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## PROCESS OF CONCENTRATING ORES BY SELECTIVE FROTH FLOTATION

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This invention relates to processes of ore concentration by selective froth flotation utilizing certain chemical reagents, and is especially useful as applied to ores not heretofore readily floated, particularly the so-called oxidized metallic and submetallic ores.

While the process of the invention has outstanding utility in connection with these difficult to float ores, and achieves an unusually effective and economical beneficiation thereof, leading to efficient recovery of the metallic and submetallic values contained thereby, its usefulness is not restricted to ores of this character. I have found that the process may be applied successfully to what are generally regarded as nonmetallic ores, where the mineral values to be recovered contain no heavy metallic component, for example, a fluoritic ore whose valued mineral component is fluorite ( $\text{CaF}_2$ ). Furthermore, while its use is not generally indicated in instances of sulfide ores, which are adequately handled by conventional processes and reagents, the process of the invention is at least operable with respect thereto, and may consequently be regarded as a process of general applicability in the flotation art, subject, of course, to the usual considerations of relative economics in instances of particular ores.

The invention involves the use, in connection with a differential froth flotation procedure, of a reagent belonging to a class new to the flotation art. In some instances, the reagents employed are new products from a chemical standpoint, even though conforming to a known broad class of generally applicable chemical compounds.

Certain forms of the new class of reagents are especially applicable to particular situations as against other forms, for example, one form has proven selective with respect to the carbonate minerals as against the oxide minerals, and such form may be utilized, for example, to selectively float off the lime constituent of an oxide ore having a high lime content from a flotation pulp of such ore, while another form may be employed in a subsequent flotation operation on the de-limed residual ore pulp to selectively recover the valued oxide mineral component thereof.

The new class of reagents conforming to this invention embodies the phosphines, both inorganic and organic, and the hydrides of phosphorous generally, whether occurring in the gaseous, liquid, or solid state.

One of the most useful members of the class from the standpoint of reagent preparation is the inorganic phosphine ( $\text{PH}_3$ ), which is normally a gas. While the gas may be introduced directly into the ore pulp, or may be produced therein in several different ways, e. g. by introduction of a metallic phosphide, such as tri-calcium diphosphide ( $\text{Ca}_3\text{P}_2$ ), to the aqueous pulp, yielding  $\text{PH}_3$  as a decomposition product, or by introduction of a phosphonium halide ( $\text{PH}_4\text{X}$ ), which also yields  $\text{PH}_3$  as a decomposition product, I prefer to first intermix the gaseous  $\text{PH}_3$  with an organic liquid, and to utilize the resulting product as a direct addition to the ore pulp, either in the grinding circuit, conditioner, or flotation circuit.

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A liquid which I have found to be particularly well suited as a vehicle for the phosphine gas in the production of an effective flotation reagent is ordinary kerosene. This reagent may be easily made by pouring a quantity of kerosene upon a body of water in an open vessel, and by dropping a number of pieces of tricalcium diphosphide through the layer of kerosene into the body of water. Phosphine gas will be evolved as the calcium phosphide hydrolyzes, and, rising through the kerosene, will be absorbed thereby. The kerosene may then be decanted for use, or the entire body of liquid may be made into an emulsion and used in that form.

Alcohols also serve as effective agents for intermixture with the phosphine gas in the preparation of reagents suitable for purposes of the invention. Thus, calcium phosphide may be introduced into amyl alcohol and water in a manner similar to that described above for kerosene, and used as a straight alcohol solution or as an emulsion.

In both of the above instances, the preferred proportions of the respective ingredients are fifty percent each of the liquids, by volume, and calcium phosphide in the amount of one and one-half percent of the weight of the combined liquids.

Another form of the reagent is prepared by reacting calcium phosphide with an aqueous solution of the proprietary reagent product bearing the name "Emcol 4150" produced by Emulsol Corporation. This product is a sulfate ester of alcohols containing eight to ten carbon atoms, and, for purposes of this invention, is made up in preferably a five percent (by weight) aqueous solution prior to the addition of the phosphide in amount equivalent to five tenths of one percent of the weight of the solution.

All of the above reagents require from eight to twelve hours for preparation, and are preferably stirred intermittently during such time.

A variety of other useful reagents may be made up for application in accordance with the invention. Thus, oleic acid may be included as an additional reactant in the preparation of the above reagents, resulting in complex organic compounds exhibiting additional useful qualities in the flotation process.

A sulfonated cresylic acid reagent of phosphinic character has been prepared by mixing cresylic acid (75% by volume) with concentrated sulfuric acid (25% by volume), and diluting the resulting solution by addition of fifty percent of its volume of water. Approximately three grams of calcium phosphide was reacted with one hundred cubic centimeters of the dilute solution for a period of from twenty to twenty-four hours, with intermittent stirring. Both solid and liquid reaction products were produced, and were found to be satisfactory when used either separately or together as reagents in the flotation process.

Calcium phosphide has been successfully reacted with a mixture of benzyl chloride and water to produce another reagent conforming to the general class concerned. Thus, three grams of calcium phosphide was added to one hundred cubic centimeters of a solution made up of equal parts by volume of benzyl chloride and water. The reaction was allowed to proceed for from thirty-six to forty-eight hours, with intermittent agitation. Here, however, noxious fumes were produced, so care had to be exercised.

In all these prepared reagents the reaction products are organic phosphines of varying complexity. The specific examples noted above are to be regarded as indicative merely. Satisfactory reagents may be prepared in a variety of ways.

In the use of the inorganic hydrides of phosphorous other than the gaseous phosphine ( $\text{PH}_3$ ), the liquid or solid hydride may be introduced directly into the ore pulp,

or may first be intermixed with an organic vehicle. In this connection it should be noted that even through such hydrides may not be readily soluble, there is generally sufficient dissolution or reaction to fulfill the needs of the process.

With respect to the gaseous phosphine ( $\text{PH}_3$ ), it might be noted that in addition to the several ways of producing it mentioned hereinbefore, an acid such as hypophosphorous acid will decompose when added to a flotation pulp, yielding  $\text{PH}_3$ , and elemental phosphorous will react with an alkali in the pulp to also make  $\text{PH}_3$  available for the purposes of the invention. While these are not preferred methods of introducing the reagent in an ore pulp, they are mentioned herein as possibilities in line with the general inventive concepts.

Any process of selective froth flotation involves the generation of numerous and persistent air bubbles within an aqueous pulp containing mixed particles of values and so-called gangue or waste. The bubbles rise to the surface as a froth, carrying along material particles which have selectively become attached thereto. Removal of the resulting material-bearing froth effects a separation of those material particles which have become attached to the bubbles, from those which have not.

It is a principal purpose of the flotation process, therefore, to so treat the ore pulp as to insure as clean a separation as possible between the wanted particles and those that are not wanted.

As one aspect of the process, it is necessary that there be present in the ore pulp an agent capable of selectively rendering certain of the particles amenable to bubble attachment. Such an agent is generally termed a "collector" or "promoter," and normally consists of a hydrocarbon, or contains a hydrocarbon as an essential part thereof.

Often it is advisable that the finely divided ore be treated by other agents, to render certain components thereof reactive to the collector or promoter, or more reactive than would otherwise be true. These agents are generally termed "activators" or "modifiers." If, however, the reverse condition be desired, namely, the rendering of certain normally reactive components of the ore non-reactive to the collector or promoter, so that they will not float, an agent capable of accomplishing this result is added. Such an agent is generally called a "depressant."

The process of the present invention, in its various phases as hereinafter set forth, is concerned with all of these aspects of the flotation art.

Thus, I have found that a reagent conforming to the general class of compounds set forth hereinbefore, applied to an ore pulp either by a conditioning treatment in advance of the flotation operation, or accompanying other reagents during the flotation operation, serves as an activator or modifier with respect to many minerals not heretofore considered susceptible of separation from gangue constituents of their ores by the froth flotation process, or heretofore floated only with difficulty. Furthermore, I have found that such a reagent has a decided and beneficial depressing action in some instances, notably on certain compounds of iron, as iron oxides, and on particles stained by iron.

In the froth flotation of sulfide minerals from their ores, or of oxide minerals which have their surfaces effectively altered to an ecca-sulfide (sulfidized) state by appropriate chemical treatment with a suitable activator or modifier, a great variety of chemical reagents have been found to exhibit marked collecting or promoting properties for the valued minerals as against gangue. The most practical and the most widely used of these reagents belong to a class known as "sulphydric," of which the xanthates are the principal members. Thus, for example, in his "Handbook of Mineral Dressing," page 12-07, Arthur F. Taggart cites as collectors or promoters certain organic sulphydric compounds having a type for-

mula  $\text{X-SH}$ , in which X is any one of a great variety of loadings containing hydrocarbon groups.

In these compounds, or their corresponding salts, the reactive bond S determines capacity for filming surfaces of the mineral particles, whether acting through physical adsorption or chemical replacement of H or of the alkali ion, while the hydrocarbon group provides the film which gives to such mineral particles a hydrophobic or water repellent character and thereby determines their adhesion to the air-water interface of the bubbles, and, consequently, their attachment to and their floating with the bubbles in the froth, selectively with respect to the gangue materials present in the ore pulp.

Thus, it may be said that the sulphur component of these sulphydric collectors determines their preferential affinity for the sulfide particles of the ore, or for other particles which have been effectively altered to an ecca-sulfide condition by appropriate activation treatment.

In accordance with the present invention, however, it appears that phosphorous provides the reactive bond between the desired mineral particles and the hydrocarbon, and that various mineral surfaces may be "phosphidized" in a manner analogous to sulfidization, being thereby rendered amenable to collection or promotion in much the same way as in sulfide flotation. Collectors used in conjunction with such activated or modified minerals may be either of the anionic or cationic type, but the former generally give more satisfactory results and are ordinarily preferred. It might be said, furthermore, that sulphydric collectors are not normally indicated for use with the process of the invention, this being obvious from the above discussion.

In some instances, the success of the invention may be due to the cleansing of the mineral surfaces by reason of the strong reducing action of phosphine. Regardless of what phenomenon is involved, however, practice of the invention is productive of unique and highly useful results, as will be apparent from the examples of actual tests detailed below.

While, ordinarily, the reagents of the invention are best employed as activators or as so-called collector-modifiers in association with other conventional reagents of collector or promoter type, there are instances where the organic reaction products of phosphine gas, or of the other phosphorous hydrides, and the organic phosphines have sufficient collecting or promoting action in themselves to effect recovery without the addition of conventional collectors.

Following are several typical examples of the process of the invention applied to a variety of different ores, many of which have not heretofore been susceptible of economical treatment by froth flotation:

#### Example No. 1

The ore treated was an oxide manganese type from the Caselton properties of Combined Metals Reduction Company in the Pioche District of Nevada. This ore is composed largely of the manganese minerals psilomelane,  $\text{H}_4(\text{Ba, Mn, Mg, Ca})_2\text{Mn}_2\text{O}_{20}$ , and manganite,  $\text{MnO}(\text{OH})$ . The gangue minerals are quartz, iron oxides, clay, calcite, and mica. Minor quantities of sulfides are present in the form of pyrite, sphalerite, and galena.

Since the reagents of the invention are not ordinarily selective as between the oxidized minerals and the sulfides, the sulfide minerals were first removed from the ore pulp by customary sulfide flotation procedures. The pulp residue, or tailings, from this operation were then subjected to flotation procedures in accordance with this invention as indicated below, it being noted that the kerosene phosphine reagent described above was employed in a preliminary conditioning operation as well as in the subsequent flotation, together with conventional carboxyl collectors. This was a series test.

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| Reagent<br>(Lb./Ton) | Condi-<br>tioner | Rougher         | Cleaner<br>A | Cleaner<br>B | Cleaner<br>C |
|----------------------|------------------|-----------------|--------------|--------------|--------------|
| Sodium Silicate      | 1.3              |                 | 0.25         | 0.25         | Nothing.     |
| Sodium Carbonate     | 4.5              |                 |              |              |              |
| Sodium Cyanide       | 0.4              |                 |              | 0.13         |              |
| Kerosene             | 5.3              | 0.5             | 0.5          | 1.0          |              |
| phosphine Reagent    |                  |                 |              |              |              |
| Oleic Acid           | 2.9              | 1.0             | 0.7          | 1.0          |              |
| Sodium Oleate        | 0.07             | 0.07            | 0.07         | 0.07         |              |
| pH                   | 9.6              |                 |              |              |              |
|                      | 10 min-<br>utes  | 12 min-<br>utes |              |              |              |

The following results were obtained:

| Product                        | Percent<br>Weight | Percent Assay |       |       | Percent Distri-<br>bution |       |
|--------------------------------|-------------------|---------------|-------|-------|---------------------------|-------|
|                                |                   | Iron          | Insol | Mang. | Iron                      | Mang. |
| Manganese<br>Concen-<br>trates | 52.6              | 9.5           | 9.4   | 33.1  | 37.3                      | 73.0  |
| Tailing                        | 47.4              | 17.7          | 38.5  | 13.5  | 62.7                      | 27.0  |
| Calculated<br>Head             | 100.0             | 13.4          | 23.3  | 23.8  | 100.0                     | 100.0 |

#### Example No. 2

The same ore was treated in a similar manner, but employing an organic phosphine, namely, triphenyl phosphine ( $\text{Ph}_3\text{P}$ ), as the reagent of the invention. The procedure in floating the manganese minerals was as follows:

| Reagent<br>(Lb./Ton)     | Condi-<br>tioner | Rougher | Cleaner<br>A | Cleaner<br>B | Cleaner<br>C |
|--------------------------|------------------|---------|--------------|--------------|--------------|
| Sodium Carbonate         | 8.0              |         |              |              |              |
| Sodium Silicate          | 2.0              |         | 0.3          | 0.15         | Nothing.     |
| Sodium Cyanide           | 0.5              |         |              |              |              |
|                          | 5 min-<br>utes   |         |              |              |              |
| Triphenyl Phos-<br>phine |                  | 0.45    | 0.1          | 0.05         |              |
| Oleic Acid               |                  | 0.3     | 0.5          | 0.5          |              |
| Kerosene                 |                  | 1.7     | 0.3          | 0.3          |              |
| pH                       |                  | 9.5     |              |              |              |
|                          | 15 min-<br>utes  |         |              |              |              |

The results were as follows:

| Product                     | Percent<br>Weight | Percent Assay |       |      |       | Percent Distri-<br>bution |       |
|-----------------------------|-------------------|---------------|-------|------|-------|---------------------------|-------|
|                             |                   | Iron          | Insol | Lime | Mang. | Iron                      | Mang. |
| Manganese Concen-<br>trates | 49.0              | 8.6           | 11.2  | 9.6  | 26.45 | 39.0                      | 70.1  |
| Tailing                     | 51.0              | 12.9          | 53.4  | Tr.  | 10.80 | 61.0                      | 29.9  |
| Calculated Head             | 100.0             | 32.7          | 10.8  | 4.7  | 18.5  | 100.0                     | 100.0 |

In this instance the reagent of the invention was utilized only in the flotation phase of the operation for illustrative purposes. It is to be understood that it could just as well have been employed in the conditioning stage as in Example No. 1. In fact, it is preferred in practice to condition prior to the flotation operation in order to reduce the flotation time.

#### Example No. 3

The same ore was subjected to batch treatment utilizing the sulfonated cresylic acid phosphine reagent described

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hereinbefore, the flotation of the manganese minerals being carried out as follows:

| Reagent<br>(Lb./Ton)                         | Condi-<br>tioner | Rougher | Cleaner<br>A | Cleaner<br>B | Cleaner<br>C |
|----------------------------------------------|------------------|---------|--------------|--------------|--------------|
| Sodium Silicate                              | 2.0              |         | 0.2          | 0.2          | Nothing.     |
| Sodium Carbonate                             | 10.0             |         | 0.5          | 0.5          |              |
| Sodium Cyanide                               | 0.5              |         |              |              |              |
|                                              | 5 min-<br>utes   |         |              |              |              |
| Sulfonated Cres-<br>ylic Acid Phos-<br>phine |                  | 0.6     | 0.1          | 0.1          |              |
| Oleic Acid                                   |                  | 3.5     | 0.4          | 0.4          |              |
| Kerosene                                     |                  | 1.6     | 0.2          | 0.2          |              |
| pH                                           |                  | 9.4     |              |              |              |
|                                              | 15 min-<br>utes  |         |              |              |              |

The following results were obtained:

| Product                     | Percent<br>Weight | Percent Assay |       |       | Percent Distri-<br>bution |       |
|-----------------------------|-------------------|---------------|-------|-------|---------------------------|-------|
|                             |                   | Iron          | Insol | Mang. | Iron                      | Mang. |
| Manganese Concen-<br>trates | 16.3              | 9.8           | 10.0  | 35.5  | 15.2                      | 32.7  |
| Cleaner Tail-<br>ing C      | 5.7               | 12.3          | 20.4  | 28.8  | 6.7                       | 9.3   |
| Cleaner Tail-<br>ing B      | 16.4              | 15.9          | 25.0  | 24.0  | 24.9                      | 22.2  |
| Cleaner Tail-<br>ing A      | 21.8              | 15.7          | 45.6  | 15.95 | 32.6                      | 19.6  |
| Tailing                     | 39.8              | 5.45          | 75.0  | 7.2   | 20.5                      | 16.2  |
| Calculated<br>Head          | 100.0             | 10.5          | 50.0  | 17.7  | 100.0                     | 100.0 |

#### Example No. 4

The same ore was subjected to similar batch processing utilizing the benzyl chloride phosphine reagent described

hereinbefore, the manganese flotation being carried out as follows:

| Reagent<br>(Lb./Ton)         | Condi-<br>tioner | Rougher      | Cleaner<br>A | Cleaner<br>B | Cleaner<br>C |
|------------------------------|------------------|--------------|--------------|--------------|--------------|
| Sodium Silicate              | 2.0              |              | 0.2          | 0.2          | Nothing.     |
| Sodium Carbonate             | 10.0             |              | 0.5          | 0.5          |              |
| Sodium Cyanide               | 0.5              |              |              |              |              |
|                              | 5 min-<br>utes   |              |              |              |              |
| Benzyl Chloride<br>Phosphine |                  | 5.0 (Staged) | 1.0          | 0.5          |              |
| Oleic Acid                   |                  | 5.0 (Staged) | 0.7          | 0.7          |              |
| Kerosene                     |                  | 1.8 (Staged) | 0.3          | 0.3          |              |
| pH                           |                  | 9.8          |              |              |              |
|                              | 15 minutes       |              |              |              |              |

The following results were obtained:

| Product                     | Percent Weight | Percent Assay |       |       | Percent Distribution |       |
|-----------------------------|----------------|---------------|-------|-------|----------------------|-------|
|                             |                | Iron          | Insol | Mang. | Iron                 | Mang. |
| Manganese Concentrates..... | 14.3           | 15.9          | 12.0  | 36.45 | 20.6                 | 29.9  |
| Cleaner Tail-<br>ing C..... | 4.7            | 14.55         | 20.1  | 30.60 | 6.2                  | 8.2   |
| Cleaner Tail-<br>ing B..... | 15.2           | 16.70         | 21.0  | 27.65 | 23.4                 | 24.2  |
| Cleaner Tail-<br>ing A..... | 20.5           | 12.70         | 43.8  | 17.05 | 23.7                 | 20.0  |
| Tailing.....                | 45.3           | 6.30          | 72.2  | 6.80  | 26.1                 | 17.7  |
| Calculated<br>Head.....     | 100.0          | 11.0          | 47.7  | 17.5  | 100.0                | 100.0 |

It should be noted that the oxidized manganese ore treated in the above examples had theretofore never been satisfactorily floated, see U. S. Bureau of Mines "Report of Investigations No. 4111" of August 1947 entitled "Concentration of Manganese Ores from Lincoln County, Nev.," particularly pages 4 and 5, where the particular ore corresponding to that of the foregoing examples is the highly oxidized Zero Gap variety. The results obtained by the tests indicate that this ore can be profitably treated in commercial operations based upon the process of this invention.

The depression of iron by the reagents of the invention is well indicated by the foregoing examples. This features of the invention is, however, shown more significantly in connection with an ore embodying a greater proportion of the iron component relative to the other ore constituents. The following example is directed particularly to this aspect of the invention.

#### Example No. 5

The ore was an oxide manganese type from the Comet District of Nevada. As in the preceding examples, psilomelane and manganite are present as principal manganese minerals. Another principal manganese mineral in the present instance is pyrolusite,  $MnO_2$ . Iron oxides make up the major portion of the gangue constituents, only minor portions of quartz and other silicates being present. The batch procedure followed in this test was as follows:

| Reagent (Lb./Ton)                  | Ball Mill  | Rougher    | Cleaner A | Cleaner B |
|------------------------------------|------------|------------|-----------|-----------|
| Sodium Carbonate.....              | 10.0       |            |           |           |
| Sodium Silicate.....               | 1.5        |            | 0.3       | Nothing.  |
| Sodium Cyanide.....                | 0.5        |            |           |           |
| Kerosene Phosphine<br>Reagent..... | 3.2        | 3.2        | 3.2       |           |
| Oleic Acid.....                    | 15 minutes | 2.0        | 1.0       |           |
| pH.....                            |            | 9.8        |           |           |
|                                    |            | 15 minutes |           |           |

The following results were obtained:

| Product                     | Percent Weight | Percent Assay |       |       | Percent Distribution |       |
|-----------------------------|----------------|---------------|-------|-------|----------------------|-------|
|                             |                | Iron          | Insol | Mang. | Iron                 | Mang. |
| Manganese Concentrates..... | 7.7            | 20.85         | 5.8   | 27.8  | 4.2                  | 23.5  |
| Cleaner Tail-<br>ing B..... | 21.1           | 32.85         | 7.4   | 16.3  | 18.2                 | 37.8  |
| Cleaner Tail-<br>ing A..... | 45.7           | 42.75         | 10.8  | 5.5   | 51.3                 | 27.6  |
| Tailing.....                | 25.5           | 39.30         | 17.4  | 4.0   | 26.3                 | 11.1  |
| Calculated<br>Heads.....    | 100.0          | 38.1          | 11.4  | 9.1   | 100.0                | 100.0 |

#### Example No. 6

This test demonstrates the selectivity of the alcohol or alcohol derivative reagent of the invention with respect to the carbonates as against the oxides.

An oxide manganese ore having a high lime content was used in this test. The ore is known as "Columbia Manganese," and is from the Ely District of Nevada. The principal manganese minerals present are psilomelane and manganite, there being minor quantities of manganese silicates. Calcite,  $CaCO_3$ , is the principal gangue constituent along with quartz.

In this instance it was desired to remove the calcite prior to the recovery of the manganese minerals. The procedure employed involved two successive flotation operations, each of which represented a series test. The initial operation utilized the alcohol derivative reagent of the invention described above as made up from "Emcol 4150" for selectively floating the lime constituent, namely, the calcite, from the remainder of the ore pulp. The subsequent flotation operation utilized the kerosene phosphine reagent for floating off the manganese oxide minerals from the gangue constituents remaining from the initial operation.

The initial procedure for the elimination of lime was as follows:

| Reagent (Lb./Ton)                      | Conditioner | Rougher       | Cleaner |
|----------------------------------------|-------------|---------------|---------|
| Sodium Silicate.....                   | 2.8         |               | 0.4     |
| "Emcol 4150" Phosphine<br>Reagent..... | 5 minutes   | 0.21 (Staged) |         |
| Oleic Acid.....                        |             | 3.8 (Staged)  |         |
| pH.....                                |             | 8.3           |         |
|                                        |             | 10 minutes    |         |

The subsequent flotation operation for the separation of the oxide manganese minerals from associated gangue was carried out on the tailings or pulp residue of the foregoing operation, as follows:

| Reagent (Lb./Ton)                  | Conditioner | Rougher    | Cleaner A | Cleaner B | Cleaner C |
|------------------------------------|-------------|------------|-----------|-----------|-----------|
| Sodium Carbonate.....              | 4.0         |            |           |           |           |
|                                    | 10 minutes  |            |           |           |           |
| Sodium Silicate.....               |             |            | 0.3       | 0.3       |           |
| Kerosene Phosphine<br>Reagent..... |             | 3.5        | 0.5       | 1.0       |           |
| Oleic Acid.....                    |             | 4.1        | 0.6       | 0.8       | 0.6       |
| pH.....                            |             | 9.0        |           |           |           |
|                                    |             | 10 minutes |           |           |           |

The net results of the above flotation operations were as follows:

| Product                     | Percent Weight | Percent Assay |      |       | Percent Distribution |       |
|-----------------------------|----------------|---------------|------|-------|----------------------|-------|
|                             |                | Insol         | Lime | Mang. | Lime                 | Mang. |
| Lime Concentrates.....      | 27.1           | 5.04          | 45.8 | 3.25  | 99.0                 | 3.3   |
| Manganese Concentrates..... | 50.4           | 17.0          | 0.2  | 39.8  | 0.8                  | 76.4  |
| Tailing.....                | 22.5           | 44.7          | 0.1  | 23.7  | 0.2                  | 20.3  |
| Calculated<br>Head.....     | 100.0          | 20.0          | 12.5 | 26.3  | 100.0                | 100.0 |

While the "Emcol 4150" alcohol derivative reagent of the invention has been found to be especially useful in the selective flotation of the carbonates as against the oxides, the amyl alcohol reagent of the invention may be also employed. In the latter instance, however, the frothing tendency of the amyl alcohol must be taken into consideration.

The carbonates are floated off first, inasmuch as the other reagents of the invention are not ordinarily selective as between the carbonates and oxides.

#### Example No. 7

A carbonate manganese ore from the Casleton prop-

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erties of Combined Metals Reduction Company in the Pioche District of Nevada was the subject of this test. The principal manganese mineral present in this ore is mangano-siderite ( $\text{Mn, FeCO}_3$ ). Sulfide minerals are disseminated throughout the ore in the form of pyrite, galena, and sphalerite. The principal gangue constituents are quartz, calcite, the feldspars, and, in considerably lesser quantities, mica, dolomite and carbon.

As in the first four examples, the sulfide minerals were removed by a preliminary flotation operation utilizing appropriate standard reagents.

The tailings or pulp residue from such sulfide flotation was then subjected to a flotation operation utilizing the "Emcol 4150" reagent of the invention. It should be noted that any of the other reagents of the invention could have been used, since no problem of selective separation as against oxides exists with this ore.

The procedure was as follows:

| Reagent (Lb./Ton)                          | Conditioner   | Rougher    | Cleaner A | Cleaner B | Cleaner C |
|--------------------------------------------|---------------|------------|-----------|-----------|-----------|
| Sodium Carbonate                           | 4.0           | Nothing.   |           |           |           |
| Indusol (mixture of fatty and resin acids) | 1.2           |            | 0.15      |           |           |
| "Emcol 4150" Phosphine Reagent             | 0.075 minutes |            | 0.02      |           |           |
| Sodium Silicate                            |               | 15 minutes | 0.3       | 0.25      | 0.25      |

The following results were obtained:

| Product                | Percent Weight | Percent Assay |       |      |       | Percent Distribution, Mang. |
|------------------------|----------------|---------------|-------|------|-------|-----------------------------|
|                        |                | Iron          | Insol | Lime | Mang. |                             |
| Manganese Concentrates | 75.1           | 9.4           | 10.6  | 9.8  | 19.9  | 84.5                        |
| Tailings               | 24.9           | 9.5           | 43.3  | 3.4  | 11.0  | 15.5                        |
| Calculated Heads       | 100.0          | 9.4           | 18.8  | 8.2  | 17.7  | 100.0                       |

#### Example No. 8

The ore was mangano-siderite from the same source and having essentially the same constituents as that of the immediately preceding test. The amyl alcohol reagent of the invention was employed in this test, however, in the following manner:

| Reagents (Lb./Ton)                         | Conditioner | Rougher    | Scavenger | Cleaner |
|--------------------------------------------|-------------|------------|-----------|---------|
| Sodium Silicate                            | 2.0         | Nothing    |           |         |
| Amyl Alcohol Phosphine Reagent             | 1.0         |            |           |         |
| Indusol (mixture of fatty and resin acids) | 0.5         |            | 0.25      | 0.25    |
| Sodium Di Chromate                         | 5 minutes   |            |           | 0.6     |
|                                            |             | 15 minutes |           |         |

The following results were obtained:

| Product                | Percent Weight | Percent Assay |       |      |       | Percent Distribution, Mang. |
|------------------------|----------------|---------------|-------|------|-------|-----------------------------|
|                        |                | Iron          | Insol | Lime | Mang. |                             |
| Manganese Concentrates | 54.7           | 8.2           | 9.0   | 14.4 | 17.5  | 81.5                        |
| Tailings               | 45.3           | 5.5           | 54.4  | 5.4  | 8.4   | 18.5                        |
| Calculated Head        | 100.0          | 7.0           | 29.6  | 10.3 | 11.7  | 100.0                       |

The results of the immediately foregoing two examples

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can be fairly compared with the results set forth in Table 9 on page 14 of the previously referred to U. S. Bureau of Mines "Report of Investigations No. 4111" with respect to the Caselton sample, since the ores involved came from the same properties and are of corresponding character. In this connection, it should be noted that the grade produced in the Bureau of Mines testing is non-commercial, while the respective grades of the foregoing examples are definitely commercial.

#### Example No. 9

A carbonate manganese ore from the Butterfield property of Combined Metals Reduction Company in the Bingham District of Utah was the subject of this test. The principal manganese mineral in this ore is rhodochrosite ( $\text{MnCO}_3$ ). Small quantities of rhodonite ( $\text{MnSiO}_3$ ) and mangano-calcite ( $\text{Mn, CaCO}_3$ ) are also present. The principal gangue constituent is quartz, together with small quantities of other silicates. Sulfide minerals are present in the form of pyrite, sphalerite, and galena.

The sulfide minerals were floated off from the ore pulp in customary manner. The tailings or pulp residue from that operation were then subjected to the process of the invention, as follows, this being a series test:

| Reagent (Lb./Ton)                       | Conditioner | Rougher    | Cleaner A | Cleaner B |
|-----------------------------------------|-------------|------------|-----------|-----------|
| Sodium Carbonate                        | 5.0         |            |           |           |
| Sodium Silicate                         | 2.0         |            | 0.25      | Nothing.  |
| "Emcol 4150" Phosphine Reagent          | 0.3         |            |           |           |
| Oleic Acid                              | 10 minutes  | 2.25       |           |           |
| "Emcol 4150" Phosphine Reagent (Staged) |             | 0.4        |           |           |
| pH                                      |             | 8.5        |           |           |
|                                         |             | 15 minutes |           |           |

The following results were obtained:

| Product                | Percent Weight | Percent Assay |       | Percent Distribution, Mang. |
|------------------------|----------------|---------------|-------|-----------------------------|
|                        |                | Insol         | Mang. |                             |
| Manganese Concentrates | 55.1           | 8.6           | 33.25 | 75.9                        |
| Tailings               | 44.9           | 60.0          | 13.0  | 24.1                        |
| Calculated Heads       | 100.1          | 31.7          | 24.2  | 100.0                       |

#### Example No. 10

This test was performed on an oxidized zinc ore obtained from the property of United Minerals Reserve in the Big Wood River Region of Idaho. The principal zinc minerals in this ore are smithsonite ( $\text{ZnCO}_3$ ) and calamine ( $\text{H}_2\text{ZnSiO}_5$ ) with smaller amounts of willemite ( $\text{Zn}_2\text{SiO}_4$ ). The oxidized lead mineral cerussite ( $\text{PbCO}_3$ ) is also present as a principal ore mineral. The gangue is mostly quartz and the feldspars, with smaller quantities of zircon ( $\text{ZnSiO}_4$ ).

The cerussite was sulfidized, and was then floated off from the ore pulp with normal sulfide collectors. The tailings or pulp residue of that operation was then treated in accordance with the invention, in a series test, for the recovery of the carbonate zinc mineral:

| Reagents (Lb./Ton)                           | Rougher    | Cleaner A | Cleaner B and C |
|----------------------------------------------|------------|-----------|-----------------|
| Sodium Silicate                              | 2.0        | 0.25      | Nothing.        |
| Indusol (Stage Added)                        | 6.0        |           |                 |
| "Emcol 4150" Phosphine Reagent (Stage Added) | 0.5        |           |                 |
| pH                                           | 8.6        |           |                 |
|                                              | 18 minutes |           |                 |

The following results were obtained:

| Product                | Percent Weight | Percent Assay |      |       | Percent Distribution, Zinc |
|------------------------|----------------|---------------|------|-------|----------------------------|
|                        |                | Lead          | Zinc | Insol |                            |
| Zinc Concentrates..... | 51.1           | 1.4           | 46.9 | 4.4   | 71.8                       |
| Tailing.....           | 48.9           | 0.6           | 19.2 | 58.8  | 28.2                       |
| Calculated Heads.....  | 100.0          | 1.0           | 33.4 | 31.0  | 100.0                      |

#### Example No. 11

The subject of this test was an oxide lead ore known as "Tribune Oxide" taken from the Caselton property of Combined Metals Reduction Company in the Pioche District of Nevada. The principal lead minerals are anglesite ( $\text{PbSO}_4$ ) and cerussite. Minor quantities of plumbojarosite,  $\text{PbFe}_6(\text{OH})_{12}(\text{SO}_4)_4$ , and galena are also present. The gangue is made up mostly of quartz and the feldspars, along with small quantities of iron and manganese oxides and zircon.

This was a comparative test made on a batch basis, to show the difference between standard sulfidization methods as against the process of the invention.

The ore was treated in accordance with the invention, as follows:

| Reagent (Lb./Ton)               | Ball Mill  | Conditioner | Rougher    | Cleaners |          |
|---------------------------------|------------|-------------|------------|----------|----------|
|                                 |            |             |            | A        | B        |
| Sodium Carbonate.....           | 4.0        | -----       | Nothing    | -----    | -----    |
| Kerosene Phosphine Reagent..... | 3.2        | 4.8         | -----      | 0.4      | Nothing. |
| Sodium Silicate.....            | 2.5        | -----       | -----      | 0.3      | -----    |
| Indusol.....                    | 20 minutes | -----       | -----      | -----    | -----    |
| pH.....                         | -----      | 2.5         | -----      | 0.25     | -----    |
|                                 |            | 8.3         | -----      | -----    | -----    |
|                                 |            | 5 minutes   | 15 minutes | -----    | -----    |

The following results were obtained:

| Product                     | Percent Weight | Percent Assay |       | Percent Distribution, Lead |
|-----------------------------|----------------|---------------|-------|----------------------------|
|                             |                | Lead          | Insol |                            |
| Lead Concentrates.....      | 17.7           | 23.1          | 13.6  | 66.1                       |
| Lead Cleaner Tailing B..... | 14.4           | 4.0           | 42.2  | 11.1                       |
| Lead Cleaner Tailing A..... | 27.6           | 3.3           | 64.2  | 14.7                       |
| Tailing.....                | 40.3           | 1.25          | 85.4  | 8.1                        |
| Calculating Heads.....      | 100.0          | 6.2           | 60.6  | 100.0                      |

The standard sulfidization and sulfide flotation were carried out as follows:

| Reagent (Lb./Ton)                           | Ball Mill  | Lead Rougher | Oxide Lead Rougher |
|---------------------------------------------|------------|--------------|--------------------|
| Sodium Fluoride.....                        | 3.0        | -----        | -----              |
| Sodium Carbonate.....                       | 4.0        | -----        | -----              |
| Thiocarbamide.....                          | 0.3        | -----        | -----              |
| Aerofloat 242 (thiophosphate).....          | 0.05       | -----        | 0.1                |
| Sodium Silicate.....                        | 20 minutes | 4.0          | -----              |
| Potassium Amyl Xanthate.....                | -----      | 0.2          | -----              |
| Potassium Ethyl Xanthate.....               | -----      | 0.1          | 0.3                |
| Reagent 404 (Mercaptobenzothiazole).....    | -----      | 0.1          | 0.1                |
| Cleveland Cliff #2 (Hardwood Creosote)..... | -----      | 0.1          | 0.3                |
| Sodium Sulfide.....                         | -----      | 20 minutes   | 6.0                |

The following results were obtained:

| Product                   | Percent Weight | Percent Assay |       | Percent Distribution, Lead |
|---------------------------|----------------|---------------|-------|----------------------------|
|                           |                | Lead          | Insol |                            |
| Lead Concentrates.....    | 13.4           | 22.6          | 23.5  | 57.0                       |
| Lead Cleaner Tailing..... | 21.9           | 10.9          | 47.2  | 18.0                       |
| Tailing.....              | 64.7           | 2.9           | 74.0  | 25.0                       |
| Calculated Head.....      | 100.0          | 7.3           | 62.4  | 100.0                      |

In comparing the results of the respective tests, it should be noted that the grade of lead concentrates is comparable, but that there was a considerably greater loss (over three times as great) of lead in the tailings of the conventional process, as against the process of the invention.

#### Example No. 12

The subject of this test was a calcium tungstate ore known as "Minerva Chief" from the Mount Wheeler District of Nevada. The valued mineral in that ore is scheelite ( $\text{CaWO}_4$ ), and the gangue is mostly quartz and calcite.

The process of the invention was applied in the following manner, this being a series test:

| Reagents (Lb./Ton)                  | Ball Mill  | Rougher    | Cleaner |
|-------------------------------------|------------|------------|---------|
| Sodium Carbonate.....               | 4.0        | -----      | -----   |
| Sodium Silicate.....                | 1.0        | -----      | -----   |
| Quebracho.....                      | 0.1        | -----      | 0.023   |
| "Emcol 4150" Phosphine Reagent..... | 0.5        | 0.034      | 0.01    |
| Oleic Acid.....                     | 20 minutes | 0.081      | 0.002   |
|                                     |            | 15 minutes | -----   |

The concentrate was cleaned three times, and the following results were obtained:

| Product              | Percent Weight | Percent Assay      | Percent Distribution |
|----------------------|----------------|--------------------|----------------------|
| Concentrate.....     | 1.35           | $\text{WO}_3$ 49.4 | $\text{WO}_3$ 82.05  |
| Tailing.....         | 98.65          | 0.15               | 17.95                |
| Calculated Head..... | 100.0          | 0.81               | 100.00               |

#### Example No. 13

Another type of calcium tungstate ore from the property of Midwest Development, Inc. in the Delta District of Utah was treated by this test. Like the ore of the immediately preceding example, the valued mineral ore is scheelite. The gangue is made up largely of garnet and quartz.

This was a batch test carried out in the following manner:

| Reagents (Lb./Ton)                  | Ball Mill  | Rougher    | Cleaner |
|-------------------------------------|------------|------------|---------|
| Sodium Carbonate.....               | 3.0        | -----      | -----   |
| Sodium Silicate.....                | 1.0        | -----      | 0.3     |
| Copper Sulfate.....                 | 0.5        | -----      | 0.15    |
| Quebracho.....                      | 0.5        | -----      | 0.02    |
| Sodium Cyanide.....                 | 0.1        | -----      | -----   |
| "Emcol 4150" Phosphine Reagent..... | 0.1        | -----      | 0.024   |
| Oleic Acid.....                     | 0.3        | 0.67       | 0.12    |
| pH.....                             | 9.9        | 15 minutes | -----   |
|                                     | 20 minutes | -----      | -----   |

The concentrate was cleaned three times, and the following results were obtained:

| Product                      | Percent Weight | Percent Assay      | Percent Distribution |
|------------------------------|----------------|--------------------|----------------------|
| Concentrates.....            | 0.79           | $\text{WO}_3$ 37.6 | $\text{WO}_3$ 64.71  |
| Cleaner Tailing B and C..... | 1.15           | 9.9                | 24.80                |
| Cleaner Tailing A.....       | 1.15           | 2.5                | 6.25                 |
| Tailing.....                 | 96.91          | 0.024              | 4.23                 |
| Concentrates.....            | 100.00         | 0.46               | 100.00               |

## Example No. 14

The ore treated was a manganese tungstate known as "Deer Trail" from the Mount Wheeler District of Nevada. The valued mineral is hübnerite ( $MnWO_4$ ), the gangue being principally quartz, with smaller amounts of iron oxide and garnet.

The process of the invention was applied in a batch test, as follows:

| Reagents (Lb./Ton)                                  | Ball Mill  | Rougher    | Cleaner |
|-----------------------------------------------------|------------|------------|---------|
| Sodium Carbonate.....                               | 3.0        |            |         |
| Sodium Silicate.....                                | 0.8        |            | 0.2     |
| Copper Sulfate.....                                 | 0.4        |            |         |
| Quebracho.....                                      | 0.25       |            |         |
| Kerosene Phosphine Reagent.....                     | 4.0        | 4.0        |         |
| Oleic Acid.....                                     | 2.0        | 2.0        |         |
| "Emcol 4150" Phosphine Reagent.....                 | 0.15       |            |         |
|                                                     | 20 minutes |            |         |
| Sodium Oleate.....                                  |            | 0.22       |         |
| Emcol X-25 (Sulfonated 8 to 10 carbon alcohol)..... |            | 0.01       |         |
|                                                     |            | 15 minutes |         |

The following results were obtained:

| Product                      | Percent Weight | Percent Assay | Percent Distribution |
|------------------------------|----------------|---------------|----------------------|
|                              |                | $WO_3$        | $WO_3$               |
| Concentrates.....            | 1.58           | 37.56         | 59.42                |
| Cleaner Tailing B and A..... | 2.49           | 9.73          | 24.26                |
| Tailing.....                 | 95.93          | 0.17          | 16.32                |
| Calculated Head.....         | 100.00         | 1.00          | 100.00               |

The above tests all involve ores of metallic or sub-metallic character. The invention is not restricted to ores of such character, however, but is also applicable to the recovery of various non-metallic minerals. The following example is concerned with the application of the invention to a fluoritic ore for the recovery of the non-metallic mineral fluorite ( $CaF_2$ ).

## Example No. 15

The fluoritic ore treated was from the Mount Wheeler District of Nevada, being known as "Williams Fluorite." This ore is composed principally of the mineral fluorite, the gangue constituents being quartz and calcite. This was a batch test carried out as follows:

| Reagent (Lb./Ton)                   | Ball Mill  | Rougher    | Cleaner A | Cleaner B |
|-------------------------------------|------------|------------|-----------|-----------|
| Sodium Carbonate.....               | 4.0        |            |           | Nothing.  |
| Sodium Silicate.....                | 1.0        |            | 0.5       |           |
| Copper Sulfate.....                 | 0.5        |            |           |           |
| Quebracho.....                      | 0.5        |            |           |           |
| "Emcol 4150" Phosphine Reagent..... | 0.3        | 0.9        | 0.2       |           |
|                                     | 10 minutes |            |           |           |
| Oleic Acid.....                     |            | 2.1        | 0.6       |           |
|                                     |            | 10 minutes |           |           |

The following results were obtained:

| Product                | Percent Weight | Percent Assay |            |         | Percent Distribution, $CaF_2$ |
|------------------------|----------------|---------------|------------|---------|-------------------------------|
|                        |                | $CaF_2$       | Total Lime | $SiO_2$ |                               |
| Concentrates.....      | 51.2           | 98.95         | 71.5       | 0.46    | 67.3                          |
| Cleaner Tailing B..... | 6.5            | 95.81         | 70.1       | 1.36    | 8.3                           |
| Cleaner Tailing A..... | 14.3           | 86.89         | 63.2       | 6.72    | 16.5                          |
| Tailing.....           | 28.0           | 21.25         | 16.2       | 70.5    | 7.9                           |
| Calculated Head.....   | 100.0          | 75.27         |            |         | 100.0                         |

The foregoing examples are typical of the application of the process of the invention to naturally occurring ores

which are ordinarily not susceptible to satisfactory flotation on the basis of sulfidization and of collection with those collectors normally used in sulfide flotation.

These examples indicate how the reagents of the invention may be employed in a variety of situations to effect recovery of valuable mineral constituents of an ore pulp. It should be borne in mind, however, that the process of the invention is best applied in keeping with knowledge of a general character available and commonly used in the art of flotation with respect to special problems presented by particular ores. Thus, the specific tests here presented should be regarded, in their details, as merely illustrative.

While certain of the reagents which conform to the inventive class here set forth are old in themselves as chemical compositions, it is believed that others are unique. These latter are, therefore, claimed in and of themselves herein as new compositions of matter.

Whereas this invention is here specifically described with respect to particular procedural steps and particular reagents, it is to be understood that various other practices and forms are possible within the generic concepts disclosed, and are contemplated as being within the scope of the claims which here follow.

I claim:

1. A process of concentrating ores by selective froth flotation, comprising subjecting an ore pulp to a froth flotation operation in the presence of a reagent selected from the group consisting of a hydride of phosphorous and an organic phosphine.

2. The process recited in claim 1, wherein a non-sulphydic collector reagent is present in the said flotation operation.

3. The process recited in claim 2, wherein the ore pulp embodies a mineral selected from the group consisting of an oxidized type of metallic character, an oxidized type of submetallic character, and a non-metallic type, as the value to be recovered, and the collector reagent is carboxylic in character.

4. A process of concentrating ores by selective froth flotation, comprising subjecting an ore pulp to a conditioning operation in the presence of a reagent selected from the group consisting of a hydride of phosphorous and an organic phosphine; and thereafter subjecting the so-conditioned ore pulp to a froth flotation operation in the presence of a non-sulphydic collector reagent.

5. A process of differential froth flotation, comprising subjecting an ore pulp containing an iron mineral, exclusive of iron sulfide, and at least one valued mineral, to a froth flotation operation in the presence of a reagent selected from the group consisting of a hydride of phosphorous and an organic phosphine, as a depressant for the said iron mineral, and in the presence of a collector reagent for the said valued mineral.

6. The process recited in claim 5, wherein the ore pulp is conditioned with the said depressant reagent prior to the froth flotation operation.

7. A process of differential froth flotation, comprising subjecting an ore pulp containing a carbonate mineral and an oxide mineral to a froth flotation operation in the presence of a reagent prepared by intermixing a hydride of phosphorous with an aqueous solution of an organic liquid selected from the group consisting of an alcohol and an ester of an alcohol, and in the presence of a non-sulphydic collector; recovering a float product made up of the carbonate mineral; subjecting the sink product from said flotation operation to a re-flotation operation in the presence of a reagent (other than the said reagent) selected from the group consisting of a hydride of phosphorous and an organic phosphine carried by a hydrocarbon vehicle, and in the presence of a non-sulphydic collector; and recovering a float product made up of the oxide mineral.

8. The process of producing a flotation reagent, com-

prising pouring upon a body of water in an open vessel a quantity of a liquid hydrocarbon lighter than water; introducing a quantity of an alkaline earth phosphide into said body of water; and permitting the phosphine gas evolved by hydrolysis to pass through and be absorbed by the said liquid hydrocarbon.

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