This invention relates to the provision of a new and improved composition useful as a promoter in the flotation of sulfide ores for the recovery of copper; and to a new process for preparing said composition.

More particularly, it relates to alkali metal dialkyl monothiophosphoric acid compositions which can be used economically and conveniently as promoters in the recovery of copper by froth flotation from sulfide ores.

Technical grade alkyl diesters of thiophosphoric acid and their hydrolysis products are known as flotation promoters for base metal sulfide and precious metal ores. These compounds, while of prime commercial use, present serious problems because, in the form of their free acids, they are corrosive and cannot be safely handled, shipped or stored in metal drums. Many attempts have been made to solve this problem.

One approach was to prepare concentrated aqueous solutions of ammonium salts of the dialkyl thiophosphoric acids, but these are only temporarily stable. A later proposal involved neutralization of the alkyl diesters of thiophosphoric acid, using alkali metal bases. Alkali metal salts thus formed, while relatively non-corrosive, form gelatinous pastes which are difficult to dry, and, once dried, not easily redissolved. Moreover, as hard concretions, they cannot be added directly to a froth flotation circuit.

It was then attempted to dry the alkali metal salts thus to avoid corrosion problems and allow for direct addition to a flotation circuit. This approach involved neutralizing the alkyl diesters of thiophosphoric acid with an alkali metal base, and heating with a large excess of the same base to obtain a final mixture of dry solids. These mixtures are dilute in active ingredients, and the large excess of alkali required to keep the ester stable while drying increased the cost without a corresponding improvement in efficiency as a flotation collector. Another shortcoming of this method is the loss of effective alkyl triesters during the evaporation step. These esters are produced with the alkyl diesters of thiophosphoric acids by the reaction of phosphorous pentasulfide with a primary or secondary alcohol.

The oily triesters (normally present in commercial dialkyl thiophosphoric acids), though also excellent flotation promoters, are not neutralized by alkali treatment. As a result, they are more volatile and usually distill off in the drying process. The final dry product is deprived, wholly or in part, of a valuable flotation promoting component.

A part of these problems can be effectively avoided by the teachings of U.S. Patent 3,086,653. Therein is provided an aqueous composition of the alkali metal dialkyl thiophosphoric acid with over 25% excess alkali. These liquid compositions are stable and non-corrosive. In use, they are satisfactory. However, it is, nevertheless, very desirable to have available a flotation promoter which is stable in storage and economical and effective in use, but which can be provided in a dry state. This would provide the industry with the option of choosing the physical form of a good flotation promoter to suit available shipping and/or processing equipment. Up until the present time, promoters meeting these qualifications have not been commercially available.

In view of the foregoing, it is an object of the present invention to provide a composition useful as a flotation promoter for sulfide ores of copper. More specifically, it is an object of this invention to provide a promoter which is effective, stable and economically feasible under practical operating conditions. It is an additional object to provide a recovery process in which said composition is employed to promote the flotation of copper and other base metals contained in sulfide, oxidized, or mixed sulfide-oxide ores. It is a further object of this invention to provide a new and efficient process for producing said composition from commercially available materials.

These and other objects are conveniently and economically accomplished in accordance with the present invention by the provision of a composition comprising:

(a) An alkali metal dialkyl monothiophosphate,
(b) An alkali metal chloride, and
(c) An alkali metal hydroxide.

Alkali metal dialkyl monothiophosphate constitutes from about 40% to 95%, and preferably at least 75%, of the above-noted composition. The salt-forming cation may be derived from either sodium or potassium hydroxide. Each alkyl group should have 1-6 carbon atoms, preferably 2-5, and it is most preferable to have alkali metal dialkyl monothiophosphates in which the two alkyl groups are identical. Illustrative of the useful alkali metal dialkyl monothiophosphates are sodium diethyl monothiophosphate, potassium disopropyl monothiophosphate, sodium disopropyl monothiophosphate, sodium di-sec-butyl monothiophosphate and potassium diethyl monothiophosphate.

The alkali metal halide of the composition of this invention will, in most cases, constitute about 1-30% of the entire composition. It is desirable and practical to have the alkali metal halide corresponding to the alkali metal in the alkali metal dialkyl monothiophosphate. This is to take advantage of the fact, as will be described in more detail below, that the alkali metal halide is formed directly in the reaction which can be used to prepare the alkali metal dialkyl monothiophosphate employed herein.

Free alkali metal hydroxide, preferably either sodium or potassium hydroxide, should be present and may constitute up to about 10% of the entire composition. More may be used, but is not normally necessary.

Preferred compositions of the present invention are mixtures of sodium dialkyl monothiophosphates (in which the alkyl groups are symmetrical and have 2-6 carbon atoms each), sodium chloride in a concentration of 1-25% by weight of the composition, and sodium hydroxide in a concentration of 2-10% on the same basis.

The compositions of the present invention are excellent flotation promoters highly concentrated in active component. They can be shipped and handled with safety and convenience and are especially useful in the flotation of copper from ores requiring acidic flotation circuits and in leach-precipitation-flotation processes.

It has been found that the promoter compositions of the present invention can be safely and conveniently prepared by an improved procedure, which procedure constitutes another aspect of the present invention. While the product may be other than sodium chloride, it may be difficult to control, become dangerously exothermic and make commercial operating impractical.

It is known that dialkyl monothiophosphoryl chlorides can react with two moles of aqueous caustic to give the corresponding alkali metal dialkyl monothiophosphate. In general, this reaction has been conducted by dissolving the chloride with a caustic solution and then heating the mixture. At lowered temperatures, a slow reaction takes place, but as temperature approaches reflux due to a
reaction exotherm, the reaction becomes increasingly vigorous, control becomes difficult and a dangerous exothermic condition results. The difficulty is extreme when manufacture is attempted on a large commercial scale.

In accordance with the present invention, a procedure is provided by which the aforementioned difficulties can be avoided. It consists of heating aqueous caustic to reflux temperature (before admixing it with the chloride), and, then, with good agitation, adding the dialkyl monothiophosphoryl chloride gradually so as to maintain the reaction during addition. Alkali metal halide precipitates out during reaction, and rate of reaction is easily controlled. After all the dialkyl monothiophosphoryl chloride has been added, heating may be continued for a short period to insure complete reaction. It is possible to add less than the stoichiometric quantity of the chloride so that the reaction product contains excess unreacted alkali metal hydroxide. In this manner, the one-step chemical reaction yields a product which contains the three components of the promoter of the present invention.

After reaction, the product containing water can be dried by evaporation without removal of the alkali metal chloride and used directly as a satisfactory flotation promoter. It is desired to have a flotation promoter with higher concentrations of the alkali metal dialkyl monothiophosphate component, precipitated alkali metal chloride can be removed through filtration or centrifugation, and water evaporated. This gives a solid product which is an excellent flotation promoter.

The solid products, resulting from the above-described reactions, are readily soluble in water and may be fed directly to flotation circuits, if desired. The aqueous solution of the reaction product remaining after removal of precipitated sodium chloride, contains 45% to 55% of the alkali metal dialkyl monothiophosphinate. This aqueous solution is used in the following preparations.

The following examples in which parts are by weight, are presented to further illustrate the present invention.

**Example 1**

A 40% solution of sodium hydroxide (16.5 parts by weight) is heated to reflux and 14.1 parts by weight of diethyl thiophosphoryl chloride is added at a rate sufficient to maintain the refluxing. About three hours are required for the addition of the chloride. The reflux temperature is about 136°C. At the start of the reaction and gradually drops to 110°C. After the addition of the chloride, heating of the reaction mixture is continued for one hour. Sodium chloride precipitates out during the reaction. The reaction mixture is evaporated to dryness under vacuum, yielding an approximately equimolar mixture of sodium diethyl monothiophosphate and sodium chloride. This product is readily soluble in water and is an effective flotation promoter. The product contains about 2.5% excess of caustic.

**Example 2**

The procedure of Example 1 is repeated. After completion of the reaction, the reaction mixture is cooled to room temperature and the sodium chloride removed by filtration. The resulting filtrate is evaporated under vacuum to dryness. The dry solid product is chiefly sodium diethyl monothiophosphate which contains about 1.5% sodium chloride. This solid product is readily soluble in water.

**Example 3**

The procedure of Example 1 is repeated, and the reaction mixture is cooled to room temperature and filtered to remove the by-product sodium chloride. The filtrate is a clear, stable, colorless-to-yellow aqueous solution, containing about 50% sodium diethyl monothiophosphate.

**Example 4**

An approximately equimolar mixture of potassium diethyl monothiophosphate and potassium chloride is prepared by following the procedure of Example 1 and using potassium hydroxide chemically equivalent to the indicated quantity of sodium hydroxide. The resulting solid product is readily soluble in water and is an effective flotation promoter.

**Example 5**

The procedure of Example 2 is followed except for the use of potassium hydroxide. Evaporation of the filtrate yields potassium diethyl monothiophosphate containing small percentages of potassium chloride. This product is readily soluble in water.

**Example 6**

A solution of about 50% potassium diethyl monothiophosphate is prepared by the procedure of Example 3, using potassium hydroxide instead of sodium hydroxide. The filtrate obtained is suitable for direct feeding to flotation operations.

**Example 7**

Following the indicated procedure as set forth in Examples 1–6, and using the required concentrations of alkali in the reaction, several sodium and potassium dialkyl monothiophosphate compositions are prepared as solutions or as dry solids for use as flotation promoters. These preparations are given in the following table:

<table>
<thead>
<tr>
<th>Product</th>
<th>Dialkyl Thiophosphoryl Chloride Used</th>
<th>Method of Preparation</th>
<th>Percent Excess Alkali Over 2:1 Mol Ratio</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Di-isopropyl</td>
<td>Example 3</td>
<td>10</td>
<td>60% solution of sodium salt</td>
</tr>
<tr>
<td>B</td>
<td>do</td>
<td>Example 2</td>
<td>7.5</td>
<td>Sodium salt, 50% solution of potassium salt</td>
</tr>
<tr>
<td>C</td>
<td>do</td>
<td>Example 5</td>
<td>10</td>
<td>Potassium salt, 50% solution of sodium salt</td>
</tr>
<tr>
<td>D</td>
<td>Di-n-butyl</td>
<td>Example 6</td>
<td>5</td>
<td>Sodium salt plus NaCl, 50% solution of sodium salt</td>
</tr>
<tr>
<td>E</td>
<td>do</td>
<td>Example 1</td>
<td>7</td>
<td>Potassium salt, 50% solution of sodium salt</td>
</tr>
<tr>
<td>F</td>
<td>Di-n-propyl</td>
<td>Example 4</td>
<td>7</td>
<td>Sodium salt plus NaCl, 50% solution of sodium salt</td>
</tr>
<tr>
<td>G</td>
<td>Di-n-butyl</td>
<td>Example 3</td>
<td>6</td>
<td>Sodium salt, 50% solution of sodium salt</td>
</tr>
<tr>
<td>H</td>
<td>Di-n-amyl</td>
<td>Example 4</td>
<td>10</td>
<td>Sodium salt, 50% solution of sodium salt</td>
</tr>
<tr>
<td>I</td>
<td>Di-n-ethyl</td>
<td>Example 5</td>
<td>10</td>
<td>Sodium salt, 50% solution of sodium salt</td>
</tr>
<tr>
<td>J</td>
<td>Di-n-propyl</td>
<td>Example 6</td>
<td>10</td>
<td>Sodium salt, 50% solution of sodium salt</td>
</tr>
</tbody>
</table>

Products A, D, G, I, and J are solutions.
Products B and C contain the thiophosphate promoter plus small percentages of sodium or potassium chloride.
Products E, F and H are approximate equimolar mixtures of the thiophosphate promoter and sodium or potassium chloride.

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Products B and C contain the thiophosphate promoter plus small percentages of sodium or potassium chloride.
Products E, F and H are approximate equimolar mixtures of the thiophosphate promoter and sodium or potassium chloride.
Example 8

This example is presented to show effectiveness of the claimed compositions as compared with known copper promoters.

(A) An alcoholic solution of diethyl dithiophosphoric acid was prepared by reacting 8 moles of anhydrous ethyl alcohol with one mole of phosphorus pentasulfide below 60°C. One mole of water was added and the mixture heated for 12 hours, during which time the temperature was gradually raised to 95°C. The alcohol was removed from the hydrolysis products by distillation under vacuum and an equal weight of anhydrous sodium carbonate was added. The water formed in the neutralization was removed by heating under vacuum at 60°C. The final product was an oil-containing paste, which was designated as Product X.

(B) Diethyl dithiophosphoric acid (206.7 parts by weight) of about 90% purity was dissolved in anhydrous ethyl alcohol. Water (18 parts by weight) was added and the mixture refluxed for two hours at 78–80°C. Alcohol was then distilled off under vacuum. The resulting hydrolysis product contained a mixture of approximately one part of diethyl dithiophosphoric acid and one part of diethyl monothiophosphoric acid together with small amounts of O.O.S- and O.O.O-trialkyl esters of these acids. This preparation was titrated and found to have an equivalent weight of 248. To 200 parts of this composition were added slowly 41 parts sodium hydroxide in 49 parts water, a 25% excess of sodium hydroxide over that required to neutralize the acids. During the addition of alkali, the mixture was maintained under agitation and kept below 50°C. The resulting solution was filtered to yield a yellow solution containing 55% of the combined diethylmono- and dithiophosphoric acids as sodium salts. The oily triesters are readily soluble in this solution. The product was designated as Product Y.

(C) The two products produced as above were compared as promoters with dialkyl monothiophosphates produced in Examples 1–7. A flotation test was conducted on a South American copper ore assaying about 2.0% Cu and 0.065% MoS₂. The ore was ground at 60% solids, conditioned at 22% solids with 4.0 lb./ton sulfuric acid, 0.15 lb./ton cresylic acid as frother, and 0.1 lb./ton promoter on an active content basis, and floated for ten minutes to produce a copper-molybdenum concentrate. The flotation tailings were assayed for copper. These assays are inversely related to efficiency as a promoter, since the copper losses are directly proportioned to the copper content of the tailings. These assays are listed for purposes of comparison in the following table. For comparison, a run was conducted with ethyl xanthogen ethyl formate, a commercial promoter. The results are presented in the following table:

<table>
<thead>
<tr>
<th>Assay of tailing, percent Cu</th>
<th>3.317,040</th>
</tr>
</thead>
</table>

Example 9

Comparative flotation tests were conducted with dialkyl monothiophosphate promoters on three South American copper ores containing mainly sulfide copper minerals together with fractional percentages of oxidized copper minerals and molybdenite.

Ore #1

Head Assay: 1.83% Cu
Grind: 65% minus 200 mesh
Flotation: 7 minutes (pH=4.7)
Reagents:
0.42 lb./ton cresylic acid
5.0 lb./ton sulfuric acid
0.12 lb./ton promoter of Example 3

This promoter yielded a copper concentrate assaying 15.66% Cu and a copper recovery of 87.3%. The tailing assayed 0.26% Cu.

Ore #2

Head Assay: 1.60% Cu
Grind: 50% minus 200 mesh
Flotation: 10 minutes (pH=4.9)
Reagents:
0.35 lb./ton cresylic acid
2.5 lb./ton sulfuric acid
0.09 lb./ton promoter of Example 2

This promoter gave a copper recovery 83.2% of the copper in a concentrate assaying 15.65% Cu. The tailings assayed 0.29% Cu.

Ore #3

Head Assay: 1.59% Cu
Grind: 75% minus 200 mesh
Flotation: 10 minutes (pH=5.0)
Reagents:
0.08 lb./ton pine oil
0.54 lb./ton cresylic acid
2.7 lb./ton sulfuric acid
0.10 lb./ton Promoter C of Example 7

A copper concentrate assaying 23.62% Cu was produced, representing a recovery of 87.6% of the total copper present in the flotation feed.

Example 10

The promoter of Example 1 was used to float a copper ore from the Western United States, which assayed 1.05% Cu mainly as sulfide copper minerals and some oxidized copper minerals. The ore was ground with 1.0 lb./ton lime to minus 65 mesh and floated at 22% solids with 0.75 lb./ton of polypropylene glycol frother and 0.20 lb./ton of Promoter E of Example 7. A copper concentrate was removed amounting of 9.35% of the weight of the ore, assaying 9.86% Cu, and representing a copper recovery of 87.6% of the total copper. The tailings assayed 0.14% Cu.

Example 11

A sulfide zinc ore containing sphalerite was ground to minus 65 mesh and conditioned at 22% solids first with 1.0 lb./ton copper sulfate as activator followed by 0.1 lb./ton of a higher alcohol frother and 0.18 lb./ton of Promoter F of Example 7. From a flotation feed assaying 2.70% Zn, a concentrate assaying 40.93% Zn was produced. This concentrate represented 6.4% of weight of the ore and a recovery of 87.0% of the total zinc.

Example 12

An ore from the Western United States, containing about 1.4% Cu as mixed sulfide and oxide copper minerals, was ground to minus 65 mesh, was leached at about 35% solids with 12 lb./ton sulfuric acid, treated with sponge iron to precipitate the dissolved copper, and floated at 22% solids to produce a flotation concentrate con-
taining both the precipitated and sulfide copper. As promoter, 0.22 lb./ton of Promoter A was used with 0.15 lb./ton pine oil as frother. Following removal of the copper, residual sponge iron with some adhering copper was removed from the ore pulp by magnetic separation methods. This fraction in commercial practice is returned along with fresh sponge iron precipitant to the next treatment cycle. The flotation concentrates, the magnetic portions, and the flotation tailings were assayed for copper. The following table summarizes these operations:

<table>
<thead>
<tr>
<th>Percent Wt.</th>
<th>Percent Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated Head</td>
<td>100.00</td>
</tr>
<tr>
<td>Copper Concentrates</td>
<td>13.28</td>
</tr>
<tr>
<td>Magnetite</td>
<td>11.58</td>
</tr>
<tr>
<td>Tailings</td>
<td>78.08</td>
</tr>
</tbody>
</table>

I claim:

1. A storage-stable flotation promoter composition consisting essentially of: (1) alkali metal dialkyl monothiophosphate, each alkyl group being selected from the primary and secondary alkyl and containing 1-6 carbon atoms, (2) alkali metal chloride in a concentration of 1-30% by weight of the entire composition and (3) alkali metal hydroxide in a concentration of above about 2 but less than 10% by weight of the entire composition.

2. A storage-stable flotation promoter composition consisting essentially of sodium diethyl monothiophosphate, less than 10% by weight of sodium chloride and above about 2 but less than 10% by weight of sodium hydroxide.

3. In the process of beneficiating ores for the recovery of copper sulfide by froth flotation, the improvement which comprises using as the flotation promoter, the composition of claim 1.

4. In the process of recovering copper from sulfide ores containing copper by froth flotation, the improvement which comprises conducting the flotation in the presence of the promoter of claim 2.

5. A process for the preparation of an alkali metal dialkyl monothiophosphate in which each alkyl group is selected from primary and secondary alkyl, for use as a flotation promoter, which comprises heating an aqueous solution of an alkali metal hydroxide to reflux temperature, gradually adding to the refluxing solution, with agitation, dialkyl monothiophosphoryl chloride at a rate sufficient to maintain reaction between said chloride and said alkali metal hydroxide, continuing the addition until no more than one mole of chloride has been added for every two moles hydroxide, heating said reaction mixture for a short period after all the chloride has been added, and recovering the product thus prepared.

6. The process of claim 5 in which precipitated alkali metal chloride is separated from the reaction product.

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<th>Inventor</th>
<th>Citable Page Range</th>
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HARRY B. THORNTON, Primary Examiner.
R. HALPER, Assistant Examiner.