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CONCENTRATION OF MINERALS

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This invention relates to the concentration of minerals contained in mineral-bearing materials such, for example, as ores and has for an object the provision of an improved process for concentrating minerals. More particularly, the invention contemplates the provision of an improved process for concentrating minerals by froth flotation. A specific object of the invention is to provide an improved process for concentrating sulphide minerals by froth flotation. Further specific objects of the invention are to provide improved processes for concentrating copper sulphide minerals, zinc sulphide minerals and lead sulphide minerals by froth flotation. Another object of the invention is to provide novel and effective flotation reagents. A further object of the invention is to provide new products, particularly, improved flotation reagents.

The invention is based on my discovery that a flotation froth containing a mineral collecting agent, produced in an operation employing normal frothing and conditioning agents as well as the mineral collecting agent, responds to the incorporation of a plasticizer therein in many respects as organic plastic materials respond to the incorporation of the same plasticizers therein, being modified by the actions or functions of the plasticizers to form resilient, flexible and workable froths when employed even in rather minute quantities in operations that would result in the production of brittle and unstable froths under otherwise identical conditions, even though the plasticizers themselves have no flotative capacities or properties or have only relatively insignificant flotative capacities or properties.

The plasticizers appear to possess the ability to create or have the property of creating a new flotative environment in which the flotation reagents employed become endowed with increased flotative powers or capacities or properties either because of improvements in one or more of the other reagents resulting from the presence of the plasticizer or because, in the flotative environment, the plasticizer itself is so influenced by the other reagents as to acquire substantial flotative qualities of an additive character.

The plasticizer accelerates distribution in flotation pulps of water-insoluble mineral collecting agents with the result that the production on the mineral particles to be recovered of films comprising the mineral collecting agent is accelerated.

The results of my researches and investigations indicate that the acceleration of distribution of the water-insoluble mineral collecting agent results from plasticization of the mineral collecting

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agent and that the improvements in the flotative properties of mineral collecting agents, both water-insoluble and water-soluble, results from incorporation therein of the plasticizers with resulting plasticization.

The plasticizers and the mineral collecting agents may be mixed together prior to their introduction into the flotation pulps, or the plasticizers and the mineral collecting agents may be introduced into the flotation pulps separately. Water-insoluble mineral collecting agents and plasticizers may be mixed together prior to their introduction into the flotation pulps or they may be introduced into the flotation pulps separately with about equal advantage. Water-soluble mineral collecting agents and plasticizers preferably are introduced into the flotation pulps without preliminary mixing. Mixing of the plasticizers and the water-insoluble mineral collecting agents may be carried out under any suitable temperature and pressure conditions. Normally, mixing of the plasticizers and the mineral collecting agents may be carried out at ordinary room temperatures and pressures prevailing in the plants in which mixing is carried out.

Incorporation of a plasticizer and a mineral collecting agent in a flotation pulp, whether mixed beforehand or added to the flotation pulp separately, results in the formation on particles of mineral to be recovered of films of plasticized mineral collecting agent comprising both the mineral collecting agent and the plasticizer.

When mixing of the plasticizer and the water-insoluble mineral collecting agent is carried out prior to introduction into the flotation pulp, a plasticized mineral collecting agent is produced, and the plasticized mineral collecting agent is introduced into the flotation pulp.

When the plasticizer and a mineral collecting agent are introduced into the pulp separately, plasticization of the mineral collecting agent may be effected largely while the mineral collecting agent is dispersed in the liquid portion of the pulp, or largely after the mineral collecting agent has formed films on the mineral particles.

When a water-insoluble mineral collecting agent is employed, the time or place of plasticization depends upon the time or order of incorporation in the pulp of the mineral collecting agent and the plasticizer. If the water-insoluble mineral collecting agent and the plasticizer are incorporated in the pulp separately, but substantially simultaneously, plasticization of the mineral collecting agent may be effected largely or

substantially entirely in the liquid portion of the pulp. When the plasticizer is incorporated in the pulp before or after incorporation of the water-insoluble mineral collecting agent, the degree or amount of plasticization effected in the liquid portion of the pulp may be greater or less than the degree or amount of plasticization effected when they are incorporated separately but substantially simultaneously. When a water-soluble mineral collecting agent is employed in conjunction with a plasticizer, plasticization may take place largely or substantially entirely after the mineral collecting agent has formed films on the surfaces of the mineral particles regardless of the time or order of incorporation in the flotation pulps.

Plasticization of the mineral collecting agent takes place substantially immediately, with substantially immediate improvement in the flotative properties of the mineral collecting agents and, in the case of water-insoluble mineral collecting agents, with substantially immediate improvement in the rates and degrees of distribution of the mineral collecting agents. A particular advantage of the invention resides in the fact that the use of a plasticizer results in distribution of the mineral collecting agent throughout the flotation pulp in a relatively short period of time, as, for example, in less than a half minute when the pulp with added mineral collecting agent and plasticizer is properly agitated. The plasticizer improves the capacity of the mineral collecting agent to coat the mineral particles, and rapid distribution of the plasticized mineral collecting agent throughout the pulp provides for multiplication of the opportunities for the mineral collecting agent to contact and forms films on the mineral particles with a consequent reduction in the time required for conditioning the pulp prior to initiation of frothing operation proper.

In a froth flotation operation, a conditioning agent such as an alkaline substance or an acid substance, a mineral collecting agent and a frothing agent usually are incorporated in an aqueous pulp of the ore, and the pulp subsequently is subjected to aeration and agitation to produce a froth containing the valuable mineral of the ore. Usually, at least a brief period of time may be required to condition the pulp, as by agitation, after incorporation of the conditioning agent and the mineral collecting agent to effect thorough distribution of the conditioning agent and the mineral collecting agent throughout the pulp prior to the incorporation of the frothing agent in the pulp. When a water-insoluble mineral collecting agent is employed, in the absence of a plasticizer, a relatively long conditioning period, for example, a half hour to an hour or longer, may be required to effect distribution of the mineral collecting agent to the extent that a substantial recovery of valuable minerals may be effected.

When a water-insoluble mineral collecting agent is employed in accordance with heretofore customary practices, the amount or percentage of valuable mineral recovered in the flotation operation is a function of the time of conditioning to effect distribution of the mineral collecting agent and filming of the mineral particles. If preliminary conditioning prior to flotation is not provided for, or, if a relatively short period of conditioning is provided for, recovery of valuable minerals may be so low as to make the operation unprofitable or uncommercial.

In flotation operations conducted heretofore, the amount of recovery, or the percentage recovery, of valuable mineral is a function of the amount of mineral collecting agent that forms films on the mineral particles, and, to some extent, the amount of mineral collecting agent that forms films is a function of both the amount of mineral collecting agent added to the pulp and the time of conditioning the pulp containing the added mineral collecting agent. If the conditioning period is not sufficiently long, only a portion of the mineral collecting agent functions to form films on the mineral particles even when an amount of mineral collecting agent sufficient to form proper films on all of the mineral particles is employed. Consequently, the amount of mineral collecting agent that can be employed effectively is restricted and recoveries are relatively poor. Also, the use of excess water-insoluble mineral collecting agent, that is, mineral collecting agent that does not form films on the mineral particles, results in the production of a poor froth in the subsequent frothing operation which further limits the recovery of valuable mineral.

The present invention permits the incorporation in the pulp and the effective use of an amount of mineral collecting agent sufficient to form proper films on all mineral particles.

A further important advantage of the invention results from the fact that rapid distribution of a water-insoluble mineral collecting agent is effected with consequent shortening or elimination of the conditioning period. For example, in a mineral recovery or concentration plant in which a conditioning period of a half hour or an hour is required to produce a suitable recovery and in which the time of flow of the pulp through the frothing operation is about fifteen minutes, conditioning facilities must be provided for handling two or four times the amount of pulp actually subjected to the frothing operation or mineral recovery operation proper, with attendant increased costs of installation, maintenance and operation. When, in accordance with the present invention, the time required for conditioning is reduced to a half minute or less, conditioning equipment can be substantially completely dispensed with, and the conditioning and mineral collecting agents can be added to the pulp in a small compartment immediately ahead of the first frothing compartment. This advantageous result of the invention permits the immediate use in plants not equipped with conditioning equipment of highly efficacious water-insoluble mineral collecting agents that otherwise cannot be employed effectively.

It is to be understood that the scope of the invention is not to be limited by theoretical discussions contained herein. Whatever the explanation may be, it is a demonstratable fact that the incorporation in a flotation pulp to which is added a mineral collecting agent and the normal frothing and conditioning agents of a plasticizer normally effective for plasticizing organic plastics in amounts even as small as five one-thousandths (0.005) of a pound per ton of ore treated may result in the production of profound improvements in the flotation operation and in the metallurgy of the mineral or metal recovery operation of which the flotation operation is a part. The addition of the plasticizer

(1) Produces a resilient, flexible and workable froth in a flotation operation that would pro-

duce a brittle and unstable froth under otherwise identical conditions,

(2) Permits the application of more mineral collecting agent for increased collecting power without detriment to the froth,

(3) Reduces the time necessary for conditioning the pulp with the mineral collecting agent,

(4) Increases the speed of the flotation operation and

(5) Yields generally improved metallurgical results.

The intimate relationship of dispersed and dispersing phases involved in the plasticizer effect is felt not only in the conditioning process but, also, in the process of froth formation and results in an over-all improvement in the mechanics of the operation.

The plasticizer preferably is employed in amounts in the range 0.01 to 0.005 pound per ton of ore treated, but it may be employed in greater or lesser amounts when conditions warrant such modification.

Among the commonly known plasticizers that I have found to be highly effective in flotation operations are included esters of phthalic acid, sebacic acid, citric acid, tartaric acid, phosphoric acid, succinic acid and hydroxybenzoic acid such as salicylic acid, such, for example, as

Diethyl phthalate,
Dibutyl phthalate,
Dihexyl phthalate,
Dibutyl sebacate,
Dihexyl sebacate,
Tributyl citrate,
Triamyl citrate,
Dibutyl tartrate,
Diamyl tartrate,
Tricresyl phosphate,
Diamyl succinate,
Amyl salicylate,
Diethyl adipate,
Dibutyl adipate, and
Dihexyl adipate.

While the plasticizers may be employed with advantage in conjunction with all mineral collecting agents, including both water-soluble and water-insoluble mineral collecting agents, employed in flotation practice with the normal frothing and conditioning agents, my researches and investigations indicate that plasticizers are most effective and better results are obtained when they are employed in conjunction with the water-insoluble alkyl xanthogen formates, both symmetrical and unsymmetrical. Other specific mineral collecting agents with which plasticizers may be employed advantageously include, for example, alkali metal xanthates and dialkyl dithiophosphates. Representative xanthogen formate compounds suitable for use as mineral collecting agents include

Ethyl xanthogen ethyl formate,
Butyl xanthogen ethyl formate,
Amyl xanthogen ethyl formate, and
Hexyl xanthogen ethyl formate.

The claims of this application are directed to methods or processes employing esters of tribasic acids and esters of tribasic acids of the types of citric acid and phosphoric acid. Methods or processes employing plasticizers in the forms of esters of others of the acids referred to herein are covered by my copending applications Serial No. 198,896, filed December 2, 1950, Serial No. 198,897, filed December 2, 1950, and Serial No. 198,898, filed December 2, 1950.

The plasticizer and the mineral collecting agent employed in any flotation operation in accordance with the invention may be added to the flotation pulp separately or in the form of any suitable mixture or solution.

In practicing a method or process of the invention, a neutral, acid or alkaline circuit may be employed.

The following examples illustrate the advantages of the reagents and processes of the invention over reagents and processes employed heretofore.

In carrying out the processes of the examples, sulphide ores of the compositions indicated with respect to copper and zinc were ground in water to form aqueous pulps which were subjected to froth flotation operations in the presence of the reagents indicated, but, otherwise, under substantially identical conditions, with the production of concentrates and tailing products of the analyses indicated:

Example I

Test No.	1	2	3
Heads, percent Cu	4.114	4.079	4.065
Concentrates, percent Cu	25.17	23.54	23.44
Tails, percent Cu	.222	.209	.190
Reagents:			
Lime, pounds per ton	10.0	10.0	10.0
Pine oil, do	.09	.09	.09
Amyl xanthogen ethyl formate, pounds per ton	.04	.04	.04
Tributyl citrate, do		.01	
Triamyl citrate, do			.01

Example II

Test No.	1	2	3
Heads, percent Cu	4.104	4.079	4.065
Concentrates, percent Cu	24.46	23.54	23.44
Tails, percent Cu	.222	.209	.190
Reagents:			
Lime, pounds per ton	10.0	10.0	10.0
Pine oil, do	.12	.09	.09
Amyl xanthogen ethyl formate, pounds per ton	.04	.04	.04
Tributyl citrate, do		.01	
Triamyl citrate, do			.01

Example III

Test No.	1	2
Heads, percent Cu	2.090	2.090
Concentrates, percent Cu	15.60	15.09
Tails, percent Cu	.293	.242
Reagents:		
Sulphuric acid, pounds per ton	10.0	10.0
Cresylic acid, do	.44	.44
Ethyl xanthogen ethyl formate, do	.20	.20
Tributyl citrate, do		.02

Example IV

Test No.	1	2	3
Heads, percent Cu	2.045	2.088	2.067
Concentrates, percent Cu	14.61	15.53	14.10
Tails, percent Cu	.300	.255	.262
Reagents:			
Sulphuric acid, pounds per ton	10.0	10.0	10.0
Cresylic acid, do	.44	.44	.44
Ethyl xanthogen ethyl formate, pounds per ton	.20	.18	.18
Tributyl citrate, do		.02	
Tricresyl phosphate, do			.02

In the tests carried out to obtain the data set forth in the above examples, the froth produced in each of the tests in which a plasticizer was employed was resilient, flexible and workable,

whereas in each of the tests carried out without the use of a plasticizer, a more brittle and less stable froth was produced.

I claim:

1. The method of concentrating a sulphide mineral which comprises subjecting the sulphide mineral-bearing material in the form of a pulp to a froth flotation operation in the presence of an anionic mineral collecting agent selected from the class consisting of alkyl xanthogen formates, alkali metal alkyl xanthates and dialkyl dithiophosphates and a plasticizer selected from the group consisting of tributyl and triamyl citrates and tricresyl phosphate.

2. The method of concentrating a sulphide mineral which comprises subjecting the sulphide mineral-bearing material in the form of a pulp to a froth flotation operation in the presence of an alkyl xanthogen formate mineral collecting agent and tributyl citrate.

3. The method of concentrating a sulphide mineral which comprises subjecting the sulphide mineral-bearing material in the form of a pulp to a froth flotation operation in the presence of an alkyl xanthogen formate mineral collecting agent and triamyl citrate.

4. The method of concentrating a sulphide mineral which comprises subjecting the sulphide mineral-bearing material in the form of a pulp to a froth flotation operation in the presence of amyl xanthogen ethyl formate and tributyl citrate.

5. The method of concentrating a sulphide mineral which comprises subjecting the sulphide mineral-bearing material in the form of a pulp to a froth flotation operation in the presence of amyl xanthogen ethyl formate and triamyl citrate.

6. The method of concentrating a sulphide mineral which comprises subjecting the sulphide mineral-bearing material in the form of a pulp to a froth flotation operation in the presence of ethyl xanthogen ethyl formate and tributyl citrate.

7. The method of concentrating a sulphide mineral which comprises subjecting the sulphide mineral-bearing material in the form of a pulp to a froth flotation operation in the presence of an alkyl xanthogen formate and tricresyl phosphate.

8. The method of concentrating a sulphide mineral which comprises subjecting the sulphide mineral-bearing material in the form of a pulp to a froth flotation operation in the presence of ethyl xanthogen ethyl formate and tricresyl phosphate.

9. A flotation agent for use in a sulphide mineral concentrating process in which sulphide mineral-bearing material in the form of a pulp is subjected to a froth flotation operation in the presence of frothing and mineral collecting agents, said flotation agent being an intimate mixture comprising (1) a water-insoluble mineral collecting agent selected from the group consisting of alkyl xanthogen formates and (2) a plasticizer selected from the group consisting of trialkyl citrates and triaryl phosphates.

10. A flotation agent for use in a sulphide mineral concentrating process in which sulphide mineral-bearing material in the form of a pulp is subjected to a froth flotation operation in the presence of frothing and mineral collecting agents, said flotation agent being an intimate mixture comprising (1) a water-insoluble mineral collecting agent selected from the group consisting of alkyl xanthogen formates and (2) a plasticizer selected from the group consisting of tributyl and triamyl citrates and tricresyl phosphates.

11. A flotation agent for use in a sulphide mineral concentrating process in which sulphide mineral-bearing material in the form of a pulp is subjected to a froth flotation operation in the presence of frothing and mineral collecting agents, said flotation agent being an intimate mixture comprising (1) a water-insoluble mineral collecting agent selected from the group consisting of ethyl, butyl, amyl and hexyl xanthogen ethyl formates and (2) a plasticizer selected from the group consisting of trialkyl citrates and triaryl phosphates.

12. A flotation agent for use in a sulphide mineral concentrating process in which sulphide mineral-bearing material in the form of a pulp is subjected to a froth flotation operation in the presence of frothing and mineral collecting agents, said flotation agent being an intimate mixture comprising (1) a water-insoluble mineral collecting agent selected from the group consisting of ethyl, butyl, amyl and hexyl xanthogen ethyl formates and (2) a plasticizer selected from the group consisting of tributyl and triamyl citrates and tricresyl phosphates.

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