Patented Oct. 31, 1933

1,933,179

UNITED STATES PATENT OFFICE

1,933,179

FLOTATION PROCESS AND MINERAL COLLECTING AGENT

Rhetherford B. Martin, Roselle, N. J.

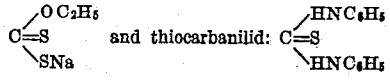
No Drawing. Application March 14, 1930
Serial No. 435,953

10 Claims. (Cl. 209—166)

This invention relates to the treatment of ores and more particularly has reference to the separation and concentration of valuable constituents from ores and like bodies containing more than one mineral by a flotation process which is facilitated by mineral collecting agents.

Heretofore, separation and concentration of valuable mineral constituents from ores by various methods have been carried out. Many of the methods heretofore employed have comprised the steps of grinding the ore to fine particles and then after dilution and modifying the ore, the mass was subjected to a flotation process in which there was employed a mineral collecting agent. After the bulk or mass had been agitated for a sufficient time, the desired mineral bearing froth was removed by any suitable means.

Some organic compounds when introduced into a flotation reaction, materially increase the efficiency thereof, resulting in a greater yield of the desired constituents under the same operating conditions or by accomplishing the same results with a smaller amount of mineral collector. Among the various substances which have been successfully used as froth flotation collectors, are thiocarbonic acid derivatives such as sodium ethyl xanthate:



and thiocarbanilid:

A major object of this invention is to devise a method of treating ores and like bodies to effect a separation and concentration of their valuable mineral constituents.

Another object of this invention is to devise a method of preparing mineral collecting agents capable of effecting a highly efficient separating and concentrating process.

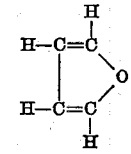
Yet another object of this invention is to provide a mineral collecting agent capable of stabilizing a mineral flotation froth.

A still further object of this invention is to prepare compounds which may be advantageously employed as mineral collecting agents.

In accordance with the present invention, an ore separation process involving flotation may be carried out, in which a suitable frothing agent or frothing aromatic substance such as cresylic acid, creosote and phenol is employed. The ore may be properly prepared by grinding, classifying, diluting, and by further conditioning, if necessary or desirable, with other modifying agents.

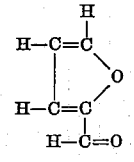
After the ore is made up into a pulp suitable for the flotation process, and at a desired time, a hetero-cyclic sulfur compound is introduced therein. This sulfur derivative of a hetero-cyclic compound differs from the well known thioureas and alkyl thiocarbonates in that it is formed from the interaction of a hetero-cyclic compound, carbon disulphide and a suitable alkali metal hydroxide, such as sodium, potassium and other hydroxides of metals having similar properties.

It is proposed in this invention to employ froth flotation collectors, compounds prepared from substances which may be said to be midway between the derivatives of methane and derivatives of benzene combined with alkalies and carbon disulphide. The particular compounds to which I have reference, are the so called hetero-cyclic compounds, and may be classified as a third great division of carbon derivatives. In this class of organic compounds, which are somewhat similar to the benzene compounds in that they contain a so called ring, these compounds differ from the benzene or homocyclic compounds in that the ring consists of unlike atoms. Among this class of compounds is a group or series known as the furfuran group. One compound in this group is furan or furfuran, which is indicated by the following structural form:



This compound in the form indicated in the above formula is of little importance, and does not readily react with carbon disulphide and an alkali hydroxide to form xanthates.

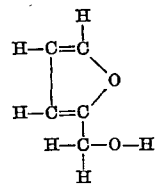
An aldehyde derivative of the above compound furfural or furfuraldehyde is generally written as follows:



This compound may be considered as a parent substance of the compounds forming the subject matter of this invention. This compound may be obtained from pentoses by the elimination of three molecules of water, which may be facilitated by the influence of a hydrolizing agent, such

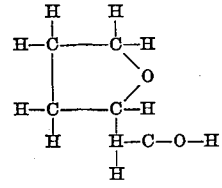
as mineral acids. Of course, other methods of preparing this compound have been developed and at present, this compound may be produced at relatively small cost.

An alcohol which may be obtained from furfuraldehyde is furfuryl alcohol, which may be represented by the following structural formula:



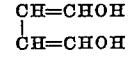
Furfuryl alcohol may be obtained from furfuraldehyde by hydrogenation of the aldehyde in the presence of nickel at approximately 190° C. This compound may be readily "thiodized" or treated to form a xanthate compound by reacting the alcohol with carbon disulphide in the presence of caustic alkali.

Another compound which may be prepared from furfuraldehyde, is tetra-hydro furfuryl alcohol. This compound may be structurally represented as follows:

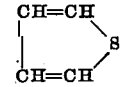


The above compound may be prepared by carrying the hydrogenation of furfuraldehyde further than in the case of the preparation of furfuryl alcohol. This alcohol reacts with carbon disulphide in the presence of caustic alkali to form xanthate compounds which form flotation collecting agents. Of the above compounds, furfuraldehyde, furfuryl alcohol and tetra-hydro furfuryl alcohol are articles of commerce, and may be obtained in the open market.

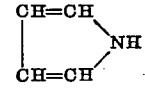
In viewing the above compounds, furfuran may be considered as the cyclic ether of an unsaturated glycol, and consequently, may be said to be a derivative of glycol. The compound represented by



is unknown, but by replacing the oxygen of furfuran with sulfur, we have thiophene, which may be indicated by the following structural formula:



By replacing the oxygen of furfuran with ammonia, pyrrol may be formed which is indicated by the following formula:

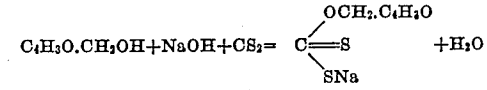


The last two substances bear a remarkable resemblance to benzene.

Alcohols, especially ethyl alcohol, react with carbon disulphide and an alkali metal hydroxide to form alkali metal xanthates. Benzene does not react with carbon disulphide and an alkali metal hydroxide to form xanthates. The reaction to form xanthates cannot be carried out with the hydroxy derivative of benzene, phenol, until it has been hydrogenated. Furfural does not react with carbon disulphide and an alkali metal hydroxide to form xanthates, but when the furfuraldehyde is hydrogenated to produce an alcohol, the alcohol resulting from the hydrogenation does react with carbon disulphide, and an alkali metal hydroxide to form the xanthates.

A xanthate compound formed from furfuryl alcohol, which has properties of a flotation collecting agent, may be prepared by subjecting furfuryl alcohol to the action of carbon disulphide and an alkali metal hydroxide. As an example, sodium furfuryl xanthate may be prepared from the interaction of furfuryl alcohol, sodium hydroxide and carbon disulphide. The compound is prepared by treating one mol. of furfuryl alcohol with one mol. of sodium hydroxide and one mol. of carbon disulphide. In carrying out the reaction, the caustic soda is dissolved in one-half its weight of water and a mixture of the furfuryl alcohol and carbon disulphide slowly added to the alkali hydroxide, while the reaction mass is constantly agitated. It has been found that proper control of the reaction may be obtained by cooling the reaction mass to 15° C. On standing, some gas was given off from the reaction. After the reaction has been completed, the mass sets to a pasty solid condition.

While results better suited for commercial practice may be obtained from other methods of preparing an alkali metal furfuryl xanthate, I have found that satisfactory results may be obtained when the reaction is carried out in accordance with the following equation:

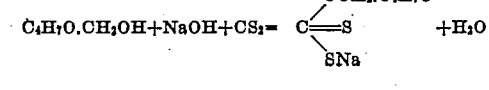


In accordance with the above formula, the reaction substances are in the following proportions:

	M. W.	Per cent
1 mol. furfuryl alcohol	98.05	45.7
1 mol. sodium hydroxide	40.01	18.7
1 mol. carbon disulphide	76.12	35.6
		100.0

A xanthate compound may be prepared from the interaction of tetra-hydro furfuryl alcohol, sodium hydroxide and carbon disulphide. As in the case of the sodium furfuryl xanthate, the sodium tetra-hydro furfuryl xanthate may be prepared by a reaction involving one molecule of each of the reacting constituents. This compound may be prepared by dissolving caustic soda or another suitable alkali metal hydroxide in one-half its weight of water, and slowly adding to the alkali solution, a mixture of tetra-hydro furfuryl alcohol and carbon disulphide. Constant agitation of the reaction mass should be insured. It has been found that this mass should be cooled to approximately 15° C. As in the case of the reaction between the furfuryl alcohol and the other reagents, gas is given off during standing. The reaction mass resulting from the preparation of sodium tetra-hydro furfuryl xanthate sets to a pasty solid, which is slightly more fluid than in the case of the sodium furfuryl xanthate.

Sodium tetra-hydro furfuryl xanthate may be prepared in accordance with the following equation:



The constituents enter into the reaction as above set forth, in the following proportion:

	M. W.	Per cent
1 mol. tetra-hydro furfuryl alcohol	102,08	=46.7
1 mol. sodium hydroxide	40.01	=18.4
1 mol. carbon disulphide	76.12	=34.9
		100.0

While in describing the preparation of the above compounds, specific reference has been made to sodium hydroxide, I wish it to be clearly understood that other alkali metal hydroxides may be employed with substantially equal results. I also wish it to be clearly understood that alcohols derived from other heterocyclic compounds which have properties similar to furfuryl alcohol and tetra-hydro furfuryl alcohol may be employed in preparing xanthate compounds suitable for flotation purposes.

In carrying out the separation of minerals in accordance with the present invention, the ore is properly prepared and is then subjected to a flotation process in which xanthate compounds prepared in accordance with the present invention are employed. The following examples of practice illustrate the results obtained when employing xanthate compounds as hereinbefore set forth.

1,000 grams of Anaconda Copper Mining Company's copper ore, crushed to about 10 mesh, were further ground in an Abbe pebble mill for 45 minutes with burnt lime at the rate of 5 pounds per ton of ore and 500 cc. of Roselle (N. J.) water. After grinding, the ore pulp was further diluted with the requisite amount of water for flotation purposes in a Littleford laboratory flotation machine. Pine oil was used as the frother, and as the collector, the reagent was added in the amounts tabulated below.

Sodium furfuryl xanthate lbs./ton of ore		Weight percent	Assay percent Cu	Recoveries percent Cu
	Heads	100.0	1.33	100.0
0.08	1st Concentrates	8.8	15.0	99.2
0.24	2nd Concentrates	22.0	.454	0.8
				100.0
	Tailings	69.0		
	Loss	0.2		

Note:—Had the 2nd concentrates been rejected into the tailings, the tailings would have contained 0.0495% Cu.

Sodium tetrahydro furfuryl xanthate lbs./ton ore		Weight percent	Assay percent Cu	Recoveries percent Cu
	Heads	100.0	1.33	100.0
0.00125	1st Concentrates	4.5	13.42	45.1
0.00500	2nd Concentrates	2.9	22.44	48.6
0.05000	3rd Concentrates	4.4	0.88	2.6
				96.3
0.02575	4th Concentrates	10.0	0.44	3.7
				100.0
0.02250	5th Concentrates	7.7	Trace	
0.05950	6th Concentrates	4.2		
	Tailings	65.1		
	Loss	1.2		

0.00625 lbs. of collector floated 93.7% of total copper.
0.08200 lbs. of collector floated all the copper.
0.164 lbs. of collector floated all the copper and iron.
First four concentrates=64.7%, containing all the copper.
Last two concentrates=35.3%, containing all the iron.
The frothing substance used was 0.3 lbs. pine oil.

From the foregoing results, it will be appreciated that the new mineral collecting agents forming the subject matter of this application, materially and advantageously affect mineral separation processes in which they are employed. Also, the compounds hereinbefore described may be rather easily prepared from relatively low cost raw materials which, together with the effectiveness of the compounds, results in low production costs of the mineral products.

These new flotation agents stabilize mineral flotation froth, have selective properties, drop iron from copper ores, are active collectors on zinc ores and are very effective even on coarsely ground ores. The latter is particularly desirable as much time can be saved in the preparation of the ores prior to treatment. Thus it will be seen that this invention makes it possible to more efficiently separate minerals from their ores than heretofore accomplished.

While I have herein shown and described a practical and satisfactory process and agent for carrying out my invention, it is, of course, obvious that various modifications may be made therein without exceeding the scope of my invention, it being understood, for example, that the homologues and analogues of the heterocyclic compounds may be employed in combination with carbon disulphide and alkali metal hydroxides to produce desirable and effective mineral collecting agents.

I claim:

1. A mineral collecting agent comprising a tetra-hydro furfuryl xanthate.

2. A mineral collecting agent comprising an alkali metal salt of tetra-hydro furfuryl xanthate.

3. A tetra-hydro furfuryl xanthate.

4. An alkali metal salt of tetra-hydro furfuryl xanthate.

5. A method of separating minerals comprising subjecting the same to a froth flotation process in the presence of a tetra-hydro furfuryl xanthate.

6. A process of concentrating ores which consists in agitating a pulp of the ore under such conditions that a froth is formed in the presence of a tetrahydro furfuryl xanthate, and separating the float.

7. A process of concentrating ores which consists in agitating a pulp of the ore under such conditions that a froth is formed in the presence of an alkali metal salt of tetrahydro furfuryl xanthate, and then separating the float.

8. A process of concentrating ores which consists in agitating a pulp of the ore under such conditions that a froth is formed in the presence of the sodium salt of tetrahydro furfuryl xanthate, and then separating the float.

9. A process of concentrating ores which consists in agitating a pulp of the ore under such conditions that a froth is formed in the presence of the potassium salt of tetrahydro furfuryl xanthate, and then separating the float.

10. The process of concentrating ores which consists in agitating a pulp of the ore under such conditions that a froth is formed with an agent consisting of a sulphur containing derivative of completely hydrogenated furan, and separating the float.

RHETHERFORD B. MARTIN.