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CONCENTRATION OF ORES.

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This invention relates to the concentration of ores, minerals, and the like, by flotation, and has for its object the provision of certain improvements in flotation processes, and more particularly the froth flotation process.

The present invention is based upon the discovery that thiocarbamic esters, thiourethanes) are effective flotation reagents. I have found that the thiocarbamic esters, and more particularly alkyl arylthiocarbamates such as methyl phenylthiocarbamate and ethyl phenylthiocarbamate, have a marked selective action on sulfide minerals, as distinguished from gangue minerals, and when used as flotation agents in the customary flotation processes cause the sulfide minerals to float readily with an attendant high recovery of the metal values.

My investigations indicate that the thiocarbamic esters are substantially lacking in frothing power, so that an appropriate frothing agent, such as pine oil, terpineol, or the like, should be employed in conjunction therewith in carrying out the flotation operation.

In general, thiocarbamic esters are called thiourethanes, being urethanes (that is, esters of carbamic acids) in which one or both oxygen atoms have been replaced by sulfur. Since the two oxygen atoms of urethanes differ in function, distinctive names are required to indicate which one is replaced, in case sulfur has been substituted for only one. When the carbonyl oxygen is replaced by sulfur, the result is a thionurethane. The thionurethane compounds are ordinarily understood to be embraced within the generic class of thiourethanes. Replacement of the other oxygen atom gives a thiolcarbamate or thiolurethane.

The derivation of the word urethane (from urea and ethane) implies an ethyl ester. Accordingly, the rational but cumbersome nomenclature should be applied to other esters. For example, the compound represented by the chemical formula

$$C_6H_5NHCSOCH_3$$

is methyl phenylthiocarbamate, or to be quite exact, methyl phenylthioncarbamate.

Dithiocarbamic esters are also known and are available for the purposes of the invention. In the case of ethyl esters, the dithiocarbamic esters may be called dithiourethanes. The invention, accordingly, contemplates the use, as flotation agents, of mono- and dithiocarbamic esters (mono- and dithiourethanes), and it is the intention throughout this specification and in the appended claims to include all these esters under the generic terms thiocarbamic esters or thiourethanes.

The general method of preparing a thiourethane consists in treating an isothiocyanate or mustard oil with an alcohol, under suitable conditions. For example, to prepare ethyl phenylthiocarbamate

$$(C_6H_5NHCSOC_2H_5),$$

or methyl phenylthiocarbamate

$$(C_6H_5NHCSOCH_3),$$

phenyl mustard oil is heated with ethyl alcohol, or with methyl alcohol, respectively, in an autoclave. The addition of an alkali, such as caustic potash, promotes the reaction, so that lower temperatures may thereby be employed. In the foregoing examples, the resulting thiocarbamic esters crystallize readily, and may thus be removed from the reaction mixture and obtained in a pure condition. If desired, the crude reaction mixture may be used in the flotation process without isolating the ester. Other methods of preparing the thiocarbamic esters may be used, as, for example, by alkylation of salts of dithiocarbamic acids.

Thiourethanes are only sparingly soluble in water, but dissolve readily in aqueous solutions of alkalies, such as caustic soda, as well as in various organic solvents. Hence, the thiourethane may be used in the flotation process either by adding it to the ore pulp prior to or during fine grinding, or it may be dissolved in aqueous alkali or in an appropriate organic solvent and the resulting solution added to the ore pulp feed entering the flotation apparatus.

As thiourethanes are mineral collecting agents only, being substantially devoid of frothing power, they should be used, in practicing the present invention, in conjunction with an appropriate frothing agent, such as pine oil, or the like. The thio-urethanes exhibit marked mineral collecting power in acid, neutral and alkaline ore pulps. My investigations indicate, however, that the thiourethanes give the best results on most

ores in pulps made alkaline, as for example by the addition of lime.

I prefer to employ the thiourethanes as flotation agents in a neutral (that is non-acid) or alkaline ore pulp. Any alkali, such as caustic soda, soda ash, or lime, may be added to the ore pulp to make the pulp neutral or alkaline. Lime, on the whole, is the most suitable and available alkali for this purpose. The alkali is preferably added to the ore pulp before the final grinding, and before adding the thiourethane to the ore pulp.

The quantity of the thiourethane to be employed in practicing the present invention depends to some extent upon the particular ester being used and the particular ore being treated. In general, I have found that one-fifth of a pound, and less, per ton of dry ore gives satisfactory results.

In the following table, I have given some typical flotation results obtained in the practice of the present invention. In each of the floats reported in this table, the thiourethane was added, in the proportion of 0.1 pound per ton of dry ore, together with the amount of hydrated lime indicated, to 500 grams of minus 40-mesh ore of the Utah Copper Company, which was then ground with 250 cc. of water in a laboratory pebble mill for 20 minutes. The ore pulp was transferred to a laboratory Callow rougher flotation machine, diluted with about 2 liters of water, and floated after adding one drop of terpineol as a frothing agent immediately preceding flotation.

Reagent.	Lime lbs. per ton dry ore.	Heads % Cu.	Tails, % Cu.	Conc. % Cu.	Recovery %
Phenyl thiourethane $C_6H_5NHCSOC_2H_5$	4	1.24	0.18	12.5	86.7
Methyl phenylthiocarbamate $C_6H_5NHCSOCH_3$	5	1.22	0.14	14.8	89.5
o-tolyl thiourethane $C_7H_7NHCSOC_2H_5$	5	1.22	0.16	16.7	87.7
Phenyl dithiourethane $C_6H_5NHCSSC_2H_5$	5	1.22	0.20	16.1	84.7

Satisfactory flotation results have also been obtained using ethyl phenylthiocarbamate (phenyl thiourethane) in acid and neutral pulp on the ore of the Magma Copper Co. Good results have likewise been obtained using ethyl phenylthiolcarbamate

$(C_6H_5NHCOSC_2H_5)$

phenyl methyldithiourethane

$(C_6H_5NCH_3CSSC_2H_5)$,

and alpha-naphthyl thiourethane

$(C_{10}H_7NHCSOC_2H_5)$

in an alkaline pulp of the ore of the Utah Copper Co. In general, I have found that uniformly good results are secured by using the alkyl arylthiocarbamates, such as ethyl phenylthiocarbamate and methyl phenylthiocarbamate, and ordinarily I prefer to use one or the other of these compounds.

It will be understood by those skilled in the art that the present invention is applicable to the treatment by flotation of various kinds of mineral mixtures both natural and artificial. In the appended claims, I have accordingly employed the terms "mineral" and "ore" in a broad sense to include ores, mineral products and all materials amenable to concentration or similar treatment by the flotation processes.

I claim:

1. The improvement in the concentration of minerals by flotation which comprises subjecting the mineral in the form of a pulp to a flotation operation in the presence of a thiourethane.

2. The improvement in the concentration of minerals by flotation which comprises subjecting the mineral in the form of a pulp to a flotation operation in the presence of an alkyl arylthiocarbamate.

3. The improvement in the concentration of minerals by flotation which comprises subjecting the mineral in the form of a pulp to a flotation operation in the presence of ethyl phenylthiocarbamate.

4. The improvement in the concentration of minerals by flotation which comprises subjecting the mineral in the form of a non-acid pulp to a flotation operation in the presence of a thiourethane.

5. The improvement in the concentration of minerals by flotation which comprises subjecting the mineral in the form of a non-acid pulp to a flotation operation in the presence of an alkyl arylthiocarbamate.

6. The improvement in the concentration of minerals by flotation which comprises subjecting the mineral in the form of an alkaline pulp to a flotation operation in the presence of a thiourethane.

7. The improvement in the concentration of minerals by flotation which comprises subjecting the mineral in the form of an alkaline pulp to a flotation operation in the presence of an alkyl arylthiocarbamate.

8. The improvement in the concentration of minerals by flotation which comprises subjecting the mineral in the form of an alkaline pulp to a flotation operation in the presence of ethyl phenylthiocarbamate.

9. The improvement in the concentration of minerals by flotation which comprises subjecting the mineral in the form of a pulp made alkaline by the addition of lime to a flotation operation in the presence of a thiourethane.

10. The improvement in the concentration of minerals by flotation which comprises subjecting the mineral in the form of a pulp made alkaline by the addition of lime to a flotation operation in the presence of an alkyl arylthiocarbamate.

11. The improvement in the concentration of minerals by flotation which comprises subjecting the mineral in the form of a pulp made alkaline by the addition of lime to a flotation operation in the presence of ethyl phenylthiocarbamate.

12. In the process of concentrating ores and minerals by flotation the step which comprises subjecting the ore in the form of a pulp to a flotation operation in the presence of aryl thiourethane.

13. In the process of concentrating ores and minerals by flotation the step which comprises subjecting the ore in the form of a pulp to a flotation operation in the presence of phenyl thiourethane.

In testimony whereof I affix my signature.

RALPH E. SAYRE.