# United States Patent [19]

# Werneke

### [54] FLOTATION PROCESS FOR RECOVERING MOLYBDENUM

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- [51]
   Int. Cl.
   B03d 1/06

   [58]
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- 1 1 203/100, 107
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# [45] Jan. 29, 1974

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## [57] ABSTRACT

A process for recovering molybdenite from a metallurgical concentrate comprising a major proportion of copper sulfide and other sulfides and a minor portion of molybdenum sulfide is provided, in which the copper and other sulfides are selectively depressed by employing a xanthate thereby enabling the molybdenite to be recovered by flotation.

#### **3** Claims, No Drawings

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#### FLOTATION PROCESS FOR RECOVERING **MOLYBDENUM**

Generally stated, the subject matter of the present invention relates to an improved flotation process for 5 recovering molybdenite. More particularly, this invention relates to a process wherein molybdenum sulfide is separated from other sulfides with which it occurs by use of a novel selective depressant.

#### BACKGROUND OF THE INVENTION

In the treatment of copper sulfide ores containing minor quantities of molybdenite  $(MoS_2)_1$  the molybdenite normally accompanies the copper sulfide in the metallurgical concentrates obtained by flotation treat- 15 ment of the raw ores. It is then necessary to separate molybdenite from the copper sulfide and any other sulfides, notably iron sulfide, in the concentrates thus obtained.

Normally, any one of three approaches may be used 20 to separate molybdenite from other sulfides. In a first approach, molybdenite can be depressed by suitable reagents and the copper recovered by reflotation. A heat treatment step involving low temperature roasting of the molybdenite bearing flotation tailings is required 25 in order to reactivate the molybdenite for upgrading by reflotation in several stages. This approach is not particularly desirable because it requires floating the major portion (usually more than 99 percent) of the metallurgical concentrate initially obtained and re- 30 quires costly heat treatment as an added step.

A second approach involves depressing copper minerals by means of steaming or low temperature roasting to remove the original copper mineral collectors, followed by flotation of molybdenite from the heat treated 35concentrate with or without the use of auxiliary copper depressants. This approach is not particularly desirable because of the added costly heat treatment steps required.

A third approach is that of depressing copper sulfide with selective reagents and recovering molybdenite by selective flotation and repeated cleaning, as necessary. This approach is highly desirable since it requires floating only a small fraction of the total weight of metallurgical concentrate (usually less than 1 percent) and it does not require the added costly, heat treating steps. The major problem associated with this third approach is providing selective and effective depressants for sulfides other than molybdenite.

In the past, a selective depressant employed was the <sup>50</sup> material obtained by reaction of sodium hydroxide with phosphorus pentasulfide commonly referred to as Noke's reagent. This reaction may erupt with great violence liberating substantial amounts of hydrogen sul-55 fide, a hazardous and toxic pollutant. The reaction is spasmodic in character, giving rise to violent bursts of activity and gas liberation at unpredictable intervals. The unpredictable nature of the reaction recently was responsible for the deaths of several workers. Thus, al-60 though this third approach as a method of recovering molybdenite from other sulfides is highly desirable from a processing viewpoint, the lack of safe and effective depressants necessitates the use of alternative recovery procedures. Other depressants which have been 65 used are sodium sulfide and sodium cyanide among others. However, the sodium sulfide requires the use of large quantities, as well as constituting a safety hazard

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in that it will liberate hydrogen sulfide under certain conditions. The sodium cyanide also presents a potential safety hazard because of the inherent nature of cyanide compounds.

The present invention represents the culmination of a long series of investigations directed to providing a safe and effective process for recovering molybdenite from the metallurgical concentrates obtained by the flotation treatment of raw copper sulfide ores.

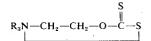
Accordingly, it is an object of the invention to provide a process for recovering molybdenite from the metallurgical concentrates in which it occurs.

An additional object of the invention is to provide a safe and effective process for recovering molybdenite. It is yet another object of the invention to provide a relatively cheap process for recovering molybdenite.

Additional objects and advantages will be set forth in part in the description which follows and in part will be obvious from the description or maybe learned by the practice of the invention, the objects and advantages being realized and attained by means of the processes and improvements, particularly pointed out in the appended claims.

#### THE INVENTION

To achieve the foregoing objects and in accordance with its purposes as embodied and broadly described, the present invention provides a process for recovering molybdenite from a metallurgical concentrate of sulfide minerals in which the molybdenite constitutes a minor amount which comprises depressing minerals other than molybdenite with from about 0.1 to 10 pounds per ton of concentrate of a xanthate having the formula



 $_{40}$  wherein R is selected from hydrogen, methyl, ethyl and mixtures thereof; selectively froth floating molybdenite from the depressed sulfides and recovering the flotation concentrate thus obtained.

Choline xanthate prepared in the following manner is preferred as a selective depressant for the sulfide 45 minerals other than molybdenite:

a. 
$$(CH_3)_3N + CH_2CH_2 + H_2O$$
  
 $O \longrightarrow (CH_3)_3N - CH_2CH_2 - OH$   
b.  $1 + CS_2$   
 $\longrightarrow (CH_3)_3NCH_2CH_2OC - S + H_2O$ 

The invention consists of the novel methods, processes, steps and improvements herein shown and described.

(1)

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory and are not restrictive of the invention.

In accordance with the present invention, the novel depressants selectively depress sulfide minerals other than molybdenite enabling much cleaner froth flotation

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concentrates to be obtained than was formerly possible. In addition, the present process avoids costly added heat treatment steps and enables the desired recovery to be effected while froth floating only a minor portion of the metallurgical concentrate initially employed. In addition, the reagents are safe to use and present no significant threat to health and the environment. Still further, the present process enables more efficient recovery of molybdenite to be achieved than was previously possible.

It is believed that the mode of action of the depressant involves ionization in water, i.e.,

$$(CH_3)_3NCH_2CH_2O - C - S \qquad 15$$

$$(CH_3)_3NCH_2CH_2O - C - S$$

$$(CH_3)_3NCH_2CH_2O - C - S$$

whereby the ionic species attaches to the mineral via its 20 xanthate group, leaving the quaternary amine group projecting into the aqueous phase, giving the mineral a hydrophilic surface. Therefore, on flotation the surface of the depressed mineral has been made hydrophilic and is rendered unfloatable. It is conceivable that the <sup>25</sup> reagents used in this invention may function generally as depressants for many sulfide minerals and could be useful, for example, for depressing pyrite in coal flotation, to give low sulfur coal, a commodity much in de-30 mand for ecological reasons. It is also possible that they may serve to depress undesirable sulfides during nonmetallic mineral flotation, for example, in the recovery of fluorspar, barite, silica, feldspar, and the like from their ores.

Applications of other materials as depressants could <sup>35</sup> include the use of hydrophilic polycarboxylic acids or sulfonates to depress minerals which are normally promoted by fatty acids or petroleum sulfonates. Hydrophilic polyamines may be used as depressants for minerals which are promoted by fatty amines. <sup>40</sup>

In carrying out the process of the present invention a copper ore in which the metal occurs as a sulfide is first processed in accordance with conventional procedures to separate the valuable minerals from the gangue materials. Generally, such separation is effected by grinding the ore to a suitable size for flotation and effecting flotation using a collector such as a xanthate, dithiophosphate, dithiocarbamate, or a derivative thereof. The concentrate thus collected is suitable for use directly in the process of the present invention. The particular method by which the metallurgical concentrate is obtained is not critical and forms no part of the present invention.

The metallurgical concentrate is prepared as a 15–40 percent aqueous slurry in a flotation cell and conditioned with from about 0.1 to about 10 pounds per ton of solids with a novel depressant of the present invention. The most effective concentration can be determined by testing. Conditioning is continued until copper sulfide is no longer floated to the surface by a stream of air. The use of a hydrocarbon oil in sufficient amount to aid in the flotation of the molybdenum sulfide to the surface where it can be collected is also possible. Hydrocarbon oils such as kerosene, fuel oil, and the like are normally used for such purpose and are effective in the present process.

The floated molybdenum sulfide concentrate is then recovered and, if necessary, subjected to cleaning. In many instances the concentrate obtained is of sufficient purity to be processed without the need for additional cleaning. When cleaning is contemplated, a reflotation of the concentrate using a novel depressant of the present invention is beneficial.

The following examples are provided for illustrative purposes and may include particular features of the invention. However, the examples should not be construed as limiting the invention, many variations of 10 which are possible without departing from the spirit or scope thereof.

#### EXAMPLE 1

A 400 gm. sample of mixed copper molybdenum sulfides containing 0.317% MoS<sub>2</sub> was conditioned in a laboratory scale flotation cell at ~18 percent solids with 1.7 lbs./ton of choline xanthate and 0.6 lbs./ton of fuel oil for 2½ minutes. The froth was collected for seven minutes. Metallurgical results were as follows:

,	Weight	Percent	Distribution
Product	Percent	MoS <sub>2</sub>	Percent MoS <sub>2</sub>
Concentrate	19.38	1.545	94.32
Tailing	80.62	0.022	5.68

#### **EXAMPLE 2**

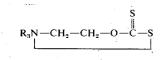
A 600 gm. sample of previously activated copper/molybdenum sulfides containing 0.555% MoS<sub>2</sub> was conditioned in a laboratory flotation cell at ~28 percent solids with 1.8 lbs./ton of choline xanthate as copper depressant and 0.5 lb./ton of fuel oil for  $2\frac{1}{2}$  minutes. The froth was collected for 7 minutes, then placed in a cleaning cell, conditioned for  $2\frac{1}{2}$  minutes with an additional 0.5 lb./ton of choline exanthate and 0.25 lb./ton of fuel oil. The froth was collected for 7 more minutes. Metallurgical results include:

		Weight	Percent	Distribution
	Product	%	MoS <sub>2</sub>	% MoS,
	Cleaner		-	· · · <b>- 1</b>
	Concentrate	31.64	1.572	89.55
	Cleaner tail	9.42	0.291	4.86
0	Rougher tail	58.93	0.053	5.59

As can be seen from both examples, the choline xanthate acts as an effective depressant for copper sulfide in the presence of molybdenum sulfide, allowing the molybdenum sulfide content to be increased, while lowering the overall copper content.

I claim:

1. A process for recovering molybdenite from a metallurgical concentrate which comprises depressing copper and iron sulfide minerals with from about 0.1 to 10 pounds per ton of concentrate solids of a xanthate having the formula:



wherein R is selected from hydrogen, methyl, ethyl and mixtures thereof; selectively froth floating molybdenite from the sulfides and recovering the flotation concentrate thus obtained.

2. A process according to claim 1 wherein the xanthate is choline xanthate.

3. A process according to claim 1 wherein a hydrocarbon oil is used to aid in the flotation and recovery of the molybdenite.

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