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ORE FLOTATION AND FLOTATION REAGENT

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The present invention relates to certain improvements in the froth flotation process of minerals by the use of nitrogenous base salts of certain organic thiophosphoric acid compounds which contain naphthalene, or analogous substances, as part of the molecular structure, as herein set forth. The invention embraces both the product and the method of making the same, as well as the use of the product in the froth flotation of minerals.

More particularly our invention is based upon the discovery that materials having flotation value can be prepared by a three-step reaction, in which a (preferably polynuclear) hydrocarbonaceous substance such as naphthalene is made to react with phosphorus pentasulfide (or with phosphorus and sulfur) to form a naphthalene thiophosphoric acid anhydride intermediate product which in turn is caused to react with phenol (or certain other substances mentioned below), to produce a naphthalene thiophosphoric acid compound which in turn is combined with an organic nitrogenous base to form a compound which may be described as a nitrogenous base salt of a naphthalene thiophosphoric acid compound.

The organic thiophosphoric acid compounds that can be employed in the preparation of the flotation reagent according to the present invention are completely described and specifically claimed in application Serial No. 199,625, which has issued as U. S. Patent 1,772,386, filed June 17, 1927, and dated August 5, 1930. The present case, however, relates to the compounds of the acid as specified in said patent, or the analogues thereof with the nitrogen bases hereinafter more fully set forth.

While the naphthalene thiophosphoric acid anhydride compound is the preferred intermediate in the preparation of the flotation reagent of the present invention, other hydrocarbonaceous substances may be employed equally well, such as, for example, the coal tar crystalline substances acenaphthene, anthracene, carbazol, phenanthrene, or mixtures of the same as they normally occur in the refining of tar, or a coal tar oil consisting essentially of hydrocarbonaceous substances. We use the term "hydrocarbonaceous substance" hereinafter to cover the group of substances mentioned in this paragraph.

As phenol equivalents to combine, for example, with the naphthalene thiophosphoric acid anhydride compound, we 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 five carbon atoms such as for example, ethyl alcohol, n-propyl alcohol, n-butyl alcohol, n-amyl alcohol as well as isomeric alcohols of the same.

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

Substances as specified in the above classification may be embraced in the term "a phenol-like substance" in that said substances all react in a similar or analogous manner in the present process, and structurally they may be regarded as ROH (or RSH) the OH or SH group containing a labile hydrogen atom.

The naphthalene thiophosphoric acid compounds, for example, obtained by the reaction of the naphthalene thiophosphoric acid anhydride compound with the compounds of the above classification are excellent flotation reagents of themselves as disclosed in our application Ser. No. 199,625, above referred to.

When, however, these thiophosphoric acid compounds are combined with organic nitrogenous bases to form nitrogenous base thiophosphoric acid salts, a flotation reagent is obtained which, on some ores, is superior to the original thiophosphoric acid compound obtained; particularly is it more effective on oxidized ores.

We give the following classification of the nitrogenous bases that may be employed in the production of the nitrogenous base thiophosphoric acid salts of our invention, namely:

(*a*) Aliphatic amines such as, for example, the ethyl, propyl, butyl, and amyl amines or closely related homologues of the same.

(*b*) Aromatic amines such as, for example, aniline, methyl or ethyl aniline, dimethyl or diethyl aniline, toluidine, alpha-naphthylamine, benzyl amine or closely related homologues of the same.

(*c*) Pyridine bases such as, for example, pyridine, quinolin, or the mixed pyridine bases obtained from coal tar oils.

Substances which are included in the foregoing classification are hereinafter embraced in the term "an organic nitrogenous base". Such bases are of course capable of combining with acids, including the specific acids above referred to, containing an organic thiophosphoric acid group

and containing one of the hydrocarbonaceous substances above noted.

These nitrogenous base salts of an organic thiophosphoric acid comprising hydrocarbonaceous substances, such as for example, naphthalene, as a part of the molecular structure, possess a very high selective or collecting power for metalliferous materials in froth flotation operations; particularly are they effective on sulfide and oxide ores. A suitable frothing agent such as pine oil or tar acids may be employed in conjunction with the above reagents, although they possess some frothing action of themselves.

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

We give the following examples, but we do not restrict the invention thereto:—

In the preparation of the flotation reagent of our invention, the first step in the process consists in the preparation of the naphthalene thiophosphoric acid anhydride intermediate as follows:

Fifty (50) 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 rate of addition of the phosphorus may be conveniently governed by the temperature of the reaction mixture, regulating the flow of phosphorus so that said temperature does not rise above a certain temperature limit, such as 210° C. When the addition of the phosphorous is complete the reaction of the phosphorus and sulfur to form phosphorus sulfide may be said to be complete. The process then 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, until there is a loss of 6.5 parts, or thereabout, of sulfur as hydrogen sulfide, which may require from one to two hours time. 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 sulphur, 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.

Although an excess of sulfur over phosphorus pentasulfide is not essential, we prefer to use a small excess, not limiting ourselves, however, to the amount employed above, nor do we limit ourselves to the above specified temperature and time.

We have found it convenient to use an excess of naphthalene over that required for the reaction with phosphorus pentasulfide, the excess of naphthalene serving as a convenient solvent medium for the naphthalene thiophosphoric acid anhydride formed.

Working under substantially the same conditions, the naphthalene of the above preparation may be replaced with an equal weight (50 pts.) 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 our disclosure.

The next step in our process consists in combining the organic thiophosphoric acid anhydride compounds, as prepared above, as for example the naphthalene derivative, with various substances (phenol or equivalent as above specified) to form the corresponding organic thiophosphoric acid derivatives as illustrated by the following example.

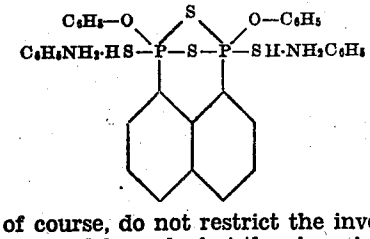
Fifty (50) parts of the naphthalene-thiophosphoric acid anhydride reagent as prepared above are slowly mixed with 50 parts of anhydrous tar acid, the temperature, during the mixing, not being allowed to rise above 70° C. or thereabout. The reaction takes place readily and may be considered to be complete 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 in a liquid condition, any excess tar acid also serving as a very good frothing reagent.

In the above preparation we do not limit ourselves to a reaction temperature, but may use a little higher temperature such as 125° C. to bring about a complete combination of these substances.

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

To produce the final product of the present invention 80 parts, or thereabout, of the reaction product from the preceding example are combined with about 20 parts of aniline, toluidine, alpha-naphthylamine, coal tar pyridine bases, etc. at 70° C. or thereabout. The nitrogenous base is preferably added slowly to the tar acid naphthalene thiophosphoric acid preparation with stirring. The reaction may be considered to be complete as soon as the last of the nitrogenous base has been added.

The product produced (anilin being employed in the proportions and under the conditions given in this example) is an amber colored syrupy liquid. When using different proportions it is possible to make semi-solid, or substantially solid products. The formula of the anilin compound produced in accordance with example may be



We, of course, do not restrict the invention to any theoretical formula, but the above is what we believe may be the correct one. We give this formula by way of illustration of one specific formula falling within the scope of the invention, believing said formula to be accurate.

The general procedure outlined in the above examples may be applied in chemically combining P_2S_5 with any of the various classes of compounds outlined in the early part of the specifications to form nitrogenous base salts of

certain organic thiophosphoric acid compounds as herein disclosed, these reactions taking place readily at the temperatures indicated, or thereabout, in the presence preferably of an excess of the reacting organic liquid substance (or other suitable inert organic liquids) to serve as a solvent.

In the froth flotation of ores by the use of the above products as collecting agents the said products, although possessing some frothing action, may require the use of a suitable frothing agent such as, for example, pine oil, terpineol, cresylic acid or the like. The said reagents and frothing agents may be introduced into the pulp in any convenient manner and at any appropriate stage preceding or during the flotation operation. Thus, for example, it may be mixed with the ore pulp in a tube mill or other device in which the ore is being pulverized; and the amount of said reagent may be varied between wide limits depending upon the nature of the ore under treatment. Good results are obtained in many cases by the use of 0.1 to 0.2 pound of the reagent per ton of ore.

The pulp is then subjected to the ordinary aeration or froth flotation operation, producing a foam carrying the mineral from the ore. The flotation can be conducted in any type of froth flotation apparatus and in a neutral, alkaline or acid circuit, as desired.

As illustrative of the practice of the invention, 0.15 pound per ton of ore of the toluidine salt of the tar acid naphthalene thiophosphoric acid compound was employed in conjunction with the froth flotation of a difficultly floatable copper sulfide bearing ore (containing some oxidized copper mineral) of the Phelps-Dodge Corporation, together with a 0.1 pound of terpineol as a frothing agent and an alkaline circuit (2.0 pound of lime per ton). A recovery of 75%, or thereabout, of the copper bearing mineral was obtained, together with a high grade concentrate.

The same reagent employed in conjunction with the flotation concentration of Utah Copper Company ore, under substantially the same conditions, gave a recovery of better than 90% of the copper bearing mineral in the form of a high grade concentrate.

This application is a continuation in part of our application Serial Number 96,061 filed March 19th, 1926.

We claim:

1. A process which comprises floating ore material in the presence of an organic nitrogenous base salt of a hydrocarbon compound of an organic thiophosphoric acid.

2. The froth flotation of metalliferous material while in the presence of an organic nitrogenous base salt of a hydrocarbon compound of an organic thiophosphoric acid.

3. The froth flotation of metalliferous material while in the presence of an organic nitrogenous base salt of an organic thoiphosphoric acid united with a hydrocarbon as a part of the molecular structure.

4. The froth flotation of metalliferous materials while in the presence of an aniline salt of an organic thiophosphoric acid united with a hydrocarbon as a part of the molecular structure.

5. The froth flotation of metalliferous materials while in the presence of an aromatic amine salt of an organic thiophosphoric acid united with a hydrocarbon as a part of the molecular structure.

6. The froth flotation of materials while in the presence of a naphthylamine salt of an organic thiophosphoric acid united with a hydrocarbonaceous substance as a part of the molecular structure.

7. The froth flotation of materials while in the presence of a pyridine base salt of an organic thiophosphoric acid united with a hydrocarbonaceous substance as a part of the molecular structure.

8. Froth flotation of ores while in the presence of an organic nitrogenous base salt of an organic thiophosphoric compound of naphthalene combined with an alcohol.

9. Froth flotation of ores while in the presence of an organic nitrogenous base salt of an organic thiophosphoric compound of naphthalene combined with a phenol.

10. Froth flotation of ores while in the presence of an organic nitrogenous base salt of an organic thiophosphoric compound of naphthalene combined with a tar acid.

11. A new flotation reagent comprising an organic nitrogenous base salt of an organic thiophosphoric acid compound united with a hydrocarbon as an essential part of its composition.

12. A new flotation reagent comprising the reaction product of naphthalene thiophosphoric acid anhydride; with a substance selected from the herein described group of compounds, (*a*) phenolic compounds, (*b*) hydrogenated phenolic compounds, (*c*) aliphatic alcohols containing from 1 to 5 carbon atoms, and (*d*) the aliphatic and aromatic mercaptols and their homologues; and with an organic nitrogenous base.

13. A new flotation reagent comprising the reaction product of naphthalene thiophosphoric acid anhydride, with tar acid; and with an organic nitrogenous base.

14. A process which comprises reacting with phosphorus and sulfur on a hydrocarbonaceous substance capable of forming a thiophosphoric acid compound of said hydrocarbonaceous substance, reacting on the latter with a phenol-like substance to form an organic thiophosphoric acid compound of said hydrocarbonaceous substance, and reacting on the latter with an organic nitrogenous base to form an organic nitrogenous base salt of said last mentioned acid, the latter being capable of use as a flotation reagent.

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