Patented Jan. 7, 1936

2,027,357

UNITED STATES PATENT OFFICE

2,027,357

FLOTATION OF MINERALS

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No Drawing. Application May 13, 1927, Serial No. 191,260

24 Claims. (Cl. 209—166)

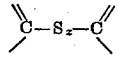
This invention relates to the separation of minerals and the concentration of ores by froth flotation processes, and is particularly directed to such separation and concentration carried out with the utilization of certain organic sulfides as flotation agents.

According to the present invention, improved results can be obtained in the separation of minerals and the concentration of ores by carrying out the flotation operation with the addition to the mineral pulp or ore of a carbocyclic organic sulfide of the aromatic series which contains no nitrogen and no ogygen in its composition.

The aromatic carbocyclic sulfides employed as flotation agents or adjuvants in the process of the present invention are those aryl sulfides represented by the formula

$$R—S_x—R'$$

wherein R and R' represent the same or different aromatic carbocyclic hydrocarbon radicals which may contain substituents but which contain no nitrogen and no oxygen in their composition, and x denotes the number 1 or a number greater than 1. These sulfides comprise in their composition the grouping



wherein each carbon atom is a component member of an aromatic carbocyclic ring or nucleus. The nitrogen-free and oxygen-free aryl disulfides of the formula

$$R—S—S—R$$

are particularly important, and especially those of the benzene series.

In general, the sulfides employed in the present invention can be prepared in any suitable manner, for example, by the action of a diazotized amine on an alkali metal sulfide or polysulfide; by the action of sulfur or of a sulfur chloride on an aromatic hydrocarbon in the presence of aluminum chloride; by the oxidation of thiophenols; by the action of sulfur on a diaryl sulfone; by the decomposition of the salts of an aryl-thiosulfuric acid; by the action of an aryl halide on certain metallic salts of a thiophenol; by the action of sulfur chloride on thiophenols; and by dissolving sulfur in the corresponding aryl mono- and di-sulfides. Other suitable methods may also be employed. They may be used as flotation agents in the pure or purified state; and, in general, they may be also employed in the impure or crude state.

In carrying out the flotation process, the flotation agent comprising the nitrogen-free and oxygen-free aromatic carbocyclic sulfide may be incorporated with the ore or the mineral pulp in any suitable manner and at any suitable time which will insure a satisfactory flotation operation. For example, it may be introduced in the free state or it may be dissolved, suspended or dispersed in any suitable solvent or dispersing agent as, for example, water, or one or more of the usual flotation oils or oil mixtures, or any suitable organic solvent, and incorporating the resulting solution, suspension or dispersion with the ore or the ore pulp. While the agents of the present invention show marked action as flotation agents in ore concentration, many of them possess insufficient frothing qualities and, in such cases, are used to advantage in conjunction with a suitable or well known frothing agent, e. g., pine oil, terpineol, tar acids, etc. They may be also sometimes used to advantage in admixture with each other or in conjunction with other flotation agents, and more especially with those flotation agents which are miscible with or are capable of dissolving considerable quantities of the sulfides of the present invention to give solutions which are liquid at ordinary temperatures. In general, liquid mercaptans and particularly liquid thiophenols, are good solvents for the sulfides of the present invention and give solutions which can be used to advantage as flotation agents in the flotation operation.

In the differential separation of various minerals, such as zinc blende from associated minerals, the presence of an alkali metal cyanide, or of copper sulfate or other salts, is sometimes advantageous.

The process of the present invention can be carried out in any suitable apparatus, for example, those of the pneumatic type such as the Callow cell, or those where the air is incorporated with the mixture by mechanical agitation such as the Janney apparatus, or the like.

It is of advantage in many cases, as with certain copper ores, to subject the ore pulp to the action of an amount of alkali sufficient to give it a neutral or an alkaline reaction before subjecting it to flotation with the aid of the flotation agents of the present invention. The alkali may be caustic alkali such as caustic soda, or an alkaline salt such as soda ash, or it may be calcium oxide or hydrate, etc.

The amount of flotation agent required to be used in the flotation process will vary, it depending partly on the character and composition

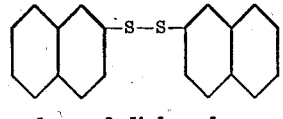
of the ore, partly on the particular sulfide employed, and partly on other factors. In many cases, one-fifth to one-half of a pound of flotation agent per ton of dry ore will be sufficient, while in other cases larger or smaller amounts than this may be required.

The invention will be further illustrated by the following specific examples, but it will be understood that the invention is not limited thereto. The parts are by weight.

Example 1.—500 parts of a copper sulfide ore (table tailings of an Anaconda Copper Company ore) assaying 1.48 percent copper was ground in a ball mill with 220 parts water, 0.0625 parts diphenyl monosulfide, $C_6H_5—S—C_6H_5$, (equivalent to one-fourth pound per ton of ore), and 0.75 parts hydrated lime (equivalent to 3 pounds hydrated lime per ton of dry ore) until practically all of the mixture was sufficiently fine to pass a 40 mesh screen. The ground pulp was diluted with sufficient water to give a mixture containing about 16 percent solids and subjected to flotation in a Janney flotation apparatus. After agitating for two or three minutes, a small amount, e. g., about 0.02 to 0.03 parts, of pine oil was added. A satisfactory mineral froth was produced. During the next 20 minutes of agitation, an amount of pine oil was added to make a total of about 0.06 to 0.08 parts. Mechanical agitation of the pulp was continued for about 5 minutes after all of the pine oil had been added. 41.6 parts of a concentrate assaying 13.35 per cent copper was obtained. A recovery of 87 percent of the copper was therefore obtained in the concentrate. The tailings assayed 0.206 percent copper. It will be noted that the equivalent of about 12.2 tons of ore was required to give about 1 ton of concentrate.

Example 2.—500 parts of copper sulfide ore (of the Miami Copper Company) assaying 1.19 percent copper was treated as described in Example 1 except that 0.0625 parts ditolyl disulfide $CH_3·C_6H_4—S—S—C_6H_4.CH_3$, was used in place of diphenyl monosulfide. 20.5 parts of concentrate assaying 22.05 percent copper was obtained. This is a recovery in the concentrate of 75.1 percent copper. The tailings assayed 0.31 percent copper. In this example, the equivalent of 24.6 tons of ore gave 1 ton of concentrate.

Example 3.—500 parts of a copper sulfide ore (Miami Copper Company) assaying 1.17 percent copper was treated as described in Example 1 except that 0.0625 parts of di-betanaphthyl disulfide,



was used in place of diphenyl monosulfide. 20 parts of concentrate assaying 15.55 percent copper was obtained which is a recovery of 53.2 percent. The tailings assayed 0.57 percent copper. In this example, the equivalent of 25.1 tons of ore gave 1 ton of concentrate.

In a similar manner, other aryl sulfides such as dinaphthyl monosulfide, diphenyl disulfide, dipenhyl polysulfide (more than two atoms of sulfur present), p.p-ditolyl tetrasulfide, etc., have been found to be effective flotation agents.

It will be thus noted that the present invention contemplates the utilization of a carbocyclic-sulfide or polysulfide of the aromatic series, and which contain no nitrogen and no oxygen in their composition, as flotation agents in the separation of minerals and the concentration of ores; that said flotation agents may be incorporated in or with the ore or mineral pulp in any well-known or suitable manner; that they may be used in admixture with each other or with mercaptans or in conjunction with other flotation agents or with frothing agents, or with mixtures of the same; and that they may be employed in the free condition or in solution, suspension or dispersion in any suitable solvent or medium.

It will be understood that the present invention is applicable to the treatment of various kinds of mineral mixtures, both natural and artificial, which are amenable to concentration by flotation processes.

It will be further understood that the invention is not limited in this specification to the use of the particular agents or ingredients mentioned as examples, and that other agents of the class mentioned can be used.

We claim:

1. In effecting the separation of minerals by flotation, the process which comprises mixing with the mineral pulp an aromatic carbocyclic sulfide which contains no nitrogen and no oxygen in its composition and subjecting the resulting mixture to a froth flotation operation.

2. In effecting the concentration of ores by flotation, the process which comprises mixing with the one pulp a sulfide represented by the probable formula

$$R—S—S—R$$

wherein R stands for a carbocyclic hydrocarbon radical of the benzene series, and subjecting the resulting mixture to a froth flotation operation.

3. A flotation process for the separation of minerals which comprises adding a diaryl sulfide of the benzene series to a mineral pulp and subjecting the resulting mixture to a froth flotation operation.

4. A flotation agent comprising a tolyl disulfide in admixture with a merctaptan.

5. A flotation agent comprising a tolyl disulfide in admixture with a thiophenol.

6. In effecting the separation of minerals by flotation, the process which comprises incorporating with the mineral pulp an oxygen- and nitrogen-free organic sulfide and a mercaptan, said sulfide having within its composition the following probable group

$$—S_x—$$

wherein said group is bound on each side to an aromatic carbocyclic carbon atom and x has a numerical value of 1 or more.

7. In effecting the separation of minerals by flotation, the process which comprises incorporating with the mineral pulp an oxygen- and nitrogen-free organic sulfide and a thiophenol, said sulfide containing the probable group

$$—S_x—$$

wherein said group is bound on either side to an aromatic carbocyclic carbon atom, and x has a numerical value of 1 or more.

8. In effecting the separation of minerals by flotation, the process which comprises incorporating with the mineral pulp a diaryl polysulfide and a mercaptan.

9. In effecting the concentration of ores by flotation, the process which comprises incorporating with the ore pulp a diaryl disulfide and a thiophenol.

10. A flotation agent comprising an oxygen- and nitrogen-free aromatic sulfide and a mer-

captan, said sulfide having within its composition the following probable grouping

—S_x—

wherein said grouping is bound on each side to an aromatic carbocyclic carbon atom, and where x denotes a numerical value of 1 or more.

11. A flotation agent comprising a diaryl polysulfide and a mercaptan.

12. A flotation agent comprising a diaryl disulfide and a thiophenol.

13. In effecting the concentration of a copper sulfide ore, the process which comprises subjecting a pulp of the ore to a froth flotation operation in the presence of an aromatic carbocyclic sulfide which contains no nitrogen and no oxygen in its composition.

14. In effecting the concentration of a copper sulfide ore, the process which comprises subjecting a pulp of the ore to a froth flotation operation in the presence of a diaryl sulfide of the benzene series.

15. In effecting the concentration of a copper sulfide ore, the process which comprises subjecting a pulp of the ore to a froth flotation operation in the presence of a diaryl sulfide and a mercaptan, said sulfide containing the group.

—S_x—

bound on each side to an aromatic carbocyclic carbon atom and in said group, x stands for a numerical value of 1 or more.

16. In effecting the concentration of a copper sulfide ore, the process which comprises subjecting a pulp of the ore to a froth flotation operation in the presence of a diaryl disulfide and a thiophenol.

17. A flotation agent comprising a diaryl sulfide and a mercaptan, said sulfide containing the group

—S_x—

bound on each side to an aromatic carbocyclic carbon atom and in said group x stands for a numerical value of 1 or more.

18. The process of concentrating ores which consists in agitating a pulp of the ore with diphenyl-disulphide under such conditions that a float is formed, and separating the float.

19. The process of concentrating ores which consists in agitating a pulp of the ore under such conditions that a float is formed with an agent each of whose molecules includes two phenyl ring radicals containing only hydrogen and carbon and also includes two sulphur atoms, a carbon atom in each ring being directly united to a sulphur atom, and the sulphur atoms being directly united to each other; and separating the float.

20. The process of concentrating ores which consists in agitating a pulp of the ore with ditolyl disulfide under such conditions that a float is formed; and separating the float.

21. In effecting the separation of minerals by flotation, the process which comprises mixing with the mineral pulp a diaryl sulfide in which the aryl radicals are the same or different aromatic carbocyclic hydrocarbon radicals which may contain substituents but which are free from nitrogen and oxygen in their composition, and subjecting the resulting mixture to a froth flotation operation.

22. In effecting the concentration of ores by flotation, the process which comprises mixing with the ore pulp a diaryl sulfide in which the aryl radicals are carbocyclic hydrocarbon radicals of the benzene series which may contain substituents but which are free from nitrogen and oxygen, and subjecting the resulting mixture to a froth flotation operation.

23. In effecting the concentration of ore by flotation, the process which comprises subjecting an ore pulp to a froth flotation operation in the presence of a nitrogen-free and oxygen-free diaryl sulfide in which the aryl radicals are different aromatic carbocyclic radicals and nuclear carbon atoms are directly linked to sulfur.

24. In effecting the concentration of a copper sulfide ore, the process which comprises subjecting a pulp of the ore to a froth flotation operation in the presence of a diaryl sulfide in which the aryl radicals are the same or different aromatic carbocyclic hydrocarbon radicals which may contain substituents but which contain no nitrogen and no oxygen in their composition.

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CERTIFICATE OF CORRECTION.

Patent No. 2,027,357.

January 7, 1936.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 32, for "13.35" read 15.35: second column, line 30, claim 2, for "one" read ore; and line 42, claim 4, for "merctaptan" read mercaptan; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 25th day of February, A. D. 1936.

(Seal)

Leslie Frazer

Acting Commissioner of Patents.