Patented Nov. 21, 1939 2,180,926

UNITED STATES PATENT OFFICE

2,180,926

SUBSTITUTED BIGUANIDES AS FLOTATION REAGENTS

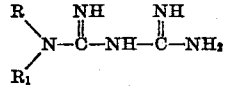
David Walker Jayne, Jr., Old Greenwich, and Arvid Emil Anderson, New Canaan, Conn., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application November 19, 1938, Serial No. 241,394

6 Claims. (Cl. 209—166)

This invention relates to the froth flotation of metallic minerals, and particularly to the froth flotation of minerals containing copper.

We have found that substituted biguanides, their salts and their aldehyde condensation products have a specific flotation promoter action, particularly on copper minerals, when used in an alkaline circuit. The cheapest types of biguanides are those having the following formula:



in which R and R_1 are either hydrogen, an alkyl radical or an aryl radical. These materials are very effective and constitute the preferred embodiment of the invention.

In the past, flotation of copper present in a mixed ore containing, for example, lead and zinc minerals, has been effected by floating off the copper and lead in the presence of a depressant for zinc, such as sodium cyanide, and then separating copper from lead. This procedure is often unsatisfactory because it is difficult to get sufficient depression of the undesired constituents of an ore without affecting the copper recovery. The use of the biguanides of the present invention, however, produces excellent recoveries of high grade copper minerals without any appreciable flotation of the undesired constituents although no depressants are added.

No selective flotation of copper minerals occurs when the standard potassium or sodium ethyl xanthate reagents are used as promoters, and it is believed that the surprising result obtained with the compounds of the present invention is due to the formation of water-insoluble copper salts which are readily floatable. This has not been definitely determined, however, and it should be understood that the invention is in no sense limited to any particular theory of action.

The mono-aryl substituted biguanides such as phenyl biguanide, tolyl biguanide, xylyl biguanide, cymyl biguanide, naphthyl biguanide, and the like, or the aldehyde condensation products thereof such as ethylidene o-tolyl biguanide, furfurylidene (mixed) xylyl biguanide, and the like, are the preferred modifications of the present invention, but other compounds such as ethyl, isopropyl, butyl, etc., biguanides, diphenyl biguanide, phenyl tolyl biguanide, diethyl biguanide, diisopropyl biguanide, phenyl ethyl biguanide, phenyl isopropyl biguanide, and the like, and their condensation products with acetaldehyde, furfuraldehyde, benzaldehyde, etc., may also be used and are included within the scope of the invention.

We have found a progressive increase in copper recovery as alkyl loading on the phenyl group is increased up to at least four carbon atoms in the side chains, i. e., cymyl biguanide, but the higher cost of the cymyl derivatives renders their use uneconomic and the cheaper phenyl and tolyl derivatives are preferred. The simple aldehyde derivatives of the preferred mono-aryl substituted biguanides are more effective than the biguanides from which they are derived, the ethylidene derivatives in turn being more efficient than the methylene derivatives, and they are cheap enough to be practicable. The invention is, however, not limited to these preferred embodiments.

Good copper recoveries are obtained if the reagents of the present invention are used in a circuit having a pH of about 9.5, but the best results are obtained at a pH of about 11–12.

It is an important advantage of the present invention that it can be applied to a flotation process without necessitating any changes in the flow sheet of the mill. Thus, for example, it makes no difference whether the reagent is added in the grinding circuit or in the flotation machine and the advantages of the present invention may be enjoyed by merely substituting the biguanides for whatever flotation agent was formerly used. It is also possible to use ordinary frothing agents since the products of the present invention do not in any way affect their action.

While we have been referring to the use of the free substituted biguanide bases for the flotation of copper minerals, acid salts of these bases, such as the monohydrochloride, can also be used and are included in the present invention. Whether the substituted biguanide is employed in the form of the free base or acid salt makes no difference since the circuit is sufficiently alkaline to convert the salt to the free base immediately upon addition thereto.

The invention will be described in greater detail in conjunction with the following specific examples which illustrate the application of the invention to certain typical ores.

Example 1

Five —20 mesh samples, weighing 600 grams each, of a copper ore containing chalcocite, bornite, enargite and pyrite as the principal sulfide minerals and assaying 2.71% copper, 9.08% iron,

11.04% sulfur and 73.72% insoluble, were ground in a steel rod mill so that substantially all of the ore would pass through a 65 mesh sieve, the resulting pulp containing 76.31% of −200 mesh product. The pulp was then transferred to a Fagergren flotation machine; a promoter and frother were added, and the material was floated. The results of comparative flotation tests, wherein the only variable was the type of promoter added, are given in the following Table I.

TABLE I

Metallurgical results

Promoter used	Heads	Concentrate		Tailing	
	Cu, percent	Assay Cu, percent	Rec., percent	Assay Cu, percent	Dist. Cu, percent
Sodium ethyl xanthate	2.68	33.90	86.81	0.38	13.19
Mixed xylyl biguanide hydrochloride	2.68	24.80	82.33	0.52	17.67
2-cymyl biguanide hydrochloride	2.64	23.00	92.20	0.23	7.80
Ethylidene o-tolyl biguanide hydrochloride	2.68	28.16	87.32	0.37	12.68
Ethylidene (mixed) xylyl biguanide hydrochloride	2.72	25.30	96.04	0.12	3.96

Example 2

Comparative flotation tests similar to those of Example 1 were made on a sulfide lead ore containing galena and assaying 8.54% lead, 3.10% iron, 1.86% sulfur and 10.22% insoluble. When 0.02 lb./ton of the standard potassium ethyl xanthate was used as the promoter, an 80% lead recovery was obtained in a concentrate which assayed 73% lead while 0.068 lb./ton of ethylidene o-tolyl biguanide hydrochloride as the promoter gave 16% lead recovery in a concentrate which assayed 43.3% lead.

Thus, it can be seen that the reagents of the present invention do not, in general, promote the flotation of metallic minerals other than copper minerals, or those activated with copper.

Example 3

Three −20 mesh samples, each weighing 600 grams, of a copper-gold ore containing chalcopyrite, pyrite, bornite, chalcocite, covellite, bournonite, limonite, quartz and free gold, and assaying 0.02% lead, 0.12% zinc, 2.51% copper, 20.85% iron, 2.20 ozs. gold per ton, 0.20 oz. silver per ton, and 53.6% insoluble, were ground in a steel rod mill, transferred to a Fagergren flotation machine and diluted to flotation density. The results of comparative flotation tests are given in the following Table II, the biguanide reagents being added in the grinding circuit and the fifty-fifty mixture of sodium diethyl and disecondary butyl dithiophosphates in the flotation machine. Other conditions are constant in the three tests.

TABLE II

Metallurgical results

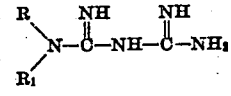
Promoter used	Heads		Concentrate						Tailing, assays	
	Cu, percent	Au, oz./ton	Weight		Gold		Copper		Au, oz./ton	Cu, percent
			Grams	Percent	Assay, oz./ton	Rec., percent	Assay, percent	Rec., percent		
50:50-mixture of sodium diethyl and disecondary butyl dithiophosphates	2.48	2.20	121.5	20.03	8.86	80.72	11.81	95.48	0.53	0.14
Ethylidene o-tolyl biguanide	2.51	2.25	65.1	10.76	8.84	42.36	13.48	79.35	1.45	0.58
Ethylidene mixed xylyl biguanide	2.54	2.36	147.8	24.50	5.97	61.95	9.88	95.25	1.19	0.16

The above results show that the ethylidene mixed xylyl biguanide and ethylidene o-tolyl biguanide give more selective flotation of copper in a gold-copper ore than the dithiophosphate reagent. The fifty-fifty mixture of sodium diethyl and disecondary butyl dithiophosphates, however, is a more powerful promoter for gold than either of the reagents covered by the present invention. This permits a more effective separation of copper from gold. Since copper compounds are well known cyanicides, the present invention permits important savings in cyanide where gold-copper ores are treated by a combined flotation and cyanide process. In such cases, the value of the present invention does not lie in the recovery of copper; on the contrary, in many low grade gold-copper ores, the copper is more an undesired impurity than a real metallic value. The economics of treating many such ores depend on the amount of cyanide which must be used as in such cases, cyanide constitutes one of the major costs. The present invention removes a large portion of the undesired copper impurity without serious gold losses and permits the economic treatment by a combined flotation and cyanidation process of low grade ores which otherwise could not be profitably mined and refined.

When copper-containing precious metal ores which are relatively rich in silver are treated by the process described in Example 3, similar results are obtained, the substituted biguanides showing the same selective action in the case of ores containing silver as they do with ores containing gold. The economic importance in the case of silver ores is not usually as great as with low grade gold ores, but the savings are nevertheless material and the present invention can be effectively used in treating copper-containing silver ores or silver and gold ores.

What we claim is:

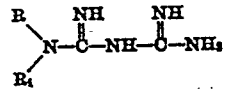
1. A method of froth flotation which comprises subjecting an aqueous pulp of a metalliferous mineral to froth flotation in the presence of a reagent included in the group consisting of substituted biguanides having the following formula:



in which R and R_1 are members of the group including hydrogen, alkyl radicals and aryl radicals, their acid salts, and their aldehyde condensation products.

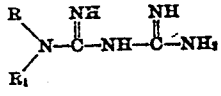
2. A method of froth flotation which comprises subjecting an aqueous pulp of an ore containing copper to froth flotation in the presence of a

reagent included in the group consisting of substituted biguanides having the following formula:



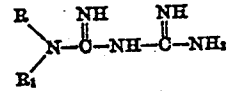
in which R and R_1 are members of the group including hydrogen, alkyl radicals and aryl radicals, their acid salts, and their aldehyde condensation products, removing therefrom the concentrate rich in copper and rejecting the tailing poor in copper.

3. A method of differential froth flotation which comprises subjecting an aqueous pulp of an ore containing copper and other metallic minerals to froth flotation in the presence of a reagent included in the group consisting of substituted biguanides having the following formula:



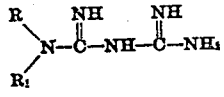
in which R and R_1 are members of the group including hydrogen, alkyl radicals and aryl radicals, their acid salts, and their aldehyde condensation products, removing therefrom the concentrate rich in copper and rejecting the tailing poor in copper and rich in the other minerals.

4. A method of differential froth flotation which comprises subjecting an aqueous pulp of an ore containing copper, lead and zinc to froth flotation in the presence of a reagent included in the group consisting of substituted biguanides having the following formula:



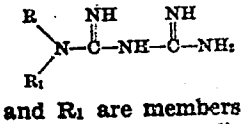
in which R and R_1 are members of the group including hydrogen, alkyl radicals and aryl radicals, their acid salts, and their aldehyde condensation products, removing therefrom the concentrate rich in copper and rejecting the tailing poor in copper and rich in zinc and lead.

5. A method of froth flotation according to claim 3 in which the reagent used is an aldehyde condensation product of a substituted biguanide having the following general formula:



in which R and R_1 are members of the group including hydrogen, alkyl radicals and aryl radicals.

6. A method of froth flotation according to claim 3 in which the reagent used is an aldehyde condensation product of a substituted biguanide having the following general formula:



in which R and R_1 are members of the group including hydrogen, alkyl radicals and aryl radicals.

DAVID WALKER JAYNE, JR.
ARVID EMIL ANDERSON.

CERTIFICATE OF CORRECTION.

Patent No. 2,180,926. November 21, 1939.

DAVID WALKER JAYNE, JR., ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 14, claim 5, for the claim reference numeral "3" read 1; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 16th day of January, A. D. 1940.

Henry Van Arsdale,

(Seal) Acting Commissioner of Patents.