

[54] **FROTHERS FOR THE FLOTATION OF SULFIDIC ORES**

[75] Inventors: **Elmer C. Tveter, deceased**, late of Walnut Creek, Calif. by Cora Belvin Judd Tveter, executrix; **Guy H. Harris**, Concord, Calif.; **Lowell B. Lindy**, Midland, Mich.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[22] Filed: **Dec. 7, 1972**

[21] Appl. No.: **313,155**

[52] **U.S. Cl.** **209/166**

[51] **Int. Cl.** **B03d 1/02**

[58] **Field of Search** 209/166, 167; 252/61

[56] **References Cited**

UNITED STATES PATENTS

2,065,053	12/1936	Christmann.....	209/166
2,302,338	11/1942	Moellen	209/166
2,335,485	11/1943	Christmann.....	209/166
2,797,808	7/1957	Tueten	209/166

3,595,390 7/1971 Booth 209/166

FOREIGN PATENTS OR APPLICATIONS

542,966	7/1957	Canada	252/61
1,001,652	1/1957	Germany	209/166
1,004,442	9/1959	Germany	209/166

OTHER PUBLICATIONS

Chem. Abst., 1966, Vol. 65, 18218d.
Chem. Abst., 1969, Vol. 70, 98894n.

Primary Examiner—Robert Halper
Attorney, Agent, or Firm—J. R. Lockhead

[57] **ABSTRACT**

A process involving the use of a new and improved class of frothing agents in the froth flotation of ores such as the sulfide ores of copper, molybdenum, lead, nickel and zinc, as well as for separating coal fines by flotation. The class comprises the non-hydroxylated ether derivatives of dialkylene glycols such as ethylene glycol and propylene glycol. Especially good results are obtained when these frothers are employed in the treatment of complex copper-molybdenum ores.

6 Claims, No Drawings

FROTHERS FOR THE FLOTATION OF SULFIDIC ORES

BACKGROUND OF THE INVENTION

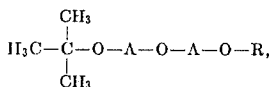
Heretofore, a large number of different compounds have been employed as frothing agents. Alcohols such as methyl isobutyl carbinol and pine oil received early use in this area. Non-hydroxylated compounds have also been employed: for example, U.S. Pat. Nos. 2,591,289, 2,687,214 and 2,982,787 illustrate the use of compounds containing ether linkages.

It is also known that reaction products of alcohols with one or more moles of alkylene oxide can be employed as frothing agents. For example, in U.S. Pat. No. 2,611,485, Tveter describes the use of monoethers of propylene glycol and of polypropylene glycols as frothers. In U.S. Pat. No. 2,950,818, Moeller teaches the use of monoethers of ethylene glycol and polyethylene glycols as frothers.

DESCRIPTION OF THE INVENTION

The invention comprises subjecting an aqueous pulp of an ore containing copper, molybdenum, lead, nickel, zinc, and the like to froth flotation in the presence of a collector and a particular organic frothing agent. The invention further comprises removing coal fines by the froth flotation of same utilizing the frothers taught herein.

The organic frothing agents utilized herein correspond to the formula



wherein each A is an alkylene group having 2 or 3 carbon atoms, and R is methyl, ethyl, n-propyl, i-propyl, i-butyl or t-butyl.

Examples of frothing agents useful alone or in admixture include diethylene glycol methyl, t-butyl ether; dipropylene glycol ethyl, t-butyl ether; diethylene glycol n-propyl, t-butyl ether; dipropylene glycol di-t-butyl ether; and dipropylene glycol i-butyl, t-butyl ether.

Frothing agents of the invention may be employed as pure compounds or, instead of using the purified compounds, reaction mixtures obtained by the usual methods of making the compounds, or mixed fractions thereof, may also be used. The frothers of the invention can also be employed in conjunction with additives such as fuel oil or other frothing agents.

Frothers employed in the invention are prepared by known methods. One such method is a multi-step process which involves reacting 1 or 2 moles of ethylene or propylene oxide with an alcohol having 1 to 4 carbon atoms or a mixture of such alcohols. A specific example of such a reaction is described in U.S. Pat. No. 2,611,485 incorporated herein by reference. The resulting hydroxy ether is "capped" by reacting the hydroxyl group to form an ether, as, for example, by reacting the hydroxy ether with isobutylene using macroreticular ion exchange beads as a catalyst (see U.S. Pat. No. 3,037,052).

In using the frothing agents, the amount employed is from about 0.001 to about 1.00 pound per ton of ore, and preferably is from about 0.01 to 0.20 pound per

ton of ore. The ore is ground to a particle size suitable for flotation. Flotation is carried out at a pulp density of from about 15 to about 40 percent solids. Acidity in the pulp is controlled to provide a pH range of from about 7 to about 12.

The frothers are employed with any of the standard collectors such as xanthates (e.g., ethyl xanthate), dithiophosphates, phosphocresylic acids, or diphenyl thiourea. The frothers are especially suitable for use with collectors such as those described in U.S. Pat. Nos. 3,590,997, 3,590,998 and 3,590,999.

The frothing agents of the invention are applicable to sulfidic ores, primarily ores of such metals as lead, zinc, copper, molybdenum, nickel, cobalt, or antimony, which are often associated with other elements such as silver, mercury, gold, cadmium or arsenic. The frothers find particularly useful application in the beneficiation of complex molybdenum-copper ores containing on the order of about 0.2 to about 1.5 weight percent of copper and about 0.01 to about 0.1 weight percent of molybdenum. Such ores are found in the southwestern United States (Arizona, Utah, Nevada), Western Canada (British Columbia) and in western South America (Peru, Chile). They may also find utility with copper-cobalt ores, such as are formed in southern Africa. In addition, they are useful in the froth flotation of coal fines.

The frothers disclosed herein are effective producers of a strong froth possessing the physical properties required for supporting mineral particles and permitting a relatively clean separation from gangue. As compared with chemically similar standard frothers such as hydroxylated mono ethers of alkylene glycols (e.g., mono and poly propylene glycol mono ethers), the new agents are capable of producing an equivalent froth with a materially smaller quantity of frothing agent, hence are markedly superior in specific frothing power. In the case of many ores (e.g., complex Mo-Cu sulfidic) they show a greater selectivity, producing a richer concentrate with a lower content of acid-insoluble gangue materials. The frothers are not effective as mineral collectors but function solely as frothing agents. The art has long recognized, however, that it is disadvantageous for frothing agents to possess good collecting properties, as better selectivity is found when the two functions are separately performed by appropriate agents.

The following example illustrates the improved results obtainable by use of the invention.

EXAMPLE 1

A series of tests was made with a copper-molybdenum ore assaying 0.68 percent copper and 0.034 percent molybdenum. The particle size of the ore was minus 20 mesh. Five hundred gram samples of the ore were ground in a ball mill with 300 ml. of water and with lime in proportion of 1.5 pounds per ton of ore to prepare a pulp in which 47 percent of the solids passed a 325 mesh screen. The pulp was conditioned in a flotation cell with a collector in the amount of 0.021 pound/ton of ore, and with the amount of frothing agent shown in the following table, after which the concentrate was removed in 6 minutes of frothing. The collector was a xanthate-derived compound corresponding generally to the formula

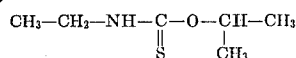


Table I shows the analysis of the concentrate and percentage recovery of copper and molybdenum. As a comparison, tests were carried out using standard frothing agents. These agents were the diacetate ester of ethylene glycol and also a mixture of polypropylene glycol monomethyl ethers available commercially as Dowfroth 250 (a product of The Dow Chemical Company).

The amounts of frother used in the tests were those required to produce approximately the same volume of

passes a 200 mesh screen. The pulp was conditioned for 1 minute in a flotation cell with the amount of frother shown in Table II, after which the concentrate was removed in 3 minutes of frothing. In each case duplicate tests were conducted, the arithmetic average values for the analysis of the concentrates and the percentages of recovery of copper and molybdenum being reported. As a comparison, methyl isobutyl carbinol (M.I.B.C.), which is customarily used in this process, and Dowfroth 250 were also tested as standards.

TABLE I

Run	Frother	Lbs. of Frother/Ton of Ore	Concentrate Analysis (Wt. %)		% Recovery	
			Cu %	Mo %	Cu	Mo
1	Diacetate ester of ethylene glycol	0.202	9.1	0.251	85.7	50.8
2	Dowfroth 250	0.120	11.7	0.499	86.0	56.4
3	Diethylene glycol methyl, t-butyl ether	0.090	8.1	0.335	88.4	65.5

TABLE II

Run	Frother	Lbs. of Frother/Ton of Ore	Concentrate Analysis (Wt. %)		% Recovery	
			Cu %	Mo %	Cu	Mo
4.	MIBC	.078	25.35	0.68	65.1	46.2
5.	do.	.109	26.00	0.62	67.7	42.1
6.	do.	.140	22.10	0.64	74.6	55.1
7.	Dowfroth 250	.094	25.10	0.66	70.1	48.9
8.	do.	.125	22.00	0.84	79.1	77.0
9.	Diethylene glycol methyl, t-butyl ether	.084	20.60	0.71	83.4	71.6
10.	do.	.180	20.20	0.74	83.2	76.1

froth. From the results depicted in Table I, it can be seen in comparison with standard frothers that use of an exemplary frother of the invention resulted in increased copper and molybdenum recovery even though smaller amounts of said agent were employed.

EXAMPLE 2

An additional series of tests was made with a copper-molybdenum ore similar to that of Example 1 and assaying 0.77 percent copper and 0.030 percent molybdenum. Five hundred gram samples of this ore were ground with 275 ml. of water, with lime in proportion to 0.4 pound per ton of ore, and with isopropyl ethyl thionocarbamate in proportion of 0.064 pound per ton of ore to prepare a pulp in which 5 percent of the solids were retained on a 100 mesh screen and 50 percent

EXAMPLE 3

In another series of tests, an ore containing 0.33 percent of copper and 0.22 percent of molybdenum was subjected to a procedure similar to the above. Twelve hundred fifty gram samples of the ore were ground in a ball mill with water to give a slurry containing 60 percent solids and with lime added in proportion to 4.8 pounds per ton of ore, stove oil equivalent to 0.040 pound per ton of ore and allyl amyl xanthate equivalent to 0.012 pound per ton of ore, to prepare a pulp in which 75 percent of the solids passed a 100 mesh screen. The pulp was conditioned in a flotation cell with the amount of frothing agent shown in Table III, after which the concentrate was removed in 2 minutes of frothing. At this point an amount of potassium amyl

TABLE III

Run	Frother	Lbs. of Frother/Ton of Ore	Concentrate Analysis (Wt. %)		% Recovery	
			Cu %	Mo %	Cu	Mo
11.	MIBC	.089	5.58	0.421	90.25	86.21
12.	Diethylene glycol methyl, t-butyl ether	.033	4.14	0.190	90.35	81.55

xanthate equivalent to 0.005 pound per ton of ore was added and concentrate was removed during an additional 3 minutes of frothing. Table III shows the analysis of the concentrate and the percentage of recovery of the copper and molybdenum.

EXAMPLE 4

The procedure of Example 2 was repeated on a new ore sample from the same location. This sample analyzed 0.68 percent copper and 0.015 percent molybdenum. Again duplicate tests were made and Table IV shows the arithmetic average results for concentrate analysis and metal recoveries.

TABLE IV

Run	Frother	Lbs. of Frother/Ton of Ore	Concentrate Analysis (Wt. %)		% Recovery	
			Cu	Mo	Cu	Mo
			%	%		
13.	MIBC	0.156	23.6	.322	55.7	34.0
14.	do.	0.125	24.6	.370	50.7	34.5
15.	Dowfroth 250	0.150	21.8	.571	69.8	85.8
16.	Diethylene glycol methyl, t-butyl ether	0.096	23.6	.422	55.9	47.1
		0.120	22.7	.453	64.9	59.7

screen and 60 percent of the solids passing a 200 mesh screen. The pulp was conditioned for 1 minute with the frother in amount shown in the Table following, and concentrate was removed in 5 minutes of frothing. In this series, a mixture of a frother containing chiefly C₇ and C₈ primary alcohol (Aerofroth 71, a product of American Cyanamid Co.) was blended with MIBC in a ratio of 3:1, was tested as a comparison, this blend being the customary practice used in treating this ore. In each case duplicate tests were made with each frothing agent and the results tabulated are the arithmetic averages.

TABLE V

Run	Frother	Lbs. of Frother/Ton Of Ore	Concentrate Analysis (Wt. %)		% Recovery	
			Cu	Mo	Cu	Mo
			%	%		
17.	3:1 Aerofroth 71/MIBC	.072	10.3	0.96	81.3	89.2
18.	Diethylene glycol methyl, t-butyl ether	.072	9.4	0.88	83.4	90.1

EXAMPLE 5

In this series of tests, an ore containing 0.55 percent copper and 0.047 percent molybdenum was ground in like manner with lime equivalent to 6.0 pounds per ton, stove oil equivalent, to 0.039 pound per ton and isopropyl 2-methylthio ethyl thionocarbamate equivalent to 0.034 pound per ton of ore to prepare a pulp with 10 percent of the solids being retained on a 100 mesh

EXAMPLE 6

Additional tests were made with a different ore sample but one from the same source as Example 5. The procedure was as that of Example 5 with the exception that the isopropyl 2-methylthio ethyl thionocarbamate collector was replaced as indicated in Tables VI A and VI B following. Again, duplicate tests were averaged. A. Using the equivalent of 0.0108 pound per ton of ethyl thionocarbamate plus 0.0108 pound per ton of ally amyl xanthate as the collector added in the grinding step.

TABLE VI A

Run	Frother	Lbs. of Frother/Ton Of Ore	Concentrate Analysis (Wt. %)		% Recovery	
			Cu	Mo	Cu	Mo
			%	%		
19.	3:1 Aerofroth 71/MIBC	.240	13.42	1.34	37.95	74.50
20.	Diethylene glycol methyl, t-butyl ether	.240	12.00	0.91	63.35	86.85

B. Using the equivalent of 0.0216 pound per ton of isopropyl 2-ethoxyethylthionocarbamate as the collector added in the grinding step.

fractions. The coal generally floats naturally, although occasionally fuel oil or kerosene is added to render the coal more hydrophobic. Frothing agents such as MIBC

TABLE VI B

Run	Frother	Lbs. of Frother/Ton of Ore	Concentrate Analysis (Wt. %)		% Recovery	
			Cu %	Mo %	Cu	Mo
21.	3:1 Aerofroth 71/ MIBC	.240	12.04	1.10	46.20	71.30
22.	Diethylene glycol	.240	11.06	0.72	69.00	86.80

EXAMPLE 7

In a manner similar to the procedure of the previous Examples, an ore containing 3.83 percent total copper of which 0.74 percent was as acid soluble copper, plus 0.227 percent of cobalt, 500 gram samples of this ore were ground with 300 ml. of water, lime equivalent to 0.2 lb. per ton of ore and isopropyl 2-ethoxyethylthionocarbamate equivalent to 0.06 lb./ton of ore to prepare a pulp in which 22 percent of the solids were retained on a 200 mesh screen. This pulp was transferred to a flotation cell and conditioned 1 minute with the amount of frother shown in the Table. Concentrate was collected during 4 minutes of frothing. For comparison tests were made with 1,1,3-triethoxybutane, known as Powell Accelerator (National Chemical Products), the frother customarily used in treating this ore. The results of duplicate tests arithmetically averaged are presented in the following Table.

TABLE VII

Run	Frother	Lbs. of Frother/Ton of Ore	Concentrate Analysis (Wt. %)		% Recovery	
			Cu %	Mo %	Cu	Mo
23.	1,1,3-triethoxy- butane	0.184	40.9	1.37	70.0	39.7
24.	Diethylene glycol methyl, t-butyl ether	0.120	37.1	1.32	76.4	45.5

EXAMPLE 8

Crude coal is generally treated in a preparation plant to reduce the ash content resulting from continuous mining procedures. The process involves washing, screening and gravity separation of the coarse (+600 micron) fractions and froth flotation of the fine coal

and pine oil are used to produce the froth. In order to demonstrate the ability of the frothers of the instant invention to froth and float coal fines, diethylene glycol methyl, t-butyl ether and MIBC were added to "oxidized" coal in roughly equivalent doses and flotation was carried out until all the coal fractions appeared to have floated. In the case of the former, this consumed 5-10 minutes, whereas with MIBC 20-30 minutes were required, demonstrating the superior ability of the frother of the instant invention in separating coal fines.

EXAMPLE 9

In order to illustrate the frothing ability of a representative group of the frothers disclosed herein, tests were made on a copper-containing ore from Arizona, the ore assaying 1.06 percent Cu. As in Example 2, 500 gram samples were ground with 300 ml. of water, with lime in proportion to 0.2 pound per ton of ore, and with iso-

propyl ethyl thionocarbamate in proportion of 0.032 pound per ton to prepare a pulp in which 7 percent of the solids were retained on a 65 mesh screen. The pulp was conditioned for 2 minutes in a flotation cell with the amount of frother shown in Table VIII, after which the concentrate was removed in 5 minutes of frothing. The calculations were the same as in Example 2.

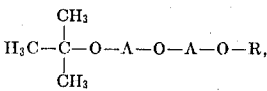
TABLE VIII

Run	Frother	Lbs. of Frother/ Ton of Ore	% Cu Recovered
25.	MIBC	.181	59.35
26.		.226	60.26
27.	Diethylene glycol methyl,	.207	66.19
28.	t-butyl ether	.259	67.17
29.	Dipropylene glycol methyl,	.121	60.11
30.	t-butyl ether	.181	63.45
31.	Diethylene glycol	.125	62.43
32.	ethyl, t-butyl ether	.175	61.84
33.	Dipropylene glycol	.100	55.44
34.	di-t-butyl ether	.200	64.15
35.	Diethylene glycol	.133	63.95
36.	di-t-butyl ether	.182	65.54

We claim:

1. The method which comprises subjecting an aqueous pulp of a sulfidic ore of one or more of the metals lead, zinc, copper, molybdenum, nickel, cobalt, antimony, silver, mercury, gold, cadmium and arsenic to froth flotation in the presence of a collector and one or

more organic frothing agents corresponding to the formula



wherein each A is an alkylene group having 2 or 3 carbon atoms, and R is methyl, ethyl, n-propyl, i-propyl, i-butyl or t-butyl.

2. The method of claim 1 wherein, in the formula, R is t-butyl.

3. The method of claim 1 wherein, in the formula, R is methyl.

4. The method of claim 1 wherein the frothing agent is diethylene glycol methyl, t-butyl ether.

5. The method of claim 1 wherein the frothing agent is diethylene glycol di-t-butyl ether.

6. The method of claim 1 wherein the frothing agent is diethylene glycol ethyl, t-butyl ether.

* * * * *