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PROCESS OF FROTH FLOTATION AND MATERIAL EMPLOYED TO EFFECT THE SAME

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This invenion relates to the concentration of materials, particularly metalliferous materials by the froth flotation operation, and has for its object the provision for certain improvements involving the use of a certain class of organic substances as collecting agents in the concentration of such materials as ores and minerals. The invention embraces both the products and the methods of making the same as well as the use of the products in the froth flotation operation.

The present invention is based on the discovery that materials exerting a useful collecting action in froth flotation can be prepared when certain unsaturated fatty acid compounds such as, for example, oleic acid, are reacted with certain hydrocarbonaceous thiophosphoric acid compounds (particularly those described and disclosed in U. S. Patent 1,772,386), which hydrocarbonaceous thiophosphoric acid compounds are obtained by first reacting a hydrocarbonaceous substance (such as naphthalene or other aromatic polynuclear hydrocarbonaceous substance herein disclosed) with phosphorus pentasulfide (or with phosphorus and sulfur) to form what may be termed a "hydrocarbonaceous thiophosphoric acid anhydride substance" which in turn is made to react with phenol (or certain other substances herein classified as phenol equivalents) to produce an acid compound, namely, the hydrocarbonaceous thiophosphoric acid compound as above specified.

In the above reaction the unsaturated fatty acid substances are chemically transformed into what will herein be termed "hydrocarbonaceous thiophospho-fatty acid compounds", which compounds, I believe, are somewhat similar in nature to those described in my copending application Ser. No. 517,126.

Although oleic acid has been indicated as a preferred unsaturated fatty acid substance for preparing the flotation reagent of the present invention, other unsaturated fatty acids, (containing from 4 to 22 carbon atoms) or mixtures of the same can also be employed, such as, for example, crotonic acid, decylenic acid, undecylenic acid, elaidic acid, rapic acid, ricinoletic acid, linoleic acid, brassidic acid, erucic acid, etc.

Instead of a fatty acid, the fatty acid esters may be employed, such as, for example, butyl oleate. Of interest also are the fatty acid substances which consist essentially of glyceride esters of the unsaturated fatty acids such as, for example, olive oil, fish oils, cottonseed oils, tung oil, etc.

Hereinafter I employ the term "unsaturated fatty acid compound" to embrace any one or more of these acids or their esters as above referred to and of which certain typical examples are mentioned.

In the preparation of the hydrocarbonaceous thiophosphoric acid substance involved in the production of the hydrocarbonaceous thiophospho-fatty acid compounds of the present invention, the preferred hydrocarbonaceous substances to be employed therein are naphthalene, carbazol, acenaphthene, phenanthrene, anthracene, or mixtures of the same, which normally occur in coal tar.

Further, in the use of naphthalene and other of the crystalline substances from coal tar or any other hydrocarbonaceous substance the invention is not limited to the use of pure materials, but partially refined materials may be employed with equally good results, as, for example, a naphthalene crude which has been whizzed and washed preparatory to its final purification by sublimation.

Hereinafter I employ the term "hydrocarbonaceous substances" to embrace the compounds of the types herein given.

As phenol equivalents that may be employed in the preparation of the hydrocarbonaceous thiophosphoric acid compounds, I give the following classification of compounds:

(*a*) Phenolic compounds, such as carbolic acid, cresols, xylenols, tar acids or closely related homologues of the same.

(*b*) The hydrogenated phenolic compounds.

(*c*) The aliphatic alcohols, containing from one up to six carbon atoms such as, for example, ethyl alcohol, n-propyl alcohol, n-butyl alcohol, n-amyl alcohol, n-hexyl alcohol, as well as isomers of these alcohols.

(*d*) The aliphatic and aromatic mercaptols such as the ethyl, propyl, etc. mercaptols, phenyl mercaptol or closely related homologues of the same.

(*e*) The aliphatic and aromatic amines such as, for example, ethyl amine, aniline, toluidine, alpha-naphthylamine or closely related homologues.

It is understood that any mixtures of the above classified compounds may also be employed, such mixtures being considered as phenol equivalents.

Hereinafter I employ the term "phenol-like substance" to embrace any one or more of the substances included in the above classification.

The hydrocarbonaceous thiophospho-fatty acid compounds prepared by the reaction of an unsaturated fatty acid substance with a hydrocarbonaceous thiophosphoric acid as herein set forth, constitute a class of flotation reagents that possess high collecting activity toward minerals and metalliferous materials in the froth flotation operations. Particularly are they effective toward so-called oxidized ores, that is, ores containing some non-sulfide minerals such as, for example, carbonates, basic carbonates, oxides, silicates, etc., as well as sulfide ores.

It is not necessary that chemically pure substances be used in the preparation of the above reagents since unrefined products may be employed with metallurgical results practically as good as those obtained with pure chemicals.

In the preparation of the hydrocarbonaceous thiophosphoric acid compound involved in the production of the hydrocarbonaceous thiophospho-fatty acid compounds of the present invention I give the following example but do not restrict the invention thereto:

As the first step in the preparation, 50.0 parts of pure or partially refined naphthalene and 37.9 parts of sulfur are melted together and heated to 200° C., or thereabout, with stirring. At this temperature the sulfur and naphthalene will form a homogeneous solution. To this solution, preferably in an inert atmosphere, is then slowly added 12.1 parts of melted yellow phosphorus with stirring;—the temperature of the reaction mixture not being allowed to rise above 210° C., or thereabout. When the addition of the phosphorus is finished the reaction of the phosphorus and sulfur to form phosphorus sulfide may be said to be complete. The next step of the process consists in bringing about the reaction of the phosphorus sulfide thus formed with the naphthalene by maintaining the temperature of the reaction mixture at 210° C., or thereabout, the stirring being continued until there is a loss of 6.5 parts, or thereabout, of sulfur as hydrogen sulfide. The product obtained is an amber colored resinous material, liquid at 100° C. or thereabout (or it may separate as a crystalline product), which may be described as a naphthalene thiophosphoric acid anhydride compound.

Instead of starting with phosphorus and sulfur, 43.5 parts of phosphorus pentasulfide (P_2S_5) and 6.5 parts of sulfur may be combined with 50 parts of naphthalene with equally good results. This can readily be accomplished by adding the phosphorus sulfide (with the additional sulfur if desired) to the molten naphthalene while maintained at about 210° C., and stirring the mass at about that temperature until there is a loss of about 6.5 parts of sulfur in the form of H_2S. Phosphorus trisulfide and sulfur could also be used.

In the appended claims the expression "reacting with sulfur and phosphorus" is intended to cover the use of the two elements, as such, as well as compounds thereof.

Although an excess of sulfur over phosphorus pentasulfide is not essential I prefer to use a small excess, not limiting myself, however, to the amount employed above, nor do I limit myself to the above specified proportion of naphthalene and phosphorus pentasulfide.

Working under substantially the same conditions, the naphthalene of the above preparation may be replaced with an equal weight (50 parts) or thereabout, of pure or partially refined acenaphthene, carbazol, anthracene, phenanthrene or mixtures of the same, or a coal tar oil consisting essentially of a hydrocarbonaceous substance, the organic thiophosphoric acid anhydride compounds thus obtained being equally good as the corresponding naphthalene compound in the preparation of the flotation reagent of my present invention.

The next step consists in combining the naphthalene thiophosphoric acid anhydride compound with a phenol (or various other substances listed as phenol equivalents) to form a naphthalene thiophosphoric acid compound of a phenol as illustrated by the following example:

Fifty (50) parts of the naphthalene-thiophosphoric acid anhydride reagent, as prepared above, are slowly mixed with 50 parts of anhydrous tar acid, (mixture of phenols), the temperature, during the mixing, not being allowed to rise above 70° C. or thereabout. The temperature is preferably about 50° C., at the beginning, and the reaction is exothermic. The reaction takes place readily and may be considered to be complete when the mixture has become homogeneous. The product is a syrupy liquid. The amount of tar acid used may be varied arbitrarily so long as there is sufficient present for the reaction, it being preferable to use enough in excess to leave the reaction product as a liquid.

In like manner the various substances listed above as phenol equivalents may be combined with the naphthalene thiophosphoric acid anhydride reagent, namely,—hydrogenated phenolic compounds, the aliphatic alcohols, the aliphatic and aromatic mercaptols, and the aliphatic and aromatic amines.

To produce the final hydrocarbonaceous thiophospho-fatty acid product of the present invention, 60 parts, or thereabout, of the naphthalene thiophosphoric acid compound of a phenol of the above preparation are chemically combined with 40 parts, or thereabout, of a fatty acid substance such as, for example, oleic acid;—a ready reaction being obtained at 115° C., or thereabout, and the reaction being complete after about three hours.

Working under substantially the same conditions, the thiophosphoric acid compound in the above preparation may be replaced with an equal weight (60 parts, or thereabout) of a naphthalene thiophosphoric acid compound of any of the various phenol equivalents listed above, or in place of oleic acid other unsaturated fatty acid substances, as above indicated, may be employed. Phosphorus trisulfide may be used instead of the pentasulfide in the example given, being employed in equi-molecular proportion under very much the same reaction conditions. Additional sulfur may be added or not, as desired, in this modification.

If, as in the above example, an unsaturated fatty acid is employed in producing a hydrocarbonaceous thiophospho-fatty acid flotation product according to the present invention, the reaction product thus obtained may be reacted with an alkali or alkaline earth hydroxide to form the alkali and alkaline earth metal salts of said hydrocarbonaceous thiophospho-fatty acid product, which with some ores may be a preferable reagent to the free acid compound.

In the above preparation I do not limit myself to the reaction temperatures given, nor to the proportion of reacting materials employed. In some cases a reaction temperature of 50° C., or thereabout, and a longer reaction period may advantageously be employed in the oleic acid reaction, while in other cases a temperature of 150° C., or thereabout, is preferable. It is conceivable that even lower or higher temperatures than those given may be more suitable for certain of these reactions.

As illustrative of the practice of the use of the reagent in froth-flotation .06 pound per ton of the hydrocarbonaceous thiophospho-oleic acid compound, made after the manner of the example cited above, was employed in conjunction with the froth flotation of difficultly flotable Utah Copper Company ore (containing some oxidized copper mineral), together with 0.3 pound of tar acid frothing agent; an alkaline circuit being employed therewith. A recovery of about 85%, or thereabout, of the copper bearing mineral was obtained, together with a good grade concentrate.

The reagents herein set forth may also be employed in an acid or neutral circuit.

I claim:

1. A process which comprises froth flotation of ore material in the presence of a reaction product of a hydrocarbonaceous substance, phosphorus, sulfur, a phenol-like substance and an unsaturated fatty acid compound.

2. A process which comprises froth flotation of ore material in the presence of a reaction product of a hydrocarbonaceous substance, phosphorus, sulfur, a phenol-like substance and an unsaturated fatty acid compound, the acid radical of which contains from four to twenty-two carbon atoms.

3. A process which comprises froth flotation of ore material in the presence of a reaction product of a hydrocarbonaceous substance, phosphorus, sulfur, a phenol-like substance and an unsaturated fatty acid compound containing the oleic acid radical.

4. A process which comprises froth flotation of ore material in the presence of a reaction product of a hydrocarbonaceous substance, phosphorus, sulfur, a phenol and an unsaturated fatty acid compound.

5. A process which comprises froth flotation of ore material in the presence of a reaction product of a hydrocarbonaceous substance, phosphorus, sulfur, a tar acid and an unsaturated fatty acid compound.

6. A process which comprises froth flotation of ore material in the presence of a reaction product of a hydrocarbonaceous substance, phosphorus, sulfur, an alcohol and an unsaturated fatty acid compound.

7. A process which comprises froth flotation of ore material in the presence of a reaction product of a hydrocarbonaceous substance, phosphorus, sulfur, a butyl alcohol and an unsaturated fatty acid compound.

8. A process which comprises froth flotation of ore material in the presence of a reaction product of a hydrocarbonaceous substance, phosphorus, sulfur, an organic amino compound and an unsaturated fatty acid compound.

9. A process which comprises froth flotation of ore material in the presence of a reaction product of a polynuclear aromatic hydrocarbon, phosphorus, sulfur, a phenol-like substance and an unsaturated fatty acid compound.

10. A process which comprises froth flotation of ore material in the presence of a reaction product of naphthalene, phosphorus, sulfur, a phenol-like substance and an unsaturated fatty acid compound.

11. A process which comprises froth flota-

tion of ore material in the presence of a reaction product of a hydrocarbonaceous substance, a sulfide of phosphorus, a phenol-like substance and an unsaturated fatty acid compound.

12. A process which comprises froth flotation of ore material in the presence of a reaction product of naphthalene, phosphorus, sulfur, a tar acid, and oleic acid.

13. A new class of chemical products, suitable for use as a collecting agent in froth flotation, comprising a reaction product of a hydrocarbonaceous substance, phosphorus, sulfur, a phenol-like substance and an unsaturated fatty acid compound.

14. A process which comprises reacting with sulfur and phosphorus on a hydrocarbonaceous substance, reacting thereupon with a phenol-like substance, and reacting on the product with an unsaturated fatty acid compound.

In testimony whereof I have signed my name to this specification.

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