremely exact control.

The depressants of the present invention may be prepared in wet form and used immediately in froth flotation or they may be reduced to dry form by suitable means such as spray drying or other methods. The dry product has an advantage that it can be shipped more readily and economically than can the wet slurries. The form in which the depressants of the present invention will be used in any particular case is largely a matter of economics. In some instances it is cheaper to prepare the depressant at the place of use. In other cases, shipment of the dry material prepared at a central point is more economical. The possibility of use of the depressants of the present invention in these various

forms adds greatly to the flexibility of the process of recovering molybdenum, carbon or strongly hydrophobic hydrous silicates containing magnesium or aluminum and is one of the additional advantages of the invention.

When bulk sulfide concentrates are treated, it is often of advantage to subject the concentrate to a preliminary treatment with acid and alkali; for example, sulfuric or sulfurous acids and then lime. This often removes frother collector coatings from the minerals and aids in the subsequent selective separation. Other mineral acids may be used such as hydrochloric acid. The sequence of treatment appears more or less immaterial. Thus the acid conditioning may be first or an alkaline conditioning with alkali may precede it. When treatment with acid and alkali is used on a concentrate, the addition of the depressant, collector, and frother, if necessary, are ordinarily made after the acid and alkali conditioning is completed.

We have found that in molybdenite flotations somewhat improved results are obtainable if the ore is conditioned before floating with a salt of a polyvalent metal, particularly a salt of calcium such as calcium chloride. This conditioning is in place of the treatment with acid described above.

The invention will be described in the following specific examples which set forth the preparation of typical depressants and their use in the process of the present invention.

#### EXAMPLE 1

40 gm. of sodium hydroxide (NaOH) is dissolved in 80 ml. water. 25 gm. of thiophosphoryl chloride is added to the solution, the entire contents being shaken until all thiophosphoryl chloride has reacted. This may require as long as two or three hours, depending upon the intensity of agitation.

#### EXAMPLE 2

13 gm. of sodium hydroxide is dissolved in 75 ml. of water. 10 gm. of phosphorus sulfide (chiefly  $P_2S_5$ , but containing other homologues among which may be  $P_4S_3$ ) is added slowly to the solution so as to keep the reacting temperature under control. This reaction proceeds rapidly, being completed in about 5 minutes.

#### EXAMPLE 3

12 gm. of calcium oxide (CaO) is reacted with 50-80 ml. of water. To the slurry is added 10 gm. of phosphorus sulfide (chiefly  $P_2S_5$ ) and the mass vigorously stirred at 70-75° C. until reaction is complete.

#### EXAMPLE 4

To 7 parts by weight of sodium hydroxide (NaOH) add 4 parts by weight of sulphur (S) and 5 parts by weight of water. Stir and heat until all sulfur has gone into solution (that is combined with the sodium hydroxide in aqueous solution). Adding a small amount of additional water, as heating continues, generally facilitates the dissolution of the sulfur. After all sulfur is in solution, add sufficient water to bring the total water added up to 70 parts by weight. Then add 8 parts by weight of arsenic trioxide ( $As_2O_3$ ) and boil until the reaction is complete. The quantities of sodium hydroxide, sulfur, and arsenic trioxide may vary within certain limits without decreasing the efficiency of the resulting depressant beyond the point of practicability.

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## EXAMPLE 5

To 10 parts by weight of arsenic sulfide add 11.6 parts by weight of lime (CaO); add 75 ml. of water and boil; finally dilute to the desired concentration.

## EXAMPLE 6

To 7 parts by weight of potassium hydroxide, add 25 parts by weight of water. Boil. To the boiling solution add small increments of sulfur alternating with small increments of antimony trioxide until a total of 2 parts by weight of sulfur and 10 parts by weight of antimony trioxide have been added.

## EXAMPLE 7

A material obtained by flotation concentration consisting of molybdenite and other sulfides, chiefly those of copper and iron (Utah Copper Company general flotation concentrate) was tested in a 5000-gm. minerals separation flotation machine. To the charge of about 5000 gms. of suitably prepared material were added the following agents:

10 ml. sulfuric acid (commercial)—66° Bé.  
12 gm. calcium oxide (commercial)  
250 ml. depressant of Example 3  
20 drops kerosene

The pulp was thoroughly agitated in a minerals separation flotation machine after the addition of each of the agents, and the pH values were taken after the incorporation of the first three and at the conclusion of the roughing period.

pH after calcium oxide addition ..... 11.6  
pH after sulfuric acid addition ..... 6.6  
pH after depressant of Ex. 3 addition ..... 9.9  
pH at end of roughing period ..... 9.7

Flotation (10 minutes' floating time) produced a rougher concentrate, a middling and a rougher tailing. The rougher concentrate was cleaned twice in a Fagergren flotation machine making a first cleaner tailing, a second cleaner tailing, and a cleaner concentrate. Most of the sulfides of copper and iron were depressed in the flotation machine and drawn off as rougher tailing, while most of the molybdenite was removed as a froth concentrate. The Fagergren flotation machine was used for grading up or cleaning the flotation machine rougher concentrate.

The effectiveness of this invention treating a flotation concentrate containing molybdenite and other sulfides such as those of copper and iron for the selective flotation separation of molybdenite from other sulfides, may be seen from the following metallurgical data.

|                          | Per Cent Weight | Per Cent Assays |                  | Per Cent Distr. |                  |
|--------------------------|-----------------|-----------------|------------------|-----------------|------------------|
|                          |                 | Cu              | MoS <sub>2</sub> | Cu              | MoS <sub>2</sub> |
| Heading.....             | 100.0           | 39.28           | 1.72             | 100.0           | 100.00           |
| Rougher Tailing.....     | 94.6            | 40.20           | .02              | 96.9            | 1.11             |
| Middling.....            | 1.7             | 34.70           | 1.24             | 1.5             | 1.22             |
| 1st Cleaner Tailing..... | 1.5             | 32.05           | 5.05             | 1.2             | 4.31             |
| 2nd Cleaner Tailing..... | .3              | 31.00           | 4.75             | .2              | .70              |
| Cleaner concentrate..... | 1.9             | 4.00            | 83.20            | .2              | 92.66            |

## EXAMPLE 8

Suitably ground material (Utah Copper Company, Arthur Plant Crude Ore Heading) was treated in a 5000-gram minerals separation flotation machine. To the charge of about 5000 gms.

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(dry basis) of ore and water were added the following agents:

5 ml. depressant of Ex. 3 (CaO, H<sub>2</sub>O, P<sub>2</sub>S<sub>5</sub>)  
6 dps. burner oil  
6 dps. frother consisting of a mixture of paraffine alcohols from 7 to 10 carbon atoms.

The pulp was thoroughly agitated and a rougher molybdenite concentrate was removed as a froth concentrate. This concentrate was later cleaned in a Fagergren flotation machine to form (1) molybdenite cleaner tailing; (2) molybdenite cleaner concentrate. To the material remaining in the minerals separation flotation machine were added 3 ml. of 2.5 per cent xanthate solution, and a rougher copper concentrate was removed as a froth concentrate. (Xanthate is the copper collector used to float the copper after the flotation of the molybdenite.) This concentrate was later cleaned in a Fagergren flotation machine to form (3) copper cleaner tailing, (4) copper cleaner concentrate. The tailing (5) was removed from the machine as waste material.

The results of the test just described may be seen from the following metallurgical tabulation:

|   | Per Cent Weight | Per Cent Assays |                  | Per Cent Distr. |                  |
|---|-----------------|-----------------|------------------|-----------------|------------------|
|   |                 | Cu              | MoS <sub>2</sub> | Cu              | MoS <sub>2</sub> |
| Heading.....                              | 100.0           | 1.254           | .050             | 100.00          | 100.00           |
| MoS <sub>2</sub> Cleaner Tailing.....     | 1.04            | 7.100           | .370             | 5.90            | 7.63             |
| MoS <sub>2</sub> Cleaner Concentrate..... | .26             | 2.900           | 8.650            | .64             | 45.09            |
| Cu Cleaner Tailing.....                   | 4.81            | 1.175           | .060             | 4.55            | 5.81             |
| Cu Cleaner Concentrate.....               | 3.79            | 27.150          | .450             | 82.05           | 34.27            |
| Tailing.....                              | 90.10           | .095            | .004             | 6.86            | 7.21             |

## EXAMPLE 9

Suitably ground material (Utah Copper Company, Arthur Plant, general flotation concentrate) was treated in a laboratory Fagergren flotation machine. To the charge of about 500 gm. (dry basis) of concentrate and water were added the following agents in amounts designated:

1.2 gm. CaO  
1 ml. of reaction product made by reacting 11.6 gm. CaO, 5 gm. red phosphorus, 4 gm. sulfur in 30 ml. water, boiling vigorously to effect solution, diluting to 100 ml. using H<sub>2</sub>O.  
2 dps. burner oil.

In the flotation that followed, substantially all the molybdenite was removed as a froth concentrate, making (1) a rougher tailing and a rougher concentrate. The rougher concentrate was cleaned making (2) a cleaner tailing, and (3) a cleaner concentrate containing substantially all the molybdenite, the depressed copper and iron sulfides remaining in the rougher tailing.

The results of this test are given in the following metallurgical tabulation:

|                          | Per Cent Weight | Per Cent Assays |                  | Per Cent Distr. |                  |
|--------------------------|-----------------|-----------------|------------------|-----------------|------------------|
|                          |                 | Cu              | MoS <sub>2</sub> | Cu              | MoS <sub>2</sub> |
| Heading.....             | 100.00          | 32.95           | 1.506            | 100.00          | 100.00           |
| Rougher tailing.....     | 92.14           | 34.00           | .03              | 95.08           | 1.86             |
| Cleaner tailing.....     | 5.80            | 23.55           | 5.84             | 4.16            | 20.58            |
| Cleaner Concentrate..... | 2.06            | 12.30           | 56.70            | .76             | 77.56            |

## EXAMPLE 10

Suitably ground material (Utah Copper Company, Arthur Plant, general flotation concen-

trate) was treated in a laboratory Fagergren flotation machine. To the charge of about 500 gm. of concentrate (dry basis) and water were added the following agents in the amounts designated:

- 1 ml. sulfuric acid ( $H_2SO_4$ ) 66° B $\acute{e}$ .
- 1 gm. lime (CaO)
- 25 ml. of the reaction product (2 gm. CaO-20 ml.  $H_2O$  and 1 gm. arsenic sulfide) made up to 50 ml. for testing
- 2 dps. molybdenite collector (burner oil, modified)

In the flotation that followed, substantially all the molybdenite was removed as a froth concentrate, making (1) a rougher tailing and a rougher concentrate. The rougher concentrate was cleaned, making (2) a cleaner tailing and (3) a cleaner concentrate containing substantially all the molybdenite, the depressed copper and iron sulfides remaining in the rougher tailing.

**Fourth.**—Adding to the pulp in the flotation machine 0.30 gm. of copper sulfate, 0.075 gm. of xanthate and 2 dps. of frother consisting of a mixture of paraffine alcohols from 5 to 10 carbon atoms, thereby recovering the zinc as a rougher froth concentrate, the rougher tailing (pulp remaining in the machine) being considered waste and drawn out of the machine. The rougher concentrates may be graded up as desired by methods known to the art.

#### EXAMPLE 12

The following test shows that by the use of this invention it is feasible to concentrate by flotation, ore containing molybdenum sulfide, copper sulfide, lead sulfide, and gangue obtaining three separate concentrates: a molybdenite concentrate, a copper concentrate and a lead concentrate.

| Product                        | Material, Per Cent Weight | Assay, Per Cent  |        |       | Distribution, Per Cent |        |        |
|--------------------------------|---------------------------|------------------|--------|-------|------------------------|--------|--------|
|                                |                           | MoS <sub>2</sub> | Cu     | Pb    | MoS <sub>2</sub>       | Cu     | Pb     |
| Heading (Computed)             | 100.00                    | 0.609            | 0.977  | 5.012 | 100.00                 | 100.00 | 100.00 |
| Rougher Tailing                | 83.15                     | .034             | 0.055  | .06   | 4.60                   | 5.25   | 1.00   |
| Rougher MoS <sub>2</sub> Conc. | 1.30                      | 40.803           | 1.190  | 1.35  | 87.02                  | 1.60   | .24    |
| Rougher Cu Conc.               | 5.52                      | .670             | 10.700 | .95   | 6.08                   | 67.39  | 1.50   |
| Rougher Pb Conc.               | 10.03                     | .140             | 2.250  | 48.60 | 2.30                   | 25.76  | 97.26  |

The results of this test may be seen from the following metallurgical tabulation:

|                   | Per Cent Weight | Per Cent Assays |                  | Per Cent Distr. |                  |
|-------------------|-----------------|-----------------|------------------|-----------------|------------------|
|                   |                 | Cu              | MoS <sub>2</sub> | Cu              | MoS <sub>2</sub> |
| Heading           | 100.00          | 31.76           | 1.130            | 100.00          | 100.00           |
| Rougher Tailing   | 83.68           | 31.50           | .040             | 83.19           | 2.34             |
| Cleaner Tailing   | 14.17           | 37.10           | 2.280            | 16.56           | 22.26            |
| Cleaner Concentr. | 1.95            | 4.20            | 66.100           | .25             | 75.40            |

#### EXAMPLE 11

The following test shows that by the use of this invention, it is feasible to concentrate by flotation an ore containing molybdenum sulfide, copper sulfide, zinc sulfide, and gangue, obtaining three separate concentrates: a molybdenite concentrate, a copper concentrate and a zinc concentrate.

| Product                        | Material, Per Cent Weight | Assay, Per Cent  |        |       | Distribution, Per Cent |        |        |
|--------------------------------|---------------------------|------------------|--------|-------|------------------------|--------|--------|
|                                |                           | MoS <sub>2</sub> | Cu     | Zn    | MoS <sub>2</sub>       | Cu     | Zn     |
| Heading (Computed)             | 100.00                    | 0.328            | 0.856  | 3.554 | 100.00                 | 100.00 | 100.00 |
| Rougher Tailing                | 88.03                     | .014             | .060   | .08   | 3.66                   | 6.19   | 1.97   |
| Rougher MoS <sub>2</sub> Conc. | 1.29                      | 20.700           | 2.400  | 3.500 | 81.41                  | 3.63   | 1.27   |
| Rougher Cu Conc.               | 5.14                      | .86              | 13.750 | 2.90  | 13.41                  | 82.59  | 4.19   |
| Rougher Zn Conc.               | 5.54                      | .09              | 1.175  | 49.40 | 1.52                   | 7.59   | 92.57  |

#### Procedure

**First.**—500 gm. ore ground in laboratory ball mill using 0.22 gm. lime (CaO).

**Second.**—Pulp subjected to flotation using a Fagergren laboratory flotation machine adding 5 ml. of the depressant of Ex. 3, 3 dps. of burner oil and 2 dps. of frother consisting of a mixture of aliphatic alcohols from 7 to 10 carbon atoms, thereby recovering the molybdenite (MoS<sub>2</sub>) as a rougher froth concentrate.

**Third.**—Adding to the pulp in the flotation machine 0.30 gm. xanthate and 4 dps. of frother consisting of a mixture of paraffine alcohols from 5 to 10 carbon atoms, thereby recovering the copper in the form of a rougher froth concentrate.

#### Procedure

**First.**—500 gm. ore ground in laboratory ball mill, using 0.22 gm. lime (CaO).

**Second.**—Pulp subjected to flotation using a Fagergren laboratory flotation machine adding 5 ml. of the depressant of Ex. 3, 2 dps. of burner oil and 3 dps. of frother consisting of a mixture of paraffine alcohols from 5 to 10 carbon atoms, thereby recovering the molybdenite as a rougher froth concentrate.

**Third.**—Adding to the pulp in the flotation machine 0.16 gm. xanthate and 2 dps. of frother consisting of a mixture of paraffine alcohols from 5 to 10 carbon atoms, thereby recovering the copper in the form of a rougher froth concentrate.

**Fourth.**—Adding to the pulp in the flotation

machine 0.05 gm. xanthate, 0.10 gm. of copper sulfate and 1 dp. of frother consisting of a mixture of paraffine alcohols from 5 to 10 carbon atoms, thereby recovering the lead as a rougher froth concentrate, the rougher tailing (pulp remaining in the machine) being considered waste and drawn out of the machine. The rougher concentrates may be graded up as desired by methods known to the art.

#### EXAMPLE 13

The following metallurgical results were obtained using the antimony agent and treating a mineral aggregate composed principally of

molybdenite and other sulfides such as those of copper and iron:

|                       | Per Cent Weight | Assays, Per Cent |                  | Distribution, Per Cent |                  |
|-----------------------|-----------------|------------------|------------------|------------------------|------------------|
|                       |                 | Cu               | MoS <sub>2</sub> | Cu                     | MoS <sub>2</sub> |
| Heading (computed)... | 100.00          | 34.030           | 1.67             | 100.00                 | 100.00           |
| Rougher Tailing.....  | 91.19           | 35.900           | .20              | 95.95                  | 10.78            |
| Cleaner Tailing.....  | 5.57            | 22.300           | 7.60             | 3.64                   | 25.15            |
| Cleaner Conc.....     | 3.24            | 4.250            | 33.10            | .41                    | 64.07            |

#### Procedure

500 gm. of general flotation concentrate (Utah Copper Co.) were subjected to flotation in the presence of an antimony agent (prepared by reacting 2 gm. Sb<sub>2</sub>O<sub>3</sub>, 1 gm. KOH and 1 gm. S in aqueous solution) whereby a rougher molybdenite concentrate and a rougher tailing were produced, the rougher molybdenite concentrate being subsequently cleaned, making a cleaner tailing and a cleaner concentrate.

#### EXAMPLE 14

A talcose lead-zinc ore containing galena, sphalerite and pyrite was treated with lime and copper sulfate and floated with sodium ethyl xanthate, a solution of thiocarbonyl diisocresyldithiophosphoric acid, and pine oil to give a bulk lead-zinc concentrate assaying 43.9% Pb, 4.1% Zn, 10.9% Fe and 16.5% insoluble mostly talc. This concentrate was treated with 0.33 lb./ton of the reaction product of 1 part CaO and 1 part P<sub>2</sub>S<sub>5</sub> and floated for 5 minutes without additional reagents to remove talc. Marked depression of sulfides took place resulting in a sulfide tailing assaying 52.6% Pb, 4.6% Zn, 13.0% Fe and 1.1% insoluble, representing recoveries of 90.2% of the lead, 91.1% of the zinc and 97.0% of the iron but only 4.4% of insoluble originally contained in the concentrate.

#### EXAMPLE 15

A lead concentrate was floated from a micaceous lead-zinc ore containing galena, sphalerite, and pyrite by the use of lime, sodium cyanide, copper sulfate, sodium ethyl xanthate, a solution of thiocarbonyl diisocresyldithiophosphoric acid, and pine oil. This concentrate, containing 43.1% insoluble mostly as micaceous material which floated readily with the sulfides and 19.6% Pb and 3.92% Zn, was conditioned with 0.37 lb./ton of a depressant formed by reacting in water 12 parts caustic soda with 9.0 parts sulfur, and 12 parts As<sub>2</sub>O<sub>3</sub> in 70 parts of hot water and then refloated with 0.6 lb./ton pine oil. The resulting concentrate assayed 43.9% of Pb, 3.8% Zn and 6.7% insoluble, representing a recovery of 89.7% of the lead and 1.2% of the zinc.

#### EXAMPLE 16

From a carbonaceous gold ore assaying about 0.20 oz. Au/ton and about 1.5% C. and containing gold in association with pyrite, iron oxides, chalcocite and quartz a concentrate was floated using 0.3 lb./ton potassium ethyl xanthate, 0.03 lb./ton of a 1:1 mixture of sodium diethyl and disecundary butyl dithiophosphates and 0.05 lb./ton pine oil. This concentrate assayed 1.150 oz. Au/ton, 1.72% C., and 64.7% insoluble and represented a recovery of 91.3% of the gold. This amount of carbon interfered with cyanidation of the concentrate, causing reprecipitation of the gold to give cyanidation tailings assaying .53 oz. Au/ton.

A portion of the concentrate was conditioned with 2.5 lb./ton of a depressant prepared by reacting a 1:1 mixture of CaO and P<sub>2</sub>S<sub>5</sub> at 70-80° C. in water to depress sulfides and refloated using in stages 0.12 lb./ton of a mixture of paraffine alcohols from 5 to 10 carbon atoms and 0.18 lb./ton fuel oil to remove the carbonaceous material. 89.7% of the gold remained in the sulfide tailing while the major portions of the carbon were removed in the froth. The sulfide tailing was subjected to cyanidation to give a tailing of 0.23 oz. Au/ton.

#### EXAMPLE 17

A 1:1 mixture of chalcocite and sericite and a 1:1 mixture of chalcocite and pyrophillite (all minerals minus 150 mesh and plus 325 mesh) were floated as follows:

(a) With 0.25 lb./ton of a mixture of paraffine alcohols from 5 to 10 carbon atoms alone and

(b) With 0.25 lb./ton of a mixture of paraffine alcohols from 5 to 10 carbon atoms and 1 lb./ton of a depressant formed by reacting 10 parts CaO with 1.0 part P<sub>2</sub>S<sub>5</sub> in water at 70-80° C.

(c) With 0.25 lb./ton of a mixture of paraffine alcohols from 5 to 10 carbon atoms alone and with 0.1 lb./ton sodium secondary butyl xanthate and 0.1 lb./ton sodium secondary butyl dithiophosphate

(d) As in (c) but with 2.5 lb./ton of the depressant described in (b).

| Chalcocite-Sericite |                  |          |
|---------------------|------------------|----------|
| Treatment           | per cent floated |          |
|                     | Chalcocite       | Sericite |
| a                   | 21.3             | 92.3     |
| b                   | 4.5              | 90.4     |
| c                   | 90.8             | 92.0     |
| d                   | 9.3              | 91.1     |

  

| Chalcocite-Pyrophillite |                  |              |
|-------------------------|------------------|--------------|
| Treatment               | per cent floated |              |
|                         | Chalcocite       | Pyrophillite |
| a                       | 18.9             | 90.3         |
| b                       | 6.1              | 89.7         |
| c                       | 88.9             | 90.5         |
| d                       | 11.3             | 88.4         |

#### EXAMPLE 18

One part arsenic sulfide was reacted with 4 parts sodium hydroxide in aqueous solution and diluted to a total of 100 volume parts of water. This depressant was used on a copper-molybdenite concentrate obtained by the flotation treatment of a copper ore from Utah. The following testing procedure was used on this concentrate:

An aqueous pulp of the flotation concentrate containing 500 gm. dry solids was conditioned in a laboratory Fagergren flotation machine with 14.64 lb. per ton 66° Bé. sulphuric acid, then conditioned with 9.6 lb. per ton commercial lime (CaO). Next was added sufficient depressant to give 3.0 lb. per ton (As<sub>2</sub>O<sub>3</sub> basis) followed by 0.16 lb. per ton modified burner oil and higher alcohol frother as required. The froth was removed for a period of 7 minutes, constituting the rougher molybdenite concentrate. The major portion of the copper and iron sulphides remained in the machine as the rougher tailing.

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The following table summarizes the metallurgical results obtained in this test:

| Product                            | Weight,<br>Per Cent | Assays, Per<br>Cent |                  | Distribution,<br>Per Cent |                  |
|------------------------------------|---------------------|---------------------|------------------|---------------------------|------------------|
|                                    |                     | Cu                  | MoS <sub>2</sub> | Cu                        | MoS <sub>2</sub> |
| Heading.....                       | 100.00              | 34.250              | 2.21             | 100.00                    | 100.00           |
| Rougher Tailings.....              | 89.45               | 35.350              | .13              | 92.33                     | 5.27             |
| Rougher MoS <sub>2</sub> Conc..... | 10.55               | 25.400              | 20.20            | 7.67                      | 94.73            |

## EXAMPLE 19

A depressant was prepared by treating 5.0 parts As<sub>2</sub>S<sub>3</sub> with 50 volume parts of concentrated NH<sub>4</sub>OH. The mixture was agitated and allowed to stand overnight and then excess As<sub>2</sub>S<sub>3</sub> was removed. 30 ml. of the resulting solution were used in a test on the ore employed in Example 18. Other details of the testing procedure were the same as described in Example 18. The following metallurgy was obtained.

| Product                            | Weight,<br>Per Cent | Assays, Per<br>Cent |                  | Distribution,<br>Per Cent |                  |
|------------------------------------|---------------------|---------------------|------------------|---------------------------|------------------|
|                                    |                     | Cu                  | MoS <sub>2</sub> | Cu                        | MoS <sub>2</sub> |
| Heading.....                       | 100.0               | 34.33               | 2.17             | 100.0                     | 100.0            |
| Rougher Tailings.....              | 94.8                | 35.70               | .16              | 98.6                      | 6.9              |
| Rougher MoS <sub>2</sub> Conc..... | 5.2                 | 9.30                | 38.70            | 1.4                       | 93.1             |

## EXAMPLE 20

7.5 parts NaOH, 4 parts sulfur, and 20 parts water were reacted together with gentle heating until a red solution was formed and then 10 parts As<sub>2</sub>O<sub>3</sub> were added and the reaction continued. The product was diluted to a total of 500 volume parts with water. This depressant was tested on the concentrate used in Example 18 and the test was identical to Example 18 except that the quantities of acid and lime were 7.32 lb. and 4.0 lb. instead of 14.64 lb. and 9.6 lb., respectively, per ton of ore. Results follow:

| Product                            | Weight,<br>Per Cent | Assays, Per<br>Cent |                  | Distribution,<br>Per Cent |                  |
|------------------------------------|---------------------|---------------------|------------------|---------------------------|------------------|
|                                    |                     | Cu                  | MoS <sub>2</sub> | Cu                        | MoS <sub>2</sub> |
| Heading.....                       | 100.00              | 36.450              | 1.92             | 100.00                    | 100.00           |
| Rougher Tailings.....              | 94.01               | 36.750              | 0.03             | 97.19                     | 1.32             |
| Rougher MoS <sub>2</sub> Conc..... | 5.99                | 16.700              | 35.00            | 2.81                      | 98.32            |

## EXAMPLE 21

3.0 parts quick lime (84% available CaO), 6.0 parts sulfur, 0.9 part NaOH, and 75.0 parts of water were boiled together until the lime and sulfur dissolved and the resulting product then was boiled with about 4.5 parts of As<sub>2</sub>O<sub>3</sub>. The concentrate and testing procedure were identical to Example 18 except that the quantities of acid and lime were 7.32 lb. and 6.0 lb., respectively, per ton of ore. Results are listed below:

| Product                            | Weight,<br>Per Cent | Assays, Per<br>Cent |                  | Distribution,<br>Per Cent |                  |
|------------------------------------|---------------------|---------------------|------------------|---------------------------|------------------|
|                                    |                     | Cu                  | MoS <sub>2</sub> | Cu                        | MoS <sub>2</sub> |
| Heading.....                       | 100.00              | 33.400              | 1.56             | 100.00                    | 100.00           |
| Rougher Tailings.....              | 91.56               | 35.000              | 0.02             | 97.15                     | 0.94             |
| Rougher MoS <sub>2</sub> Conc..... | 8.44                | 11.100              | 22.45            | 2.85                      | 99.06            |

## EXAMPLE 22

56 lb. sulfur, 75 lb. NaOH and 50 gallons water

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were reacted by boiling. 75 lb. As<sub>2</sub>O<sub>3</sub> were then added and boiled with the mixture. A flotation test using this depressant in the procedure and on the concentrate described in Example 18 was conducted with the following metallurgical results:

| Product                            | Weight,<br>Per Cent | Assays, Per<br>Cent |                  | Distribution,<br>Per Cent |                  |
|------------------------------------|---------------------|---------------------|------------------|---------------------------|------------------|
|                                    |                     | Cu                  | MoS <sub>2</sub> | Cu                        | MoS <sub>2</sub> |
| Heading.....                       | 100.00              | 35.700              | 1.86             | 100.00                    | 100.00           |
| Rougher Tailings.....              | 94.81               | 37.116              | 0.02             | 98.57                     | 0.86             |
| Rougher MoS <sub>2</sub> Conc..... | 5.19                | 9.850               | 42.10            | 1.43                      | 99.14            |

## EXAMPLE 23

A depressant was prepared by mixing 50 gallons of the depressant described in Example 20 and 25 gallons of the depressant described in Example 22. The resulting product was used in a flotation test on the concentrate described in Example 1 and with the same testing procedure. Metallurgical results follow:

| Product                            | Weight,<br>Per Cent | Assays, Per<br>Cent |                  | Distribution,<br>Per Cent |                  |
|------------------------------------|---------------------|---------------------|------------------|---------------------------|------------------|
|                                    |                     | Cu                  | MoS <sub>2</sub> | Cu                        | MoS <sub>2</sub> |
| Heading.....                       | 100.0               | 32.500              | 1.50             | 100.0                     | 100.0            |
| Rougher Tailings.....              | 96.2                | 32.700              | .05              | 99.2                      | 2.6              |
| Rougher MoS <sub>2</sub> Conc..... | 3.8                 | 6.900               | 47.20            | 0.8                       | 97.4             |

The above reaction products are typical of the class coming under the invention. Any alkali-forming metal may be used in place of the calcium, sodium, and ammonium radical used in these examples. Salts of strong bases and weak acids can be reacted as well as the hydroxides. Alkali and alkaline-earth cyanides form depressants, with arsenic and sulphur, and with phosphorus and sulphur of unknown composition.

## EXAMPLE 24

The preliminary acid-lime treatment is not always necessary, particularly in treating ores; however, in treating concentrates containing residual collector agents such treatment is frequently essential in obtaining commercial results. This is demonstrated in the following two tests which compare the results obtained with and without the acid-lime treatment on the concentrate and with the testing method used in Example 18. The depressant used was that used in Example 23.

|                                 |        |        |
|---------------------------------|--------|--------|
| Heading:                        |        |        |
| Per Cent Cu.....                | 33.500 | 33.500 |
| Per Cent MoS <sub>2</sub> ..... | 1.720  | 1.720  |

|  |        |        |
|--|--------|--------|
| Rougher Tailings:                      |        |        |
| Per Cent Wgt.....                      | 95.960 | 92.480 |
| Per Cent Cu.....                       | 34.000 | 34.400 |
| Per Cent Distr. Cu.....                | 98.910 | 95.070 |
| Per Cent MoS <sub>2</sub> .....        | 0.070  | 0.060  |
| Per Cent Distr. MoS <sub>2</sub> ..... | 3.530  | 3.190  |

|  |        |        |
|--|--------|--------|
| Rougher MoS <sub>2</sub> Conc.:        |        |        |
| Per Cent Wgt.....                      | 4.040  | 7.520  |
| Per Cent Cu.....                       | 9.000  | 21.900 |
| Per Cent Distr. Cu.....                | 1.090  | 4.930  |
| Per Cent MoS <sub>2</sub> .....        | 45.300 | 22.200 |
| Per Cent Distr. MoS <sub>2</sub> ..... | 96.470 | 96.810 |

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Agents added, lb. per ton:

|   |       |       |
|---|-------|-------|
| Sulphuric Acid                                    | 14.64 | ----  |
| Lime (Commercial)                                 | 10.00 | ----  |
| Depressant (As <sub>2</sub> O <sub>3</sub> basis) | 3.00  | 3.000 |
| Modified Burner Oil                               | 0.16  | 0.160 |
| Alcohol Frother                                   | 0.16  | 0.160 |

The above two tests show marked improvement in the grade of the rougher molybdenum concentrate in both tests. While better results were obtained with the acid-lime treatment, good results, in fact nearly 1300 percent increase in grade, were obtained without the use of acid and lime. The quality of the froth favors the acid-lime treatment.

## EXAMPLE 25

A copper-molybdenum concentrate obtained by flotation treatment of a Utah ore was treated in 500 gm. Fagergren flotation machine. To the charge of about 500 gm. of concentrate (dry basis) and water were added the following agents in the amounts designated:

1 ml. sulphuric (H<sub>2</sub>SO<sub>4</sub>) 66° Bé.

1 gm. lime (CaO)

25 ml. of the reaction produce (2 gm. CaO 20 ml. H<sub>2</sub>O and 1 gm. arsenic sulphide) made up to 50 ml. for testing.

2 dps. molybdenite collector (burner oil, modified)

In the flotation that followed, substantially all the molybdenite was removed as a froth concentrate, making (1) a rougher tailing and a rougher concentrate. The rougher concentrate was cleaned, making (2) a cleaner tailing and (3) a cleaner concentrate containing substantially all the molybdenite, the depressed copper and iron sulphides remaining in the rougher tailing.

The results of this test may be seen from the following metallurgical tabulation:

|                   | Per Cent Weight | Per Cent Assays |                  | Per Cent Distr. |                  |
|-------------------|-----------------|-----------------|------------------|-----------------|------------------|
|                   |                 | Cu              | MoS <sub>2</sub> | Cu              | MoS <sub>2</sub> |
| Heading           | 100.00          | 31.76           | 1.130            | 100.00          | 100.00           |
| Rougher Tailing   | 83.68           | 31.50           | .040             | 83.19           | 2.34             |
| Cleaner Tailing   | 14.17           | 37.10           | 2.280            | 16.56           | 22.26            |
| Cleaner Concentr. | 1.95            | 4.20            | 56.100           | .25             | 75.40            |

## EXAMPLE 26

Samples of the copper molybdenum concentrate described in Example 18 were obtained daily over a 14-day period and a laboratory flotation test conducted on each sample thus obtained. 14.64 lb./ton sulfuric acid and 10.00 lb./ton lime were used in each test. The depressant used was the same as that described in Example 23. The average of the 14-day laboratory test series are as follows:

| Conditioning Agents, Per Ton          | 14-Day Average Results, 14.64 Lb. H <sub>2</sub> SO <sub>4</sub> , 10.00 Lb. Lime |
|---------------------------------------|---|
| Heading:                              |   |
| Per Cent Cu                           | 34.543  |
| Per Cent MoS <sub>2</sub>             | 1.49  |
| Rougher Tailing:                      |   |
| Per Cent Wgt.                         | 94.01   |
| Per Cent Cu                           | 35.363  |
| Per Cent Distr. Cu                    | 98.46   |
| Per Cent MoS <sub>2</sub>             | 0.075   |
| Per Cent Distr. MoS <sub>2</sub>      | 3.44  |
| Rougher MoS <sub>2</sub> Concentrate: |   |
| Per Cent Wgt.                         | 5.99  |
| Per Cent Cu                           | 8.681   |
| Per Cent Distr. Cu                    | 1.54  |
| Per Cent MoS <sub>2</sub>             | 27.54   |
| Per Cent Distr. MoS <sub>2</sub>      | 96.56   |
| Agents, Lb. Per Ton:                  |   |
| Depressant                            | 3.0   |
| MoS <sub>2</sub> Collector            | 0.16  |
| Alcohol Frother                       | 0.16  |

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## EXAMPLE 27

Samples of copper-molybdenum concentrate obtained by the flotation of a Utah ore were treated as in Example 18 with a depressant consisting of a 1:1 mixture of a NaSH and As<sub>2</sub>O<sub>3</sub> in solution. A flotation test using 4.8 lb./ton of depressant according to the procedure of Example 18 was conducted. The feed to flotation assayed about 33.5% Cu and 1.27% MoS<sub>2</sub>. Metallurgical results follow:

|   |       |
|---|-------|
| Conc.-per cent Cu assay                       | 22.81 |
| Conc.-per cent MoS <sub>2</sub> assay         | 16.09 |
| Conc.-per cent Cu-distribution                | 4.47  |
| Conc.-per cent MoS <sub>2</sub> -distribution | 85.64 |

A cleaner float was conducted on the concentrate from this test to produce a concentrate assaying 9.72% Cu and 28.04% MoS<sub>2</sub>, representing a recovery of about 1% of the total copper and 74.71% of the total MoS<sub>2</sub>.

## EXAMPLE 27a

It was found that calcium chloride was an effective conditioning agent and may be used in place of acid. The 14-day samples described in Example 23 were conditioned with 6.0 lb./ton calcium chloride and then with 2.0 lb./ton lime instead of the H<sub>2</sub>SO<sub>4</sub>-lime combination used in Example 23. The depressant, MoS<sub>2</sub> collector and frother were the same as in Example 23. Average results of the 14-day test period were as follows:

## Heading:

|                           |        |
|---------------------------|--------|
| Per cent Cu               | 34.543 |
| Per cent MoS <sub>2</sub> | 1.49   |

## Rougher tailing:

|                                  |        |
|----------------------------------|--------|
| Per cent wgt.                    | 92.90  |
| Per cent Cu                      | 35.507 |
| Per cent Cu-dist.                | 97.50  |
| Per cent MoS <sub>2</sub>        | 0.055  |
| Per cent MoS <sub>2</sub> -dist. | 2.94   |

Rougher MoS<sub>2</sub> conc.:

|                                  |        |
|----------------------------------|--------|
| Per cent wt.                     | 7.10   |
| Per cent Cu                      | 11.936 |
| Per cent Cu-dist.                | 2.50   |
| Per cent MoS <sub>2</sub>        | 23.43  |
| Per cent MoS <sub>2</sub> -dist. | 97.06  |

## EXAMPLE 28

Other effective compounds for conditioning the pulp prior to the depression of copper minerals are: magnesium chloride, magnesium sulfate, sodium chloride, sodium sulfide, ammonium chloride, barium chloride, calcium acetate, and calcium hypochlorite. Following the conditioning operation with these compounds, lime is added for pH adjustment.

Examples of the use of several of these conditioning agents follow employing 500 gram charges of Utah Copper Co. general flotation concentrate in a laboratory Fagergren flotation machine. The pulp was agitated first with a specified conditioning agent, next with lime, then with 3.0 lb./ton (As<sub>2</sub>O<sub>3</sub> equivalent) of the mixed depressant of Example 23 and floated for 7 minutes with 0.16 lb./ton of modified burner oil

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(molybdenite collector) and higher alcohol frother. Metallurgical results follow:

| Product | Weight,<br>Per Cent | Assays, Per<br>Cent |                  | Distribution,<br>Per Cent |                  |
|---------|---------------------|---------------------|------------------|---------------------------|------------------|
|         |                     | Cu                  | MoS <sub>2</sub> | Cu                        | MoS <sub>2</sub> |

CONDITIONER, 2.0 GM. MgCl<sub>2</sub>; MODIFIER, 0.5 GM. LIME

|                      |        |        |       |        |        |
|----------------------|--------|--------|-------|--------|--------|
| Heading (calc.)..... | 100.00 | 28.443 | 1.91  | 100.00 | 100.00 |
| Rougher tailing..... | 90.67  | 30.150 | 0.07  | 96.11  | 3.32   |
| Rougher conc.....    | 9.33   | 11.850 | 19.80 | 3.89   | 96.68  |

CONDITIONER, 2.0 GM. CALCIUM ACETATE;  
MODIFIER, 1.0 GM. LIME

|                      |        |        |       |        |        |
|----------------------|--------|--------|-------|--------|--------|
| Heading (calc.)..... | 100.00 | 32.202 | 1.93  | 100.00 | 100.00 |
| Rougher tailing..... | 95.88  | 33.100 | 0.09  | 98.55  | 4.47   |
| Rougher conc.....    | 4.12   | 11.300 | 44.80 | 1.45   | 95.53  |

CONDITIONER, 0.1 GM. CuSO<sub>4</sub>·5H<sub>2</sub>O PLUS 1.5 GM. CaCl<sub>2</sub>;  
MODIFIER, 0.5 GM. LIME

|                          |        |        |       |        |        |
|--------------------------|--------|--------|-------|--------|--------|
| Heading (calc.).....     | 100.00 | 30.460 | 2.05  | 100.00 | 100.00 |
| Rougher tailing.....     | 94.85  | 31.500 | 0.10  | 98.09  | 4.64   |
| Rougher concentrate..... | 5.15   | 11.300 | 37.90 | 1.91   | 95.36  |

CONDITIONER, 1.5 GM. CALCIUM HYPOCHLORITE;  
MODIFIER, 0.5 GM. LIME

|                          |        |        |       |        |        |
|--------------------------|--------|--------|-------|--------|--------|
| Heading (calc.).....     | 100.00 | 37.643 | 2.23  | 100.00 | 100.00 |
| Rougher tailing.....     | 93.94  | 39.000 | 0.05  | 97.33  | 2.11   |
| Rougher concentrate..... | 6.06   | 16.000 | 36.00 | 2.67   | 97.89  |

## EXAMPLE 29

Heavy metals may replace the alkali-forming metals in the preparation of depressants. For example, the depressants may be prepared as described and then reacted with a metal salt prior to adding to the pulp as in the following comparative tests:

Identical 500 gm. samples of the concentrate described in Example 18 were floated in exactly the same manner, except that in the first test the depressant used in Example 20 was employed and in the second test the reaction product of this depressant with copper sulfate was used. Acid-lime conditioning was employed in both tests as shown in the table of results.

|  | Original<br>Depressant | Depressant<br>Reacted<br>With<br>CuSO <sub>4</sub> |
|--|------------------------|--|
| Heading:   |                        |  |
| Per Cent Cu.....                                       | 34.760                 | 34.760   |
| Per Cent MoS <sub>2</sub> .....                        | 1.178                  | 1.178  |
| Rougher Tailing:                                       |                        |  |
| Per Cent Wgt.....                                      | 95.34                  | 96.93  |
| Per Cent Cu.....                                       | 35.600                 | 35.450   |
| Per Cent Distr. Cu.....                                | 97.53                  | 98.91  |
| Per Cent MoS <sub>2</sub> .....                        | 0.04                   | 0.04   |
| Per Cent Distr. MoS <sub>2</sub> .....                 | 3.25                   | 3.29   |
| Rougher Concentrate:                                   |                        |  |
| Per Cent Wgt.....                                      | 4.66                   | 3.07   |
| Per Cent Cu.....                                       | 18.35                  | 12.40  |
| Per Cent Distr. Cu.....                                | 2.45                   | 1.19   |
| Per Cent MoS <sub>2</sub> .....                        | 24.35                  | 37.40  |
| Per Cent Distr. MoS <sub>2</sub> .....                 | 96.75                  | 96.71  |
| Agents added (lb. per ton):                            |                        |  |
| Sulphuric Acid.....                                    | 7.32                   | 7.32   |
| Lime.....  | 6.00                   | 6.00   |
| Depressant (As <sub>2</sub> O <sub>3</sub> basis)..... | 3.00                   | 3.00   |
| Modified Burner Oil.....                               | .16                    | .16  |
| Higher Alcoholic Frother.....                          | .16                    | .16  |

## EXAMPLE 30

A depressant was prepared by reacting 0.2 gm. CuS (finely powdered) with 8 cc. of the depressant described in Example 29. A trace of un-

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reacted residue was filtered off and discarded. The tests described below compare equal quantities of both depressants (As<sub>2</sub>O<sub>3</sub> basis) in the treatment of a copper-molybdenum concentrate obtained by flotation of a Utah ore.

|  | Original<br>Depressant | CuS<br>Reaction<br>Product |
|--|------------------------|----------------------------|
| Heading:   |                        |                            |
| Per Cent Cu.....                                       | 31.700                 | 31.700                     |
| Per Cent MoS <sub>2</sub> .....                        | 1.02                   | 1.02                       |
| Rougher Tailing:                                       |                        |                            |
| Per Cent Wgt.....                                      | 95.80                  | 95.87                      |
| Per Cent Cu.....                                       | 31.450                 |                            |
| Per Cent Distr. Cu.....                                | 97.32                  |                            |
| Per Cent MoS <sub>2</sub> .....                        | 0.08                   | 0.04                       |
| Per Cent Distr. MoS <sub>2</sub> .....                 | 6.49                   | 3.18                       |
| Rougher Concentrate:                                   |                        |                            |
| Per Cent Wgt.....                                      | 4.20                   | 4.12                       |
| Per Cent Cu.....                                       | 19.800                 | 21.100                     |
| Per Cent Distr. Cu.....                                | 2.68                   |                            |
| Per Cent MoS <sub>2</sub> .....                        | 26.40                  | 28.00                      |
| Per Cent Distr. MoS <sub>2</sub> .....                 | 93.51                  | 96.82                      |
| Agents added (lb. per ton):                            |                        |                            |
| Sulphuric Acid.....                                    | 7.32                   | 7.32                       |
| Lime.....  | 6.00                   | 6.00                       |
| Depressant (As <sub>2</sub> O <sub>3</sub> basis)..... | 3.00                   | 3.00                       |
| Modified Burner Oil.....                               | .16                    | .16                        |
| Higher Alcohol Frother.....                            | .16                    | .16                        |

The same depressant was reacted with zinc sulphate and the reaction product added to the pulp. The feed to the flotation machine was Utah Copper Company general flotation concentrate. Details of the testing are listed below.

|  | Original<br>Depressant | Depressant<br>Reacted<br>With<br>ZnSO <sub>4</sub> |
|--|------------------------|--|
| Heading:   |                        |  |
| Per Cent Cu.....                                       | 38.310                 | 38.310   |
| Per Cent MoS <sub>2</sub> .....                        | 1.573                  | 1.573  |
| Rougher Tailing:                                       |                        |  |
| Per Cent Wgt.....                                      | 95.78                  | 96.61  |
| Per Cent Cu.....                                       | 39.350                 | 39.350   |
| Per Cent Distr. Cu.....                                | 98.43                  | 99.18  |
| Per Cent MoS <sub>2</sub> .....                        | 0.11                   | 0.10   |
| Per Cent Distr. MoS <sub>2</sub> .....                 | 6.69                   | 6.15   |
| Rougher Concentrate:                                   |                        |  |
| Per Cent Wgt.....                                      | 4.22                   | 3.99   |
| Per Cent Cu.....                                       | 14.000                 | 9.000  |
| Per Cent Distr. Cu.....                                | 1.67                   | 0.82   |
| Per Cent MoS <sub>2</sub> .....                        | 34.70                  | 43.70  |
| Per Cent Distr. MoS <sub>2</sub> .....                 | 93.31                  | 93.85  |
| Agents added (lb. per ton):                            |                        |  |
| Sulphuric Acid.....                                    | 7.32                   | 7.32   |
| Lime.....  | 6.00                   | 6.00   |
| Depressant (As <sub>2</sub> O <sub>3</sub> basis)..... | 3.00                   | 3.00   |
| Modified Burner Oil.....                               | .16                    | .16  |
| Higher Alcohol Frother.....                            | .16                    | .16  |

Other metals tested include iron, lead, chromium, aluminum, molybdenum, etc. The products of the reactions of the above depressant with the following are specific examples: ferrous sulphate, lead nitrite, chromium nitrite, aluminum sulphate, ammonium molybdate.

## EXAMPLE 31

Other metals may replace the alkali-forming metals in the preparation of depressants. For example, the depressants may be prepared as described and then reacted with a metal salt prior to adding to the pulp as in the following comparative tests:

Identical 500 gm. samples of the concentrate described in Example 18 were floated in exactly the same manner, except that in the first test the depressant used in Example 20 was employed and in the second test the reaction product of this depressant with copper sulfate was used. Acid-

lime conditioning was employed in both tests as shown in the table of results.

|  | Original<br>Depressant | Depressant<br>Mixed with<br>CuSO <sub>4</sub> |
|--|------------------------|---|
| Heading:   |                        |   |
| Per Cent Cu.....                                       | 34.760                 | 34.760  |
| Per Cent MoS <sub>2</sub> .....                        | 1.178                  | 1.178   |
| Rougher Tailings:                                      |                        |   |
| Per Cent Wgt.....                                      | 95.34                  | 96.93   |
| Per Cent Cu.....                                       | 35.600                 | 35.450  |
| Per Cent Distr. Cu.....                                | 97.55                  | 98.91   |
| Per Cent MoS <sub>2</sub> .....                        | 0.04                   | 0.04  |
| Per Cent Distr. MoS <sub>2</sub> .....                 | 3.25                   | 3.29  |
| Rougher Concentrate:                                   |                        |   |
| Per Cent Wgt.....                                      | 4.66                   | 3.07  |
| Per Cent Cu.....                                       | 18.35                  | 12.40   |
| Per Cent Distr. Cu.....                                | 2.45                   | 1.19  |
| Per Cent MoS <sub>2</sub> .....                        | 24.35                  | 37.40   |
| Per Cent Distr. MoS <sub>2</sub> .....                 | 96.75                  | 96.71   |
| Agents added (lb. per ton):                            |                        |   |
| Sulphuric Acid.....                                    | 7.32                   | 7.32  |
| Lime.....  | 6.00                   | 6.00  |
| Depressant (As <sub>2</sub> O <sub>3</sub> basis)..... | 3.00                   | 3.00  |
| Modified Burner Oil.....                               | .16                    | .16   |
| Higher Alcohol Frother.....                            | .16                    | .16   |

### EXAMPLE 32

The metallic salt used in forming a metallic type depressant need not be soluble in water as indicated by the following:

A depressant was prepared by reacting 0.2 gm. CuS (finely powdered) with 8 cc. of the depressant described in Example 20. A trace of unreacted residue was filtered off and discarded. The tests described below compare equal quantities of both depressants (As<sub>2</sub>O<sub>3</sub> basis) in the treatment of a copper-molybdenum concentrate obtained by flotation of a Utah ore according to the procedure of Example 31.

|  | Original<br>Depressant | CuS Reaction<br>Product |
|--|------------------------|-------------------------|
| Heading:                               |                        |                         |
| Per Cent Cu.....                       | 31.700                 | 31.700                  |
| Per Cent MoS <sub>2</sub> .....        | 1.02                   | 1.02                    |
| Rougher Tailings:                      |                        |                         |
| Per Cent Wgt.....                      | 95.80                  | 95.87                   |
| Per Cent Cu.....                       | 31.450                 |                         |
| Per Cent Distr. Cu.....                | 97.32                  |                         |
| Per Cent MoS <sub>2</sub> .....        | 0.08                   | 0.04                    |
| Per Cent Distr. MoS <sub>2</sub> ..... | 6.49                   | 3.18                    |
| Rougher Concentrate:                   |                        |                         |
| Per Cent Wgt.....                      | 4.20                   | 4.13                    |
| Per Cent Cu.....                       | 19.800                 | 21.100                  |
| Per Cent Distr. Cu.....                | 2.68                   |                         |
| Per Cent MoS <sub>2</sub> .....        | 26.40                  | 28.00                   |
| Per Cent Distr. MoS <sub>2</sub> ..... | 93.51                  | 96.82                   |

Thus, even with an insoluble metallic compound such as copper sulfide a potent depressant was prepared.

### EXAMPLE 33

The same depressant was reacted with zinc sulphate and the reaction product added to the pulp,

| Metal Salts Used.....                  | None  | CuSO <sub>4</sub> | FeSO <sub>4</sub> | ZnSO <sub>4</sub> | Pb(NO <sub>3</sub> ) <sub>2</sub> | Cr(NO <sub>3</sub> ) <sub>3</sub> | Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> |
|--|-------|-------------------|-------------------|-------------------|-----------------------------------|-----------------------------------|---|
| Metal Salt Added (lb. per ton).....    | None  | 0.10              | 0.40              | 0.40              | 0.40                              | 0.40                              | 0.40  |
| Rougher Tailings:                      |       |                   |                   |                   |                                   |                                   |   |
| Per Cent Wt.....                       | 91.32 | 93.57             | 91.77             | 91.95             | 92.35                             | 92.65                             | 93.28   |
| Per Cent Cu.....                       | 37.70 | 38.00             | 37.60             | 38.10             | 37.90                             | 38.50                             | 38.00   |
| Per Cent Distr. Cu.....                | 96.31 | 98.81             | 97.05             | 97.36             | 97.63                             | 98.21                             | 98.72   |
| Per Cent MoS <sub>2</sub> .....        | .050  | .050              | .040              | .040              | .040                              | .030                              | .040  |
| Per Cent Distr. MoS <sub>2</sub> ..... | 2.66  | 3.03              | 2.46              |                   | 2.46                              | 2.50                              | 2.63  |
| Rougher Concentrate:                   |       |                   |                   |                   |                                   |                                   |   |
| Per Cent Wt.....                       | 6.86  | 6.43              | 8.23              | 8.05              | 7.65                              | 7.35                              | 6.72  |
| Per Cent Cu.....                       | 13.65 | 6.70              | 12.750            | 11.80             | 11.10                             | 8.85                              | 6.80  |
| Per Cent Distr. Cu.....                | 3.69  | 1.19              | 2.95              | 2.64              | 2.37                              | 1.79                              | 1.28  |
| Per Cent MoS <sub>2</sub> .....        | 17.40 | 23.40             | 17.80             | 18.20             | 18.90                             | 20.40                             | 20.40   |
| Per Cent Distr. MoS <sub>2</sub> ..... | 97.34 | 96.97             | 97.54             | 97.54             | 97.50                             | 98.17                             | 97.38   |

following the method of Example 31. Details of the testing are listed below.

|  | Original<br>Depressant | Depressant<br>Reacted<br>With ZnSO <sub>4</sub> |
|--|------------------------|---|
| Heading:                               |                        |   |
| Per Cent Cu.....                       | 38.310                 | 38.310  |
| Per Cent MoS <sub>2</sub> .....        | 1.573                  | 1.573   |
| Rougher Tailings:                      |                        |   |
| Per Cent Wgt.....                      | 95.78                  | 96.61   |
| Per Cent Cu.....                       | 39.350                 | 39.350  |
| Per Cent Distr. Cu.....                | 98.43                  | 99.18   |
| Per Cent MoS <sub>2</sub> .....        | 0.11                   | 0.10  |
| Per Cent Distr. MoS <sub>2</sub> ..... | 6.69                   | 6.15  |
| Rougher Concentrate:                   |                        |   |
| Per Cent Wgt.....                      | 4.22                   | 3.39  |
| Per Cent Cu.....                       | 14.000                 | 9.000   |
| Per Cent Distr. Cu.....                | 1.57                   | 0.82  |
| Per Cent MoS <sub>2</sub> .....        | 34.70                  | 43.70   |
| Per Cent Distr. MoS <sub>2</sub> ..... | 93.31                  | 93.85   |

### EXAMPLE 34

The metal salt depressants apparently are formed in the flotation pulp by treating the ore with an alkali salt depressant in the presence of a suitable metal salt compound. As illustrated by the following comparative metallurgical results, effective depressants result from this method of treatment. In obtaining the results, given in the following table, the depressant of Example 20 was used according to the procedure of Example 31. In the first test this alkali type depressant was used alone; in the second test copper sulfate was added to the cell after the acid treatment followed by treatment with the alkali depressant. Excellent results were obtained in both tests with improved recovery and grade in the second test.

Heading: 39.87% Cu; 1.742% MoS<sub>2</sub>

|  | Original<br>Depressant | Original<br>Depressant<br>with<br>CuSO <sub>4</sub><br>Added<br>to Cell |
|--|------------------------|---|
| Rougher Tailings:                      |                        |   |
| Per Cent Wt.....                       | 93.92                  | 95.50   |
| Per Cent Cu.....                       | 41.15                  | 41.20   |
| Per Cent Distr. Cu.....                | 97.11                  | 98.52   |
| Per Cent MoS <sub>2</sub> .....        | 2.15                   | 1.69  |
| Rougher Concentrate:                   |                        |   |
| Per Cent Wt.....                       | 6.08                   | 4.50  |
| Per Cent Cu.....                       | 18.90                  | 13.20   |
| Per Cent Distr. Cu.....                | 2.89                   | 1.49  |
| Per Cent MoS <sub>2</sub> .....        | 28.40                  | 37.50   |
| Per Cent Distr. MoS <sub>2</sub> ..... | 97.85                  | 98.51   |

### EXAMPLE 35

Several metal salts were added to the pulp as described in Example 34. The testing method was that used in Example 31 and the alkali depressant was that used in Example 20. The metal salts were added after the treatment with acid as indicated above. In the first test the alkali type depressant only was used; an improvement in the concentrate grade of MoS<sub>2</sub> was obtained in all following tests employing the metal salts.

Heading: 35.91% Cu; 1.529% MoS<sub>2</sub>

This application is in part a continuation of our earlier now abandoned copending application Serial No. 530,350, filed April 10, 1944.

We claim:

1. A froth flotation process which comprises subjecting an aqueous pulp containing a mineral included in the group consisting of molybdenum sulfide, carbon, strongly hydrophobic hydrous aluminum-containing silicates and strongly hydrophobic hydrous magnesium silicates and at least on sulfide mineral, to froth flotation in the presence of an inorganic compound of an element selected from the group consisting of phosphorus, arsenic and antimony, said compound containing bivalent sulfur and an inorganic cation, said compound being present in amounts sufficient to depress the sulfide minerals without substantial depression of molybdenum sulfide, carbon, strongly hydrophobic hydrous aluminum-containing silicates and strongly hydrophobic hydrous magnesium silicates and an oil collector for said minerals selected from the group consisting of hydrocarbons, water insoluble alcohols and mixtures, the collector being present in sufficient amounts to float molybdenum, sulfide, carbon, strongly hydrophobic hydrous aluminum-containing silicates and strongly hydrophobic hydrous magnesium silicates, removing a concentrate relatively rich in the said minerals and relatively poor in the depressed sulfide mineral.

2. A process according to claim 1 in which the depressant is a compound of phosphorus.

3. A process according to claim 2 in which the only mineral floated in the presence of the inorganic compound of phosphorus is molybdenite.

4. A process according to claim 3 in which the ore is conditioned with an acid and an alkali prior to flotation.

5. A process according to claim 4 in which the ore is additionally conditioned with a soluble salt of calcium.

6. A process according to claim 1 in which the only mineral floated in the presence of the inorganic compound of phosphorus, arsenic or antimony is molybdenite.

7. A process according to claim 6 in which the ore is conditioned with an acid and an alkali prior to flotation.

8. A process according to claim 7 in which the ore is additionally conditioned with a soluble salt of calcium.

9. A process according to claim 1 in which the depressant is a compound of arsenic.

10. A process according to claim 9 in which the only mineral floated in the presence of the inorganic compound of arsenic is molybdenite.

11. A process according to claim 1 in which the ore pulp contains molybdenite and a sulfide of copper.

12. A process according to claim 11 in which the depressant is a compound of phosphorus.

13. A process according to claim 12 in which the depressant is a reaction product of phosphorus pentasulfide and an alkali-forming hydroxide.

14. A process according to claim 13 in which the alkali-forming metal hydroxide is sodium hydroxide.

15. A process according to claim 13 in which the alkali-forming metal hydroxide is calcium hydroxide.

CHARLES M. NOKES.  
CHARLES G. QUIGLEY.  
ROBERT T. PRING.

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