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## MINERAL FLOTATION

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This invention relates to the froth flotation separation of sulfide minerals wherein certain flotation promoting agents are employed to facilitate separation and recovery. The principal object of the invention is to improve many such operations.

I have discovered that better recoveries of contained values and cleaner concentrates can be made from ores containing lead, copper, zinc, iron and other sulfides, by the use as promoters of certain derivatives or reaction products from thiocarbanilid (diphenyl thiourea) which products are to be used in addition to the usual or preferred frothing, inhibiting and activating agents which may be required. Subject matter herein disclosed but not claimed will be found in my copending application Serial No. 11,997.

The products or derivatives employed according to the present invention are very finely divided precipitated substances obtained by dissolving thiocarbanilid in fairly concentrated sulfuric acid and pouring into or otherwise commingling the solution with water. There forms a very fine precipitate which may be defined as peptized or partially peptized and is especially adapted for suspension in flotation pulps particularly since it acts as a highly efficient flotation promoter for sulfides. This precipitated derivative is much finer than thiocarbanilid and becomes highly dispersed upon addition to any flotation pulp, whether acid, alkaline or neutral. While it may be classed as substantially insoluble in water as is thiocarbanilid, it is nevertheless more soluble in water than is thiocarbanilid. Perhaps it is this greater solubility which renders it much more valuable for flotation purposes than thiocarbanilid, or perhaps it is a different chemical constitution or rearrangement. The product described may be separated and prepared in a dry form which will be added to the flotation pulp at any stage or to the grinding mill for the ores being treated, or it may be added as a paste containing water or a quantity of the solution or liquor in which it was precipitated, or it may be added while still suspended in the liquor in which it was precipitated so long as the acid content be not objectionable or it may be added as a solution of thiocarbanilid in sulfuric acid. Again these materials may be distributed on a carrier such as an inert carrier like diatomaceous earth, and the carrier supplied wet or dry to the flotation pulp or grinding mill, in addition of course to any necessary frothing agents and the like.

The invention therefore may be stated as residing broadly in the use in froth flotation proc-

esses, particularly processes for the differential separation of various sulfides, of the very finely divided derivatives or reaction products precipitated in water from a sulfuric acid solution of thiocarbanilid, and having much greater efficiency than thiocarbanilid, and being much finer in physical form than thiocarbanilid. It extends also to the use of the products in paste form, or in the original liquor from which precipitated, or in a dry powdered form, or in the form of the sulfuric acid solution itself. It includes also the product.

The invention particularly covered in this case is the use of the derivative from thiocarbanilid precipitated from sulfuric acid solution, this derivative being introduced into the flotation pulp or into the grinding mill for the ore from which the pulp is prepared, in accordance with the disclosures hereinafter made. The derivative from thiocarbanilid and sulfuric acid is in general produced by dissolving the thiocarbanilid in an appropriate amount of sulfuric acid sufficiently concentrated to effect ready solution, this solution being then combined with varying amounts of water to precipitate the desired derivative.

As a specific procedure for the manufacture of the thiocarbanilid derivative or reaction product, the following is given as an example: One part by weight of thiocarbanilid is added to about 20 parts of concentrated sulfuric acid and these are mixed at normal temperatures until complete solution is obtained. This solution is then poured into about 50 parts of water, whereupon the new thiocarbanilid derivative product precipitates in a very finely divided form. The proportion of thiocarbanilid to sulfuric acid may be varied; however it is noted that if the thiocarbanilid is increased much above one part of thiocarbanilid to 9 or 10 parts of sulfuric acid the resultant product tends to be lumpy; whereas if the sulfuric acid is increased above about 20 parts of acid to one part of thiocarbanilid the product becomes slightly finer, but this of course requires more acid. The proportions of water to which the solution is added may be varied within wide limits without affecting the result; for example the solution of one part of thiocarbanilid in 20 parts of acid described above may be added to as little as 25 parts of water or to as much as 400 parts of water. These are not in fact absolute limits although they may represent about the practical limits for handling. It may be said however that in general the smallest amount of water consistent with convenience should be used, especially where the acid is to be recovered from the re-

sultant solution inasmuch as this obviously cheapens acid recovery.

The sulfuric acid strength preferred may be classed as concentrated, since it is preferable that it be at least as strong as three parts of 1.84 specific gravity  $\text{H}_2\text{SO}_4$  to one part of water. The best strength seems to be about four parts of 1.84 specific gravity  $\text{H}_2\text{SO}_4$  to one part of water because the thiocarbanilid goes readily into solution. If the acid of 1.84 gravity is used without dilution, the thiocarbanilid becomes gummy before going into solution which does not occur with less concentrated acids such as the 4:1 solution. The gumminess however does not affect the product; it merely slows up the procedure. On the other hand, if the acid is too weak, precipitation begins before solution is complete; this occurs for example where the ratio is 1:1. The dilution limit for practical purposes is between about 2 and 3 parts of 1.84 specific gravity acid to one of water.

Having obtained the desired precipitation, the precipitated derivative may be recovered by decantation, filtration or otherwise, washed, dried and put up as a fine dry powder naturally resulting. It may also be put up as a wet paste containing a part of the acid solution, or washed and containing only water. When the solution is separated the acid will be recovered for further use; or the product may be used in suspension in the liquor in which it is precipitated for mineral flotation processes where the acid is desirable or at least not objectionable; or in such instances the sulfuric acid solution itself may be added to the ore pulp in which case precipitation will take place in the pulp. Such cases exist where the acid solution is added after addition of soluble cyanides to ores containing copper sulfide where cyanide is added to inhibit iron and/or zinc sulfides but acts also to depress part or all of the copper sulfide.

As to characteristics, the new derivative or reaction product is much finer than thiocarbanilid, and is more efficient. For mineral flotation uses it is vastly superior to thiocarbanilid as a promoter. Not only are the stated physical characteristics different from those of thiocarbanilid, but in view of the superior action, it appears to be and is assumed to be chemically different although I have not yet been able to determine what the chemical difference is, or whether there is a chemical rearrangement, or a different substitution, or whether there is any chemical change at all. It is conceivable that the fact of its having several times the solubility in water over thiocarbanilid, or its finer condition which makes it possible to disperse itself more widely, is the characteristic which makes it more valuable for its various uses. While both the new thiocarbanilid derivative and thiocarbanilid fall in the general classification of being substantially insoluble in water, the new derivative is nevertheless several times more soluble. It is well known in flotation practice that thiocarbanilid when fed to an ore pulp prior to flotation is not satisfactory, and that good results can be obtained only when possible to introduce it as a dry powder in the grinding mill, or to introduce it in a solvent into the flotation circuit prior to flotation. However, in the case of the new thiocarbanilid derivative of the present invention it can be introduced into the pulp in the flotation circuit in the form of a dry powder and will give very satisfactory results under those conditions

which sharply distinguishes the present product from thiocarbanilid.

It has also been discovered that if the new thiocarbanilid derivative is precipitated by the water in the presence of an inert material with large surface area such as diatomaceous earth, or after precipitation is mixed with such inert material in water, the derivative is deposited upon said material and the surface area of the derivative is thereby still further effectively increased. The proportion of derivative to inert material may vary between very wide limits, for example from as low as one per cent up to as high as 90% derivative. This phase is more fully developed hereinafter.

As above indicated, the new flotation promoter reagent obtained with sulfuric acid may be used by addition as a dry material fed to the ore pulp prior to the flotation operation, or it may be fed as a wet paste, or as a solution containing the new promoter in suspension, or it may be fed as a resulting solution from dissolving thiocarbanilid in concentrated sulfuric acid, the water in the ore pulp furnishing the water necessary for its precipitation as a practically water-insoluble promoting reagent. This new flotation promoter gives good results in alkaline, neutral or acid pulp; however, better results have been obtained in some lead ores by floating in an alkaline pulp made alkaline for example by sodium hydroxide, and better results have been obtained with some copper ores by floating in a non-basic pulp or a pulp made acid by sulfuric acid. Zinc sulfides are floated in either basic or non-basic pulp. Beneficial results are obtained on some lead ores by the addition of a cyanide compound either in the grinding mill or prior to the flotation operation, a better lead recovery being made with less detrimental zinc and/or iron sulfides in the lead concentrate. This is also the case with lead ores containing copper sulfides, in which instance a reactivator such as soluble nickel or lead compounds or  $\text{H}_2\text{SO}_4$  is added to reactivate the copper sulfides which have been partially inhibited by the cyanide. The following are examples of the invention as applied to different ores:

*Example 1.*—An ore containing approximately 15% combined lead, copper, zinc and iron sulfides in a siliceous and limestone gangue, is ground with water to liberate the sulfides from each other and from the gangue. This ground ore pulp is next introduced into a flotation machine and 2/100 of a pound per ton of ore of the new thiocarbanilid-sulfuric acid derivative product is added together with cresylic acid as a frothing agent, and a lead-copper concentrate is removed. Most of the iron and zinc sulfides remain in the tailing and are rejected with the gangue because the amount of thiocarbanilid derivative is too small to promote appreciable quantities of zinc or iron sulfides. If the zinc or iron sulfides are desired, they can be floated by any well known standard method.

*Example 2.*—The ground ore pulp from the ore of the above example was introduced into a flotation machine and  $\frac{1}{2}$  of a pound per ton of ore of sodium cyanide added to the pulp. This was such an ore, substantially free from oxidized constituents and soluble salts, that the cyanide acted not only in inhibit the iron and zinc sulfides but also considerable of the copper sulfide. One to two pounds of sulphuric acid was then added to reactivate the inhibited copper sulfide, together with 2/100 of a pound per ton of ore of the new

thiocarbanilid-sulfuric acid derivative and cresylic acid for a frothing agent, and a lead-copper froth concentrate was removed. This gave a much cleaner copper-lead concentrate than that obtained in Example 1, as the cyanide inhibited those zinc and iron sulfides that were floated with the copper sulfides in Example 1. At the same time the recovery of copper sulfide was as good as in Example 1 on account of the added  $\text{H}_2\text{SO}_4$  which reactivated the inhibited copper sulfide. Here, the amount of thiocarbanilid derivative may be increased because the cyanide maintains the iron and zinc in a depressed condition. In this example, also, the zinc and iron sulfides may be floated if desired, but in this operation they were rejected in the tailing. Soluble nickel and lead salts may be substituted for the sulfuric acid in some instances if desired.

**Example 3.**—A lead zinc iron ore containing approximately 10% lead, 10% zinc and 15 to 20% iron, as sulfides, is ground with water to liberate the sulfides from each other and from the gangue, which is a siliceous and limestone gangue. After the ore is ground with water, it is introduced into a flotation machines and  $\frac{1}{8}$  of a pound per ton of ore of the new thiocarbanilid-sulfuric acid reaction product added together with a half pound of sodium hydroxide per ton of ore and sufficient cresylic acid as a frothing agent to make the proper frothing condition, and a lead froth concentrate is removed. Sometimes it is desirable to add an additional small amount of sodium hydroxide, as for example  $\frac{1}{4}$  to  $\frac{1}{2}$  a pound and further float and remove the last of the lead froth concentrate. After the lead concentrate has all been removed, copper sulfate is added and  $\frac{1}{8}$  of a pound per ton of ore of the new thiocarbanilid-sulfuric acid product added and a zinc froth concentrate removed. Sometimes it is desirable to add additional new product, as for example  $\frac{2}{100}$  of a pound per ton of ore, and remove the last of the zinc froth concentrate. After the zinc concentrate has all been removed, the iron sulfide may be rejected with the tailing, or it may be floated with the addition of xanthate or other reagents and an iron froth concentrate removed.

**Example 4.**—The lead-zinc-iron ore of Example 3 is ground in the same way with water. It is then introduced into a flotation machine and  $\frac{1}{4}$  of a pound of sodium cyanide added together with  $\frac{1}{8}$  of a pound per ton of ore of the new thiocarbanilid-sulfuric acid reaction product and a half pound per ton of ore of sodium hydroxide and sufficient cresylic acid as a frothing agent to make the proper frothing condition and a lead froth concentrate removed. The pulp is then further froth floated as in Example 3. Sometimes it is desirable to add the sodium cyanide in the grinding mill rather than to the flotation machine.

**Example 5.**—A copper ore containing approximately 2% copper as sulfide in an iron pyrite gangue is ground with water to liberate the copper sulfide from the iron pyrite and the small amount of gangue. This ground ore pulp is introduced into a flotation machine together with  $\frac{5}{100}$  of a pound per ton of ore of the new thiocarbanilid-sulfuric acid product, together with cresylic acid as a frothing agent and the copper froth concentrate removed. A large part of the iron pyrite is rejected as tailing.

**Example 6.**—An ore containing 5% copper sulfide, 10% zinc sulfide, 70% iron sulfide and the rest gangue was ground with water to liberate the

sulfides from each other and from the gangue. It was then introduced into a flotation machine with the addition of 0.2 lb. sodium cyanide per ton of ore. This ore was substantially free from oxidized constituents and soluble salts and a considerable proportion of the copper sulfides, were inhibited along with the iron and zinc sulfides. This ore is to be distinguished from ores containing oxidized constituents or soluble salts where no copper sulfide is depressed by the cyanide. In the present instance a solution of one part of thiocarbanilid in from about 20 to 50 parts of concentrated sulfuric acid was added to the pulp in the proportion of about one to two pounds of the acid solution per ton of ore. The acid served to activate the depressed copper sulfides and the thiocarbanilid derivative of the present invention was precipitated in the pulp by the effect of the water.

After addition of a frothing agent the pulp was then subjected to flotation and a copper sulfide froth concentrate removed which was substantially free of iron and zinc sulfides. In a case like this, the iron and zinc sulfides may be separated and recovered by other methods or rejected as tailing as may be desired.

In treating an ore of the character of Example 6 where soluble cyanides, such as sodium and zinc cyanides act to depress quantities of the copper sulfide, sulfuric acid, in the amount of about 1 to 3 lbs. per ton if concentrated, or equivalent amount of dilute acid, may be added to the pulp to reactivate the depressed copper sulfide following addition of the cyanide employed to depress iron and zinc sulfides, and some other promoter or collector than the thiocarbanilid derivative of the present invention or sulfuric acid solution thereof, may be employed; for example other forms of thiocarbanilid, or xanthate, or the like. In these instances the added sulfuric acid is relied upon to reactivate the portion of copper sulfide depressed by the cyanide, such sulfuric acid not being necessarily added with the promoter.

Where the derivative is deposited on a carrier such as diatomaceous earth as hereinbefore mentioned, the distribution by the carrier is such that less derivative may be used although more of total derivative plus carrier is used. The carrier is produced by introducing it into several times its volume of water, (e. g. 5 to 25 times) that is, enough not only to wet the carrier but also to make a sufficiently thin slurry for free agitation and intermingling. The solution of thiocarbanilid may be poured in and mixing carried on for a time so that the precipitated derivative is deposited on the carrier. As in the case of the straight derivatives, the carrier modified by deposit of the thiocarbanilid derivative, may be recovered in dry powdered form or as a paste or a slurry. The derivative is found well distributed. The amount deposited is largely a matter of selection, but ranges of five to thirty per cent by weight of the earth of thiocarbanilid derivative deposited on the earth have been found to be exceptionally satisfactory.

As an example, about 20 parts of finely divided diatomaceous earth are mixed with 400 parts of water and, while agitating, a solution made from one part of thiocarbanilid dissolved in 18 or 20 parts of concentrated sulfuric acid is added to the slurry of diatomaceous earth in water. A practically insoluble thiocarbanilid derivative precipitates upon admixture with the water. This new mixture is thoroughly agitated causing the resultant practically water-insoluble precipi-

tated product to become distributed or diffused over the surface of the diatomaceous earth which is then separated from the solution and made into a wet paste, or separated from the solution and dried and made into a dry powdered product. This treated carrier is used in flotation processes in the same way that the derivative is employed according to the foregoing examples.

Where the derivative is to be deposited upon diatomaceous earth or like inert carrier, other solvents for thiocarbanilid may be substituted such as ethyl alcohol or other aliphatic alcohol or acetic acid or ortho toluidin, preferably those solvents which are freely miscible with water. In fact, in this connection thiocarbanilid itself may be distributed throughout the water slurry and deposited upon the earth.

It is to be understood that the foregoing disclosures are merely illustrative of the generic invention and that they are not to be taken as limiting.

I claim:

1. A froth flotation method comprising preparing a sulfide ore pulp, introducing a frothing agent and the product obtained by dissolving thiocarbanilid in sulfuric acid at normal temperatures and precipitating in water, and subjecting the pulp to froth flotation to recover sulfides.
2. A method for the froth flotation of sulfide minerals comprising preparing a pulp from a sulfide ore, dissolving thiocarbanilid in sulfuric acid at normal temperatures, adding the solution to water, recovering the precipitate, supplying the precipitate to the ore pulp, adding a frothing agent to the ore pulp, and subjecting the pulp to a froth flotation treatment.
3. A method for froth flotation comprising preparing a pulp from a sulfide ore and water, supplying to the pulp a sulfuric acid solution of thiocarbanilid made at normal temperatures, introducing a frothing agent to the pulp, and subjecting the resulting pulp to a froth flotation treatment.
4. A flotation process comprising producing a flotation pulp from a sulfide ore, supplying to the pulp a flotation promoter and dispersing the same throughout the pulp, the promoter being a largely water-insoluble finely divided thiocarbanilid reaction product producible as a precipitate by addition of water from a sulfuric acid solution of thiocarbanilid made at normal temperatures, adding a frothing agent, and subjecting the pulp to a froth flotation operation.
5. A method according to claim 2 where the thiocarbanilid is dissolved in sulfuric acid more concentrated than about two parts of 1.84 specific gravity  $H_2SO_4$  to one part of water.
6. A method according to claim 3 wherein the thiocarbanilid is dissolved in sulfuric acid more concentrated than about two parts of 1.84 sp. gr.  $H_2SO_4$  to one part water.
7. A method according to claim 3 wherein one part of the thiocarbanilid is dissolved in at least about ten parts of strong sulfuric acid.
8. A method according to claim 2 wherein one part of the thiocarbanilid is dissolved in not less than about ten parts of strong sulfuric acid.
9. A method for the froth flotation separation of ores containing copper sulfides and iron and/or zinc sulfides, comprising pulping the ore, add-

ing cyanide to depress zinc and iron sulfides present, adding a solution of thiocarbanilid in strong sulfuric acid made at normal temperatures whereby the acid activates depressed copper sulfides and a thiocarbanilid derivative is precipitated which serves as a promoter, supplying a frothing agent, and froth floating to recover a copper sulfide froth concentrate.

10. A method for the froth flotation separation of ores containing copper sulfides and iron and/or zinc sulfides wherein the copper sulfide is such that at least an appreciable proportion will be depressed by cyanide added to a flotation pulp, comprising pulping the ore, adding cyanide to depress zinc and iron sulfides present, supplying to the pulp sulfuric acid to reactivate depressed copper sulfides without substantially reactivating zinc and iron sulfides present, supplying as a promoter a thiocarbanilid derivative obtainable by dissolving thiocarbanilid in strong sulfuric acid at normal temperatures and precipitating by means of water, supplying a frothing agent to the pulp, and subjecting the pulp to froth flotation and recovering a copper sulfide concentrate containing substantially all the copper and substantially free from iron and zinc.

11. A method for the froth flotation separation of sulfide ores containing copper sulfides and iron and/or zinc sulfides wherein the copper sulfides are subject to at least partial depression by cyanide added to a flotation pulp, comprising preparing a flotation pulp from the ore, adding cyanide to the pulp to depress iron and zinc sulfides present, adding thiocarbanilid and sulfuric acid to provide a promoter and an agent for reactivating depressed copper sulfides without substantial activation of iron and zinc sulfides present, supplying a frothing agent, and subjecting the pulp to a froth flotation operation to separate a copper sulfide concentrate substantially free from iron and zinc sulfides.

12. A method according to claim 1 wherein the thiocarbanilid product is dispersed in diatomaceous earth.

13. A method according to claim 2 wherein the water receiving the precipitated thiocarbanilid product also receives an inert finely divided solid carrier of large surface area upon which the thiocarbanilid product is deposited, and such modified carrier is supplied to the ore pulp.

14. A method according to claim 4 wherein the reaction product is distributed in an inert finely divided solid carrier of large surface area.

15. A method according to claim 4 wherein the thiocarbanilid reaction product is distributed in diatomaceous earth.

16. A froth flotation method comprising preparing an ore pulp, adding to the pulp a frothing agent and a finely divided solid carrier material of large surface area carrying upon its surface a substantially water-insoluble promoter of the class of thiocarbanilid products including thiocarbanilid and thiocarbanilid derivatives precipitated from thiocarbanilid solutions by the action of water, and subjecting the resultant pulp to a froth flotation treatment.

17. A method according to claim 16 wherein the thiocarbanilid derivative is precipitated on the carrier from a solution of thiocarbanilid in a solvent freely miscible with water.

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