

## UNITED STATES PATENT OFFICE

2,628,716

## FLOTATION PROCESS

William H. Hill, Mount Lebanon, Pa., assignor to  
Koppers Company, Inc., Pittsburgh, Pa., a cor-  
poration of Delaware

No Drawing. Application March 15, 1946,  
Serial No. 654,817

10 Claims. (Cl. 209—166)

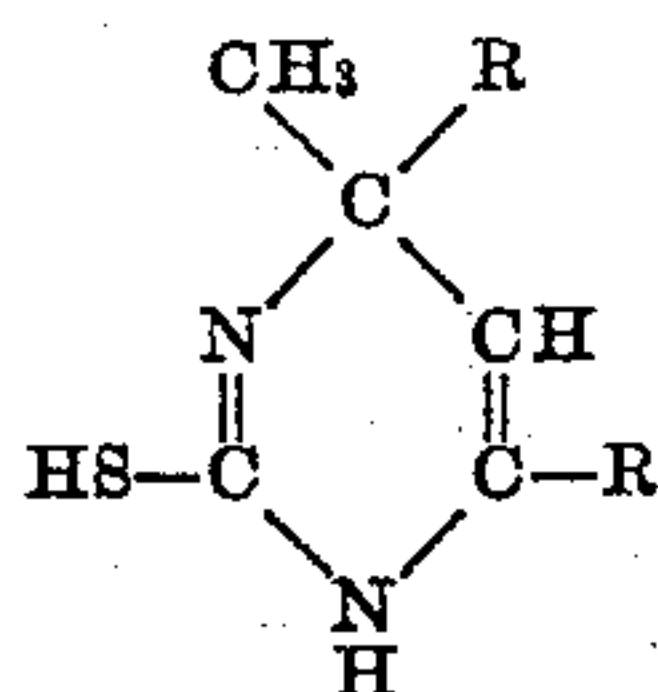
1

This invention relates to froth flotation processes and more particularly is directed to froth flotation of sulphide minerals, and still more particularly to selective froth flotation of sulphide minerals such as zinc and copper sulphides.

This invention has for its principle objects to provide new reagents for carrying out froth flotation processes, to provide new and effective collectors for sulphide minerals; to provide new collectors capable of selectively floating sulphide minerals such as copper and zinc sulphide from pyrite or pyrrhotite; to effect economies through higher recoveries, higher strength concentrates, simplified operation and/or reduced operating time; to obtain advantages as will be pointed out; and to avoid the disadvantages of the prior art. Further objects will appear as the description proceeds.

These objects are accomplished in the present invention by carrying out froth flotation in the presence of a suitable thiopyrimidine. I have found that certain thiopyrimidines are effective collecting agents in the froth flotation of minerals, particularly sulphide minerals, and, because of their relative inability to float iron sulphides are particularly valuable in selective flotation of sulphide minerals containing pyrite or pyrrhotite. By means of the collectors of the invention, I am able to float a wide variety of minerals and in many instances, as, for example, with sulphite copper-iron ores and sulphide lead-zinc-iron ores to obtain improved concentrates and improved recovery along with greater flexibility of operation and shorter flotation periods.

Thiopyrimidines which are effective according to this invention, are compounds characterized by a 2-mercapto-1,3-diazine structure as represented by the following formula:

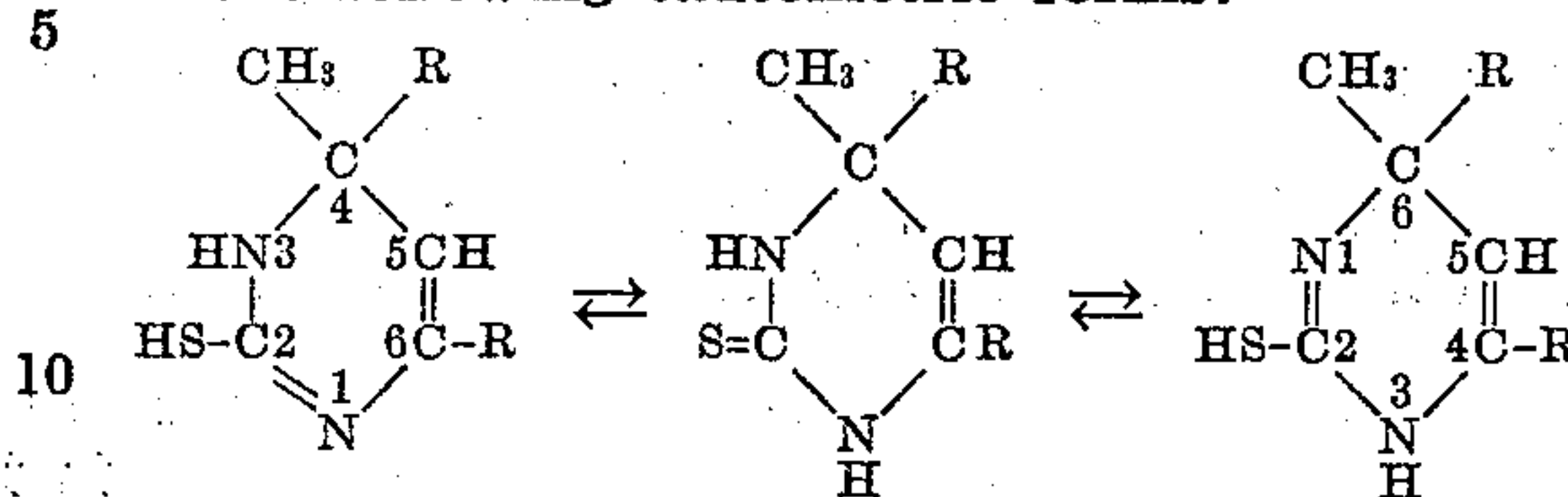


in which the R's are the same radical selected from the class consisting of methyl and ethyl radicals, such as may be obtained among other ways, by the condensation of ammonium thiocyanate with acetone or methyl ethyl ketone, or the corresponding alpha, beta unsaturated ketones resulting from the aldol condensation of acetone or methyl ethyl ketone. The products are well defined compounds being crystal-

2

line solids of low water solubility even in the form of their alkali metal salts.

These compounds may exist in one or more of the following tautomeric forms:



which accounts for the various names which have been applied to these in the prior art. The product obtained from mesityl oxide and ammonium thiocyanate, for example, is variously shown or designated as 2-mercapto-4,4,6-trimethyl-3,4-dihydropyrimidine or 2-mercapto-4,6,6-trimethyl-1,6-dihydropyrimidine (structure I); 2-thio-4,4,6-trimethyl-1,2,3,4-tetra-hydropyrimidine or 2-thio - 4,6,6 - trimethyl - 6,1,2,3 - tetrahydropyrimidine (structure II); or 2-mercapto-4,4,6-trimethyl- or 2-mercapto-4,6,6-trimethyl dihydropyrimidine or 2-mercapto - 4,4,6 - trimethyl  $\Delta^{2,5}$  metadiazine (structure III) depending on the tautomeric form and whether the ring is numbered clockwise or counterclockwise. In the enol form the mercapto hydrogen may be replaced by inorganic radicals forming salts. Suitable methods for their preparation are disclosed in U. S. Patents 2,131,790; 2,181,217; 2,234,848; and 2,244,547.

The compound 2-mercapto-4,4,6-trimethyl-3,4-dihydropyrimidine results also when acetone or diacetone is used instead of mesityl oxide. Thus the same type of compound is obtained from ketones which by self condensation (aldol condensation) or by dehydration are capable of forming alpha, beta, unsaturated ketones.

Methyl ethyl ketone or its self condensation product, 5-methyl-4-penten-3-one, similarly condenses with ammonium thiocyanate to give 2-mercapto-4,6-diethyl-4-methyl - dihydropyrimidine. In the above formula this compound is represented when R is the ethyl radical. If the ring is numbered counterclockwise, the name is 2-mercapto-4,6-diethyl-6-methyl - dihydropyrimidine as disclosed in U. S. Patent 2,356,710.

In carrying out flotation processes in accordance with the invention the thiopyrimidines as described above are utilized to condition the mineral in essentially the same manner as standard collecting agents such as xanthates, dithiophosphates and substituted thioureas. They may be incorporated in the mineral pulp in any suitable manner as, for example, in the liberation, clas-



3

sification or conditioning operations along with such other reagents as frothers, depressants, conditioners, other collectors, etc., as are commonly used or as may be desired, and the treated pulp subjected to froth flotation according to any suitable procedure.

The effectiveness of the compounds of the invention depends upon the nature of the ore, the amount used, the pH, the time and like factors. In short their efficiency depends upon the usual variables which affect the efficiency of collectors in froth flotation. In general, however, they are less susceptible to variation in pH and more effective in depressing pyrite and pyrrhotite and, in particular cases, float less insolubles and give lower tailings, higher concentrates and better over-all yields than collectors commonly used. Another advantage of the compounds of this invention is the fact that lime can be used to give the desired pH even in cases where other flotation agents now employed require the more costly soda ash as an alkalizing agent. Thus while the collectors of this invention are generally useful in collecting a wide variety of minerals, particularly sulphide minerals, they are more particularly useful in effecting selective flotation of certain sulphide minerals such as copper and zinc ores containing relatively large quantities of

4

mesh, 46.2% minus 200 mesh with 6 lbs. of lime and 0.2 lb. of 2-mercapto-4,4,6-trimethyl-3,4-dihydropyrimidine (obtained by the condensation of mesityl oxide with ammonium thiocyanate) per ton or ore. The ground ore was conditioned for 20 minutes and then subjected to a 10 minute flotation at 25% solids to which 0.1 lb. per ton pine oil was added one half at the start and the other half at five minutes. Two rougher concentrates were produced; the first taken for the first two minutes of the rougher float and the second for the last eight minutes. The results are tabulated below in Table I.

B. Procedure A was repeated except that 2-mercapto-4,4,6-trimethyl-3,4 - dihydropyrimidine was increased to 0.3 pound per ton of ore.

C. The ore was ground as in procedure A with 12 lbs. of lime per ton, conditioned for twenty minutes with 2 lbs. of sodium sulphite per ton and subjected to a ten minute flotation period at 25% solids to which 0.025 lb. Minerec B (Minerec B is a trade name for collectors obtained by dissolving a xanthate, probably potassium butyl xanthate, in ethyl chloro carbonate), 0.1 lb. of pine oil and 0.1 lb. potassium ethyl xanthate per ton were added. Two rougher concentrates were taken as in procedure A; the results are tabulated below in Table I.

Table I.—Flotation of copper sulfide according to the invention (A and B) as compared with the prior art (C)

Procedure	Weight Percent Ro. Conc.		Percent Cu. Ro. Conc.		Percent Insoluble Ro. Conc. 1	Percent Cu. Ro. Tails	Percent Cu. Recovery Ro. Conc.	
	1	2	1	2			1	2
A.....	24.9	5.7	23.29	4.73	-----	0.32	92.2	4.3
B.....	23.1	8.6	24.9	4.53	-----	0.23	91.3	6.2
C.....	23.4	14.9	24.73	2.56	-----	0.22	91.8	6.0

Ro. Conc.=Rougher Concentrate.  
Ro. Tails=Rougher Tails.

pyrite. Thus through the collectors of the invention it is possible to produce a high grade copper concentrate essentially free of pyrite with relatively low insolubles from low grade sulphide copper-iron ores and to provide high grade zinc concentrates from sulphide zinc-iron ores with unusually high recoveries of zinc. Such terms as copper-iron ores and zinc-iron ores are intended to include virgin ores, concentrates, tailings and like products which contain the named metals with or without other values in admixture with gangue.

The amount required varies according to the particular ore and according to the effectiveness of the particular compound used but is of the same order of magnitude as the required amounts of like agents of the prior art. Suitable results have been obtained within the limits of 0.0025 to 0.025% by weight of the mineral (0.05 to 0.5 lb. per ton) but greater or lesser quantities may be used. For any particular compound and any particular mineral those skilled in the art, having in mind these principles will readily be able in view of the data given below to determine suitable amounts.

The invention may be more fully understood by reference to the following examples in which the parts are by weight unless otherwise specified.

EXAMPLE I

A. An Arizona sulfide copper-iron ore containing about 6% copper was ground to 4.0% plus 65

It is significant to note from the data given in the above table that better selective flotation of copper sulphide is obtained according to the procedures of the invention than are obtained with a standard treatment using ethyl xanthate. The 14.9% by weight of the secondary concentrate of the standard test C shows a large circulating load of iron, a factor undesirable in plant operation. It should be noted also that in the procedures according to the invention it is not necessary to use sodium sulphite as a depressant for iron; moreover that these advantageous results are obtained without sacrifice in the percent recovery of copper.

EXAMPLE II

A. Standard procedure.—A sulphide lead-zinc-iron ore obtained from Park City, Utah area, was ground to 2.3% plus 100 mesh screen and 77.9% minus 200 mesh screen along with 5 lbs. soda ash, 0.2 lb. sodium cyanide, 1.0 lb. zinc sulfate and 0.025 lb. Minerec B per ton, and subjected to a three minute flotation at 25% solids with the addition at the start of 0.05 lb. B23 alcohols (B23 alcohols are a mixture of higher molecular weight alcohols, about C7, obtained by high pressure synthesis, which are commonly used in about equal admixture with pine oil in order to obtain a more brittle froth) and pine oil and 0.01 lb. potassium ethyl xanthate per ton to give lead rougher concentrate and tails. The lead rougher tails was conditioned for 10 minutes with the



5

addition of 0.05 lb. B23 alcohols and pine oil, 0.05 lb. potassium ethyl xanthate, 2.0 lbs. of lime and 0.5 lb. of copper sulfate per ton and subjected to a 10 minute flotation to give zinc rougher concentrate and tails. The results are given in Table II.

Table II.—Flotation of zinc sulfide according to the prior art

Product	Percent Wt.	Percent Composition			Percent Distribution		
		Pb	Zn	Fe	Pb	Zn	Fe
Pb. Ro. Conc.	19.1	70.2	3.42	2.4	96.2	7.1	8.7
Pb. Ro. Tails	80.9	0.65	10.50	5.94	3.8	92.9	91.3
Heads	100	13.93	9.16	5.27	100	100	100
Zn. Ro. Conc.	18.9	1.8	43.48	2.5	2.4	89.7	8.9
Zn. Ro. Tails	62.0	0.3	0.47	7.0	1.4	3.2	82.4
Pb. Ro. Tails	80.9	0.65	10.50	5.94	3.8	92.9	91.3

B. The standard procedure was repeated substituting 0.2 lb./ton of 2-mercapto-4,4,6-trimethyl-3,4-dihydropyrimidine for the 0.05 lb./ton of potassium ethyl xanthate in the zinc circuit. The results are given in Table III.

Table III.—Flotation of the sulfide according to the invention

Product	Percent Wt.	Percent Composition		Percent Distribution	
		Zinc	Fe	Zn	Fe
Pb. Ro. Conc.	19.0	2.8	1.8	5.9	6.5
Pb. Ro. Tails	81.0	10.5	6.00	94.1	93.5
Heads	100.0	9.05	5.21	100.0	100.0
Zn. Ro. Conc.	16.0	52.42	2.2	92.7	6.7
Zn. Ro. Conc.	65.0	0.20	6.95	1.4	86.8
Pb. Ro. Tails	81.0	10.5	6.00	94.1	93.5

From the data of Tables II and III it may be seen that process of the invention produced a zinc tail assaying less than half that obtained with xanthate and that the grade of concentrate was about 10% better.

The above procedures were carried out with fine ore because coarse zinc is generally difficult to float selectively. When the procedures were repeated with coarse ore, about 62% minus 200 mesh, the zinc tails in the standard increased from 0.47%, Table II, to 0.98%; whereas with 2-mercapto-4,4,6-trimethyl-3,4-dihydropyrimidine the zinc tails increased only to 0.3%.

The collectors of the invention have also been found unusually effective in the treatment of marmatite ores, natural zinc-sulfide ores containing large amounts of pyrite. The collectors of the invention are unusually effective in floating the zinc sulphides in these ores from the pyrite gangue. For example, marmatite zinc-iron ore assaying 0.04% lead and 5.42% zinc was subjected to froth flotation using 2-mercapto-4,4,6-trimethyl-3,4-dihydropyrimidine in comparison with sodium isopropyl xanthate which is commonly used as a collector for this ore. In all tests a brittle froth was obtained with the xanthate making the froth removal from both rougher and cleaner cells difficult, whereas with the collector of the invention satisfactory frothing conditions were obtained throughout. The collector of the invention proved more selective in that considerably less circulating load was involved than obtained with the xanthate. The process of the invention also produced a higher grade cleaner concentrate assaying 46% zinc as compared with 43% for the xanthate. .2 lb. per ton or less of the collector of the invention

6

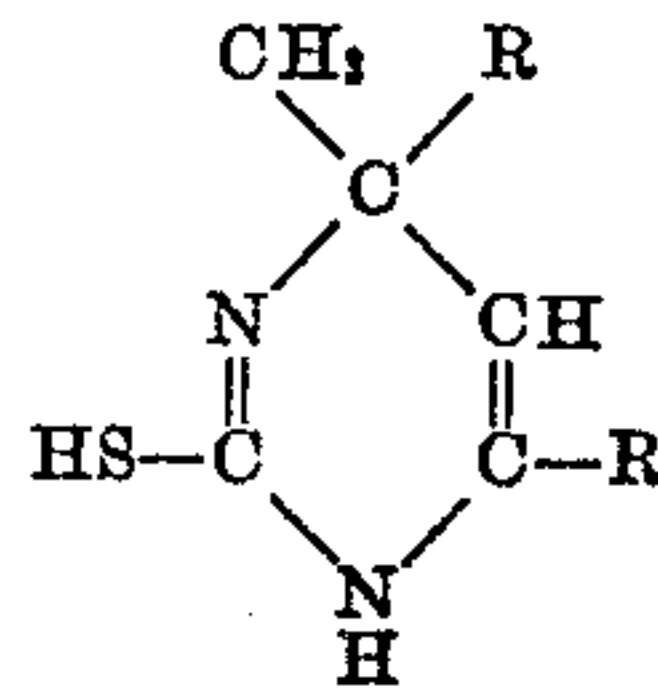
proved effective whereas .3 lb. per ton of the xanthate was required. The same collector of the invention was also found effective in floating zinc sulphide in a marmatite zinc ore assaying 15.4% zinc, 0.4% lead and 30.4% iron. With the prior art collectors such as Aerofloat 25, soda

ash is required as the alkaline reagent. By using the collector of the invention it was found possible to obtain effective flotation with this ore using lime as the alkaline reagent, moreover the collector of the invention proved more potent and more selective in the lime circuit than the Aerofloat 25 in the soda ash.

The foregoing examples serve to illustrate typical embodiments of the invention and to point out some of the advantages of the invention with respect to the prior art practices. It is to be understood, however, that the invention is not limited to these particular embodiments or to any of the details thereof but that the invention may be variously embodied within the scope of the invention as outlined above and as set forth in the appended claims.

I claim:

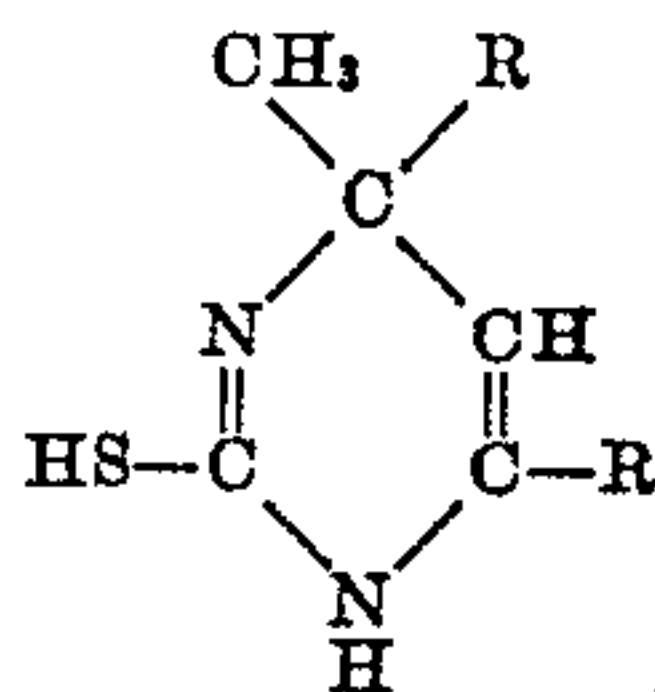
1. In a process for froth flotation the steps of preparing a mineral pulp of a sulfidic ore, incorporating therein a thiopyrimidine having the following structure:



in which the R's are the same radical selected from the class consisting of methyl and ethyl radicals and subjecting the pulp to froth flotation.

2. In a process for froth flotation the steps of preparing a mineral pulp of a sulfidic ore, incorporating therein 2-mercapto-4,4,6-trimethyl-3,4-dihydropyrimidine and subjecting the pulp to froth flotation.

3. In a process for froth flotation the steps of preparing a mineral pulp of a sulfide ore contaminated with pyrite incorporating therein a thiopyrimidine having the following structure:



in which the R's are the same radical selected from a class consisting of methyl and ethyl radicals and subjecting the pulp to froth flotation.

4. In a process for froth flotation the steps of preparing a mineral pulp of a sulphide ore contaminated with pyrite incorporating therein 2.



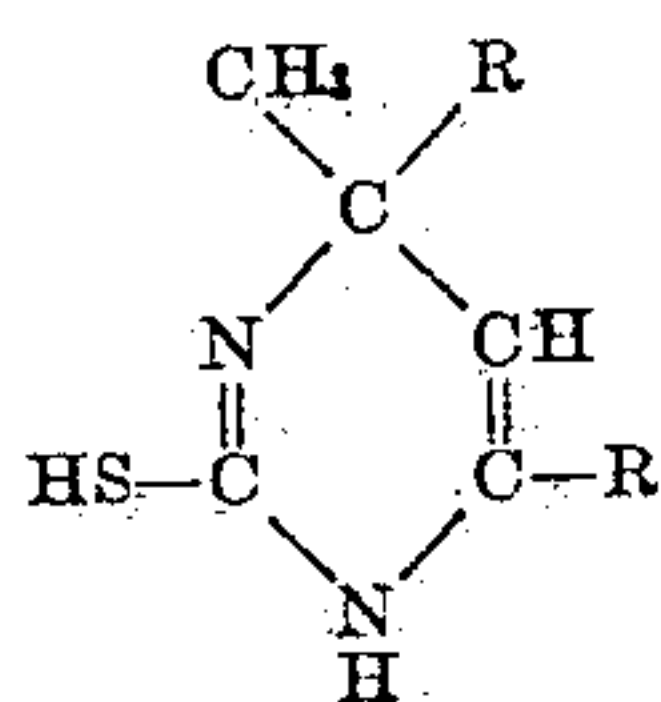
7

mercapto - 4,4,6-trimethyl-3,4-dihydropyrimidine and subjecting the pulp to froth flotation.

5. The method of claim 4 in which the mineral is selected from the class consisting of sulphide copper-iron ores and sulphide zinc-iron ores.

6. In a method for selectively floating copper sulphide in a sulphide copper-iron ore the steps of preparing a mineral pulp of the ore, incorporating therein 2 mercapto-4,4,6-trimethyl-3,4-dihydropyrimidine and subjecting the pulp to froth flotation.

7. In a method for separating lead, zinc and iron sulphides in sulphide lead-zinc-iron ores by means of froth flotation comprising the steps of selectively floating lead sulphide leaving a lead tails containing the bulk of the zinc and iron sulphides, and selectively floating zinc sulphide by subjecting said lead tails to froth flotation the improvement which comprises effecting said froth flotation of said lead tails in the presence of a thiopyrimidine of the formula:



in which the R's are the same radical selected from a class consisting of methyl and ethyl radicals.

8. In a method for separating lead, zinc and iron sulphides in sulphide lead-zinc-iron ores by means of froth flotation comprising the steps of selectively floating lead sulphide leaving a lead tails containing the bulk of the zinc and iron sulphides, and selectively floating zinc sulphide by subjecting said lead tails to froth flotation the improvement which comprises effecting said froth flotation of said lead tails in the presence of 2-mercapto-4,4,6-trimethyl-3,4-dihydropyrimidine.

9. In a process for recovering zinc sulfide by froth flotation the step of preparing a mineral

8

pulp containing the zinc sulfide, incorporating therein as a collector for said zinc sulfide a 2-mercapto - 4 - methyl-4,6-dialkyl-3,4-dihydropyrimidine in which the alkyls are the same radicals selected from the class consisting of methyl and ethyl radicals and subjecting the pulp to froth flotation.

10. In a process for recovering zinc sulfide by froth flotation the step of preparing a mineral pulp containing the zinc sulfide, incorporating therein as a collector for said zinc sulfide a 2-mercapto - 4,4,6 - trimethyl - 3,4-dihydropyrimidine and subjecting the pulp to froth flotation.

WILLIAM H. HILL.

#### REFERENCES CITED

The following references are of record in the file of this patent:

#### UNITED STATES PATENTS

Number	Name	Date
1,364,307	Perkins	Jan. 4, 1921
1,364,308	Perkins	Jan. 4, 1921
1,364,859	Perkins	Jan. 4, 1921
1,610,217	Elley	Dec. 7, 1926
1,652,060	Smith	Dec. 6, 1927
1,801,317	Moses	Apr. 21, 1931
1,801,318	Moses	Apr. 21, 1931
1,801,319	Moses	Apr. 21, 1931
1,801,320	Moses	Apr. 21, 1931
1,933,962	Bogemann	Nov. 7, 1933
2,126,269	Messer	Aug. 9, 1938
2,234,848	Horst	Mar. 11, 1941

#### OTHER REFERENCES

Giudice, Collection in Flotation, Engineering and Mining Journal, May 1934, pages 213, to 215.

Guitzeit Technical Paper No. 2077 in Mining Technology, 1946, pages 2, 3, 15.

Perry, Chemical Engineer's Handbook, second edition, © 1941, by McGraw-Hill Book Co., page 1736.

Geiser: Technical paper 401, American Inst. of Mining and Met. Engineering, pages 1 to 9.