United States Patent [19]

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Petrovich

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[54] **FROTH FLOTATION METHOD FOR RECOVERY OF MINERALS**

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[22] Filed: **Nov. 6, 1973**

[21] Appl. No.: **409,773**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 251,458, May 8, 1972, abandoned.

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

[51] **Int. Cl.²** **B03D 1/02**

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

[56] **References Cited**

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Primary Examiner—Robert Halper

[57] **ABSTRACT**

An improved method in concentration of oxide ores by froth flotation process which comprises subjecting an oxide ore of a metal which can change the valency state from lower to higher by the action of inorganic oxidizing compounds in the presence of an effective quantity of a flotation collector-frother, an olefinic, diolefinic, or triolefinic adduct of alkyl polyhydroxycarboxylic acids; the indicated compounds provide selectivity and/or recovery of oxide minerals of iron, chromium, cerium, yttrium, antimony, and phosphorous over silica and silicate gangue.

6 Claims, No Drawings

FROTH FLOTATION METHOD FOR RECOVERY OF MINERALS

This is a continuation-in-part of my prior application of Ser. No. 251,458 filed on May 8, 1972, now abandoned.

RELATED APPLICATIONS

The prior art discloses the application of oxidizing agents in conjunction with fatty acids, fatty acid sulfonates and petroleum sulfonated oils. U.S. Pat. No. 1,926,045 teaches the use of potassium permanganate, potassium dichromate, hypochlorite or bleaching powder for the concentration of fluorspar with fatty acids and sulfonated oils. U.S. Pat. No. 3,094,485 teaches the use of potassium permanganate to depress calcite, fluorite, chalcopyrite and monazite, but to float scheelite and zircon. U.S. Pat. No. 2,399,845 teaches the use of potassium permanganate and potassium dichromate in conjunction with xanthates for recovering of cobalt and nickel sulfide ores, and depressing the pyrite with ferrocyanide.

BRIEF SUMMARY OF THE INVENTION

This invention relates to the concentration of metal values from the minerals and ore. Particularly it relates to the use of olefinic, diolefinic, or triolefinic carbinol adducts of alkyl polyhydroxymonocarboxylic acids or alkyl polyhydroxydicarboxylic acids as flotation agents with collecting and frothing properties to effect a separation of metal values in ores from silica, alkali and earth alkali aluminum silicates. The minerals and ores of which the metal values are to be floated out are pretreated with strong oxidizing agents which presumably change the metal valency state at the mineral surface of respective metal, which can change the valency state. The higher oxidizing agents of the respective metal presumably activates the double bond of the olefinic collector-frother, thus effecting a succesful flotation of the desired metal values from the mineral slurry. Among such ores and minerals, to the beneficiation of which this invention is particularly adapted are the oxide ores of iron, chromium, cerium, yttrium, antimony, and phosphorous, i.e., the ferrites of iron, chromium, manganese and nickel, as are magnetite, chromite, franklinite, bixbyite, trevorite; the spinels as are hercynite, gahnite; iron titanate as is ilmenite; oxides of iron and antimony as are hematite, servantite and senarmontite; phosphate of cerium and yttrium as is monazite, as well as the phosphate rock.

Another object of the invention is a beneficiation process effective economically to recover the heretofore said metallic values from silica and silicate gangue.

One or more of the foregoing objects is achieved by the present invention.

The present invention comprises a process for the beneficiation of minerals and ores of metals which can change the valency state so that the metal at the mineral surface or a portion of the mineral surface is presumably oxidized to a higher valency state, in which state it presumably acts catalyticaly on the double carbon to carbon bond of the olefinic collector-frother, which as a π-bond compound presumably attach the olefinic collector-frother to the mineral surface. Thus the process comprises comminuting the ore to substantially completely liberation of the valuable mineral from the gangue, pretreating the comminuted ore with an inorganic oxidizing agent to modify at least a portion of the surface of the mineral which is to be floated by forming some higher metal oxide, and subjecting the comminuted surface modified ore or mineral to the beneficiation by froth flotation method in the presence of olefine, diolefine, or triolefine carbinol adduct of polyhydroxycarboxylic acid.

More particularly described, the present invention comprises contacting the comminuted ore or mineral of the afore said metals with inorganic oxidizing agents believed to effect a change in the surface oxidation-reduction potential of the ore particles, which particles are believed to exert by their acquired oxidation-reduction potential a change in the oxidation-reduction potential of the double carbon to carbon bond of the olefinic compounds which serve in this invention as collecting agents.

While it is not desired to be bound by the theory here expressed, it is believed that treatment of the comminuted ore, according to the process of this invention, results either in actual chemical oxidation of portions of the surface of the mineral of the metal which normally and naturally form higher oxide in higher valency state, or, alternatively, alters the oxidation-reduction potential of a portion of the surface of the metalliferous particles. The foregoing discussion shows that the oxidation state concept can be used to determine whether a given chemical reaction involves oxidation-reduction and further, to help in balancing the equations for such processes where balancing by inspection fails. But it is evident that the metals of the ore treated in accordance with the invention are rendered responsive to froth flotation, i.e., to levitation from siliceous gangue and collection in a froth flotation process.

In discussing oxidation-reduction reactions the species that is reduced is called the oxidizing agent or oxidant, and the species that is oxidized is called the reducing agent or reductant. Where simple ions are involved, the oxidation agent is the electron donor; the oxidation state changes can be used to identify the oxidizing and reducing agents. In the respective case, the flotation of minerals, the mineral particles in the aqueous pulp of mineral slurry may presumably exert the quality of reducing or oxidizing agents in contact with ionic oxidizing or reducing agents. Thus the mineral particle may be donor or acceptor of electron in contact with an oxidizing or reducing agent.

The oxidation correspond to an increase in oxidation state in the positive sense; reduction corresponds to a decrease in oxidation state in the positive sense. The conventional algebraic sum of the changes in oxidation states in the balanced equation for an oxidation-reduction reaction is zero.

In general, when ionic compounds are formed from their elements, electron transfer is complete, and oxidation and reduction in the modern sense can be readily discerned; but when covalent molecules results, what presumably occurs in oxidation or reduction of mineral surface in flotation in which reaction only a partial transfer of electrons from one element to the other occurs, the oxidation-reduction nature of the process is obscure. Oxidation-reduction reactions of the latter type are conveniently described using the concept of the oxidation state of an element. Oxidation state is a convention based on a set of rules, and has the advantage of applicability to oxidation-reduction reactions regardless of whether a complete or partial trans-

fer of electrons is involved. furthermore, chemical reactions involve changes in the distribution of the electrons about the nuclei of the reacting particles, whether they be atoms, molecules, or ions. Some of the changes involve a more or less complete transfer of electrons from one of the reacting particles to another. And because an oxidation is always accompanied by a reduction so that electrons are neither created nor destroyed in the transfer, it may be supposed that the carbon to carbon double bond is oxidized by supposedly higher oxide of the metal of a respective mineral so that the carbon to carbon double bond acts as reducing agent, because of which the new state of things find it solution in a presumably new compound of metal(oxide) hydrocarbon compound, for the metals of the ore treated in accordance with the invention are rendered responsive to froth flotation, i.e., levitation from siliceous gangue and collection in a froth flotation process.

The present invention embraces inorganic oxidizing agents of a high negative oxidation-reduction potential. Appropriate agents to put in practice of the present invention includes: chlorate, chromate, dichromate, ferrate, hypochlorite, and fluoride of oxygen F_2O, permanganate.

The amount of the oxidizing agents employed in practicing of the present invention may vary depending upon the nature of the ore, the conditioning time and the like operations. The oxidizing agents of this invention are preferably employed in amounts ranging from 0,05 pound per ton of ore treated to about 0,2 pound per ton of ore treated.

The consumption of acid and alkali which are employed as auxiliary reagents to bring the pH values to the necessary concentration to fulfill the oxidation in an acid or alkaline media is low and never more than two pounds per ton of ore milled. Approximately 1 pound per ton is sufficient, so that the pH of the pulp of the mineral slurry is operative between 5 to 9, which depends of the electronegativity of the metal in the mineral to be floated, i.e., of the oxidation-reduction potential involved in the process. The time of contact of the oxidizing agent and the ore may be varied depending on the particular ore treated as well as the concentration of the oxidizing agent and the concentration of hydrogen ions.

The collectors employed in this froth flotation process of my invention are: olefine carbinol, diolefine carbinol, or triolefine carbinol, adducts of alkyl polyhydroxymonocarboxylic acids, or alkyl polyhydroxydicarboxylic acids with no more than six hydroxyl groups per molecule.

The collector-frothers of the present invention which presumably functions by the chemical reaction based on the activation of the double carbon to carbon bond of an olefinic compound, i.e., with a π-bond, by the action of a metal (presumably oxide) is a higher oxidation state formed at a portion of the surface of the mineral to be floated, forming thus with the metal atoms exposed on the surface of mineral particle presumably addition compound, make the process operative.

It is obvious that the rest of the hydrocarbon compound or substituted hydrocarbon compound is oriented outward from the said particle. Thus the attachment of these (nonionic) collectors to the ore particle form a water repellent surface or barrier around at least a part of the surface of the ore particle and thereby facilitate the formation of froth when the ore slurry is agitated in the presence of air.

In view of the above outlined necessary characteristics of a good collector, it would appear that it is necessary for the organic unsaturated compound of applicant's collector-frother to be of a particular size, i.e., have an upper and a lower size limit or chain length. It has been found that the unsaturated organic compound should contain about 8 carbon atoms or more and two to six hydroxyl group in the adduct side chain attached to about 8 carbon atoms or more.

The upper limit on the size or number of carbon in the olefine, diolefine, or triolefine is determined primarily by the factors which necessitate to attach the metal in the mineral to be floated, i.e., the strength and scope of the bonding so to speak, and not to the solubility factor. The olefine portion of the molecule should have from 8 to 14 carbon atoms. The upper limit of the adduct is about 12 carbon atoms in which to maximum six carbon atoms is attached one hydroxyl group. Hence, the adducts of olefinic carbinol, diolefinic carbinol, or triolefinic carbinol, or alcohols, and alkyl polyhydroxymonocarboxylic acid or alkyl polyhydroxydicarboxylic acid contain from 16 to 24 carbon atoms.

The preferred embodiments of collector-frother in the olefinic resies are as follows:

Olefine carbinol adduct of glyceric acid, or glycerolglyceric acid, or gluconic acid, or saccharic acid.

Allyl carbinol adduct of gluconic acid

Hexenol adduct of glyceric acid

Octenol adduct of glycerolglyceric acid

Undecenol adduct of saccharic acid

Diallyl carbinol adduct of gluconic acid

Triallyl carbinol adduct of saccharic acid.

The method of making the various adducts is well known and described in the literature. Therefore, their method of preparation does not constitute a part of the present invention.

In the use of my collector-frothers, based on the π-bond activity, to float the mineral values, the ore is crushed, milled and sized to at least about 60 to 100 mesh, which depends on the particular ore treated. Milling to finer sizes is preferable. The crushed and sized ore is pulped and as a mineral slurry is ready for treatment in the flotation equipment with the oxidizing agent, which is always done prior to the addition of olefinic collector-frother.

An excess of oxidizing agents may be harmful for the collector-frother, which may oxidize to saturated hydrocarbon or split at the double bond. It is preferable to operate the flotation with fresh water after conditioning with oxidizing agents, i.e., to cycloning the oxidized mineral slurry, and then add fresh water. The used water of the flotation may be recycled as well as the used water of conditioning. After oxidizing of the mineral surface is accomplished the collector-frother and auxiliary agents, if any are to be used, are added for further treatment in the flotation equipment, i.e., in a second conditioner or directly in the first cell of a flotation stage. In the flotation cell the ore pulp is contacted with air to form a froth to achieve the separation of metal values from the gangue. Normally, the metal values present in the froth, overflow from each cell or stage. In most cases it is advantageous to use a multiple stage flotation process to treat the underflow or partially metal values barren pulp to increase the degree of separation or to enhance the degree of recovery.

Also, the use of varying amount of emulsifiers, dispersants and depressants etc. in different stages may be used to advantage to obtain the highest yields and best separations.

Having disclosed the novel collector-frothers of this invention as well as the handling of ore wherein the use of activation step as is the oxidizing, I have to say the last object of this invention is to provide a method for the flotation recovery of minerals containing oxides of iron, chromium, cerium, yttrium, antimony and phosphorous.

The above discussion illustrates my invention in a general way, but for a detailed illustration thereof the examples of flotation procedure are set forth below.

EXAMPLE 1

The activator-promoter used:
Potassium ferrate, barium ferrate, hydrochloric acid.
The collector-frother used:
Triallyl carbinol adduct of gluconic acid.
The purpose:
Recovery of magnetite from siliceous gangue.

500 grams of a lode magnetite containing 22.4 percent iron metal, was ground wet at 66 percent solids in a laboratory ball mill to pass 100 mesh sieve. In the flotation machine 0.1 pound per ton of potassium ferrate, and 0.2 pound per ton of barium ferrate, and 0.3 pound per ton of hydrochloric acid were added for oxidizing the magnetite surface. After conditioning for 5 minutes, the sample liquor was decanted and the flotation accomplished with fresh water and 0.3 pound per ton of triallyl carbinol adduct of gluconic acid. After adding the collector-frother the sample was conditioned for another five minutes and then aerated. The rougher concentrate was skimmed for 10 minutes. The rougher concentrate was cleaned with fresh water and 0.1 pound per ton of collector frother.

The results of this test were as follows:

Product	Weight percent	Assay percent	Distribution of iron percent
Concentrate	31,1	66,2	92,2
Tail, general + cleaner	68,9	2,6	7,8

EXAMPLE 2

The activator-promoter used:
Potassium chlorate.
The collector-frother used:
Diallyl carbinol adduct of saccharic acid.
The purpose:
Recovery of chromite.

500 grams of a lode chromite ore in serpentine with 26.0 percent Cr_2O_3 was ground wet at 66 percent solids in a laboratory ball mill with 1 pound per ton of sulfuric acid to pass 80 mesh sieve. In the machine 0.2 pound per ton of potassium chlorate was added at pH 6.0. Conditioned for 5 minutes; then the sample liquor was decanted and the flotation accomplished with fresh water. In the flotation machine 0.3 pound per ton of diallyl carbinol adduct of saccharic acid was added. Conditioned for 5 minutes, then aerated. The rougher concentrate was skimmed for 5 minutes. The rougher concentrate was cleaned with recycled water and 0.05 pound per ton of collector-frother.

The results of this test were as follows:

Product	Weight percent	Assay Cr_2O_3 percent	Distribution of Cr_2O_3 percent
Concentrate	53,5	46,0	94,1
Tail, general + cleaner	46,5	0,35	5,9

EXAMPLE 3

The activator-promoter used:
Potassium ferrate.
The collector-frother used:
Diallyl carbinol of saccharic acid.
The purpose:
Recovery of ilmenite.

500 grams of a lode ilmenite in crystalline schist containing 8.5 percent titanium metal was ground wet at 66 percent solids in a laboratory ball mill with 0.5 pound per ton of sulfuric acid to pass 100 mesh sieve. The sample liquor was decanted and the flotation accomplished with fresh water. In the flotation machine 0.2 pound per ton of diallyl carbinol adduct of saccharic acid was added. Conditioned for 5 minutes, then aerated. The rougher concentrate was skimmed for 5 minutes. The rougher concentrate was cleaned with used water and 0.05 pound per ton of collector-frother.

The results of this test were as follows:

Product	Weight percent	Assay Ti percent	Distribution of titanium percent
Concentrate	26,6	30,2	94,4
Tail, general + cleaner	73,4	0,67	5,6

EXAMPLE 4

The activator-promoter used:
Potassium dichromate.
The collector-frother used:
Octenol adduct of glycerolglyceric acid.
The purpose:
Recovery of antimony.

500 grams of a lode servantite and senarmontite with 14.0 percent antimony metal was ground wet at 66 percent solids in a laboratory ball mill to pass 65 mesh sieve. In the flotation machine 0.5 pound per ton of sulfuric acid and 0.2 pound per ton of potassium dichromate were added. Conditioned for 5 minutes, then the sample liquor was decanted. Transferring the sample to the flotation machine and with fresh water, 0.2 pound per ton of octenol adduct of glycerolglyceric acid was added. Conditioned for 2 minutes, then aerated. The rougher concentrate was skimmed for 4 minutes. The rougher concentrate was cleaned with used water and 0.05 pound per ton of collector-frother.

The results of this test were as follows:

Product	Weight percent	Assay Antimony percent	Distribution of antimony percent
Concentrate	16,3	74,1	93,0
Tail, general + cleaner	83,7	1,17	7,0

EXAMPLE 5

The activator-promoter used:
Potassium chlorate, Potassium ferrate.
The collector-frother used:
Undecenol adduct of gluconic acid.
The purpose:
Recovery of hematite.

500 grams of a lode specular hematite with 33.2 percent of iron metal was ground wet at 66 percent solids in a laboratory ball mill with 1 pound per ton of sulfuric acid to pass 80 mesh sieve. In the flotation mashine 0.15 pound per ton of potassium chlorate, and 0.15 pound per ton of potassium ferrate was added. Conditioned for 5 minutes, then the sample liquor was decanted. Transferring the sample to the flotation machine and with fresh water 0.3 pound per ton of undecenol adduct of gluconic acid was added. Conditioned for 3 minutes then aerated. The rougher concentrate was skimmed for 5 minutes. The rougher concentrate was cleaned with used water and 0.05 pound per ton of collector-frother.

The results of this test were as follows:

Product	Weight Percent	Assay iron percent	Distribution of iron percent
Concentrate	48.0	63.8	92.3
Tail, general + cleaner	52.0	5.0	7.7

EXAMPLE 6

The activator-promoter used:
Barium ferrate, hydrochloric acid.
The collector-frother used:
Undecenol adduct of gluconic acid.
The purpose:
Recovery of phosphate rock.

500 grams of a lode phosphate rock with 8.2 percent P_2O_5 was ground wett at 66 percent solids in a laboratory ball mill to pass 65 mesh sieve. In the flotation machine 0.5 pound per ton of hydrochloric acid, and 0.25 pound per ton of barium ferrate were added. Conditioned for 5 minutes, then the sample liquor was decanted. Transferring the sample in the flotation machine and with fresh water 0.3 pound per ton of undecenol adduct of gluconic acid was added. Conditioned for 3 minutes, then aerated. The rougher concentrate was skimmed for 3 minutes. The rougher concentrate was cleaned with used water and 0.05 pound per ton of collector-frother.

The results of this test were as follows:

Product	Weight percent	Assay P_2O_5 percent	Distribution of P_2O_5 percent
Concentrate	19.5	27.0	93.4
Tail, general + cleaner	80.5	1.0	9.6

EXAMPLE 7

The activator-promoter used:
Potassium permanganate, sodium fluoride, hydrochloric acid.
The collector-frother used:
Diallyl carbinol adduct of gluconic acid.
The purpose:
Recovery of franklinite.

The quantity of franklinite mineral was small, therefore, the flotation investigations were accomplished in a 50 grams cell with 10 grams of franklinite, and 40 grams of a mixture of quartz, calcite, and serpentine. The addition of the reagents was done dropwise. The oxidation effect of permanganate in conjunction with sodium fluoride in a hydrochloric acid media was excellent regarding the small amount of oxidant needed, as well as the speed, i.e. the rate of the reaction for the oxidation effect. This qualitative flotation test gave the float fraction assaying 95 percent of recovered franklinite by microscopic count, in a concentrate weighing 10.2 grams.

EXAMPLE 8

The activator-promoter used:
Barium ferrate, sodium fluoride, hydrochloric acid.
The collector-frother used:
Diallylpropyl carbinol adduct of gluconic acid.
The purpose:
Recovery of trevorite.

The quantity of trevorite mineral was small, therefore, the flotation investigations were accomplished in a 50 grams cell with 10 grams of trevorite, and 40 grams of serpentine. The addition of the reagents was done dropwise. The oxidation effect of barium ferrate in conjunction with sodium fluoride in a hydrochloric acid media was excellent regarding the small amount of oxidant needed, as well as the rate of the reaction. This qualitative flotation test gave the float fraction assaying 96 percent of recovered trevorite by microscopic count, in a concentrate weighing 10 grams.

EXAMPLE 9

The activator-promoter used:
Potassium chlorate.
The collector-frother used:
Octenol adduct of gluconic acid.
The purpose:
Recovery of monazite.

The quantity of monazite mineral was small, therefore, the flotation investigations as well as the representative test were accomplished in a 50 grams flotation cell with 10 grams of monazite, and 40 grams of a mixture of quartz and feldspar. The addition of the reagents was done dropwise. This qualitative flotation test gave the float fraction assaying 92.0 percent of recovered monazite by microscopic count, in a concentrate weighing 11 grams.

It is understood that the heretofore detailed discussions are for the purpose of illustration only, and is not intended as being limiting to the spirit of the invention or scope of the appended claims.

I claim:

1. An improved of (oxidic) of beneficiating ores and minerals selected from the group of oxide ores and minerals or iron, chromium, cerium, yttrium, antimony, and phosphorous by froth flotation process to produce a froth concentrate of desired metal value which improvement comprises; effecting the froth flotation of the ore by treating the comminuted ore of the mineral slurry of aforesaid ores and minerals with inorganic oxidizing agents, followed by an effective amount of a collector-frother of an olefine (alkyl vinyl) or po-

lyolefine (alkyl polyvinyl) carbinol adduct of alkyl polyhydroxycarboxylic acids, said olefine or polyolefine carbinols have from 8 to 14 carbon atoms, said adducts have from 10 to 24 carbon atoms, said alkyl polyhydroxycarboxylic acid (having at least 6) have from two to six hydroxyl groups per molecule; and recovering a froth concentrate relatively rich in the desired metal values to leave tailings relatively poor in the desired metal values.

2. A method according to claim **1,** wherein the (activator-promoter is) inorganic oxidizing agents are selected from the group (of) consisting of chlorate, chromate, dichromate, permanganate, ferrate.

3. A method according to claim **1,** wherein said oxidizing agents are added (by reducing potassium permanganate in an acid slurry made of hydrochloric acid and) in the presence of sodium or calcium fluoride in a pulp of mineral slurry acidified with hydrochloric acid or sulfuric acid in conjunction with (the) aforesaid oxidizing agents.

4. A method according to claim **1,** wherein the collector-frother is monoolefine (amylene, octylene, dodecylene, tetradecylene) carbinol adduct of (glyceric acid, glycerolglyceric acid, gluconic acid, saccharic acid, or mixture thereof) (hexane-, decane-, or tetradecaneglyceric acid, hexane-, or decanegluconic acid, hexane-, or decanesaccharic acid or mixture thereof) alkyl polyhydroxycarboxylic acids, said monoolefine have from 8 to 14 carbon atoms, said acids have from 2 to 6 hydroxyl groups, said adducts (consisting) have from 10 to 20 carbon atoms for the entire (vinyl) monoolefine carbinol adducts of alkyl polyhydroxycarboxylic acids.

5. A method according to claim **1,** wherein the collector-frother is diolefine (allyl carbinol, propylallyl carbinol, amylallyl carbinol, octylallyl carbinol, or tetramethylallyl carbinol) carbinol adduct of (glyceric acid, glycerolglyceric acid, gluconic acid, saccharic acid or mixture thereof) (hexane-, decane-, or tetradecaneglyceric acid, hexane--, or decanegluconic acid, hexane-, or decanesaccharic acid, or mixture thereof) alkyl polyhydroxycarboxylic acid, said diolefine have 10 to 14 carbon atoms, said acids have 2 to 6 hydroxyl groups, said adducts (consisting) have from 13 to 22 carbon atoms for the entire (allyl) diolefine carbinol adduct of alkyl polyhydroxycarboxylic acids.

6. A method according to claim **1,** wherein the collector-frother is triolefine (trivinyl carbinol such as heptyltrivinyl carbinol, nonyltrivinyl carbinol, undecyltrivinyl carbinol) carbinol adduct of (glyceric acid, glycerolglyceric acid, gluconic cid, saccharic acid, or mixture thereof) (hexane-, or decaneglyceric acid, hexane-, or decane-glycerolglyceric acid, or hexane-, or decanesaccharic acid, or mixture thereof) alkyl polyhydroxycarboxylic acids, said triolefine carbinols have 12 to 14 carbon atoms, said alkyl polyhydroxycarboxylic acids have 2 to 6 hydroxyl groups, said adducts have from 16 to 24 carbon atoms for the entire (trivinyl) triolefine carbinol adducts.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,909,399 Dated September 30, 1975

Inventor(s) Vojislav Petrovich

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 37, "agents" should read -- states --. Column 3, line 57, "is" should read -- in --. Claims 1 through 6, should appear as shown below:

1. An improved of beneficiating ores and minerals selected from the group of oxide ores and minerals or iron, chromium, cerium, yttrium, antinony, and phosphorous by froth flotation process to produce a froth concentrate of desired metal value which improvement comprises; effecting the froth flotation of the ore by treating the comminuted ore of the mineral slurry of aforesaid ores and minerals with inorganic oxidizing agents, followed by an effective amount of a collector-frother of an olefine or polyolefine carbinol adduct of alkyl polyhydroxycarboxylic acids, said olefine or polyolefine carbinols have from 8 to 14 carbon atoms, said adducts have from 10 to 24 carbon atoms, said alkyl polyhydroxycarboxylic acid have from two to six hydroxyl groups per molecule; and

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CERTIFICATE OF CORRECTION

Patent No. 3,909,399 Dated September 30, 1975

Inventor(s) Vojislav Petrovich

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

recovering a froth concentrate relatively rich in the desired metal values to leave tailings relatively poor in the desired metal values.

2. A method according to claim 1, wherein the inorganic oxidizing agents are selected from the group consisting of chlorate, chromate, dichromate, permanganate, ferrate.

3. A method according to claim 1, wherein said oxidizing agents are added in the presence of sodium or calcium fluoride in a pulp of mineral slurry acidified with hydrochloric acid or sulfuric acid in conjunction with oforesaid oxidizing agents.

4. A method according to claim 1, wherein the collector-frother in monoolefine carbinol adduct of alkyl polyhydroxy-carboxylic acids, said monoolefine have from 8 to 14 carbon atoms, said acids have from 2 to 6 hydroxyl groups, said adducts have from 10 to 20 carbon atoms for the entire

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

monoolefine carbinol adducts of alkyl polyhydroxycarboxylic acids.

5. A method according to claim 1, wherein the collector-frother is diolefine carbinol adduct of alkyl polyhydroxycarboxylic acid, said diolefine have 10 to 14 carbon atoms, said acids have 2 to 6 hydroxyl groups, said adducts have from 13 to 22 carbon atoms for the entire diolefine carbinol adduct of alkyl polyhydroxycarboxylic acids.

6. A method according to claim 1, wherein the collector-frother is triolefinecarbinol adduct of alkyl polyhydroxycarboxylic acids, said triolefine carbinols have 12 to 14 carbon atoms, said alkyl polyhydroxycarboxylic acids have 2 to 6 hydroxyl groups, said adducts have from 16 to 24 carbon atoms for the entire triolefine carbinol adducts.

Signed and Sealed this

sixth Day of *January 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks