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FLOTATION PROCESS OF CONCENTRATING SULPHIDE ORES.

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To all whom it may concern:

Be it known that I, HUGO EDWARD JAMES FREDRICK, a citizen of the United States, residing at San Francisco, in the county of San Francisco and State of California, have invented certain new and useful Improvements in Flotation Processes of Concentrating Sulphide Ores; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to a flotation process of concentrating sulphide ores, whether they be natural or artificial, as well as to the concentration of ores containing copper whether it be native or precipitated, and has for its object to provide a method which will be more efficient and therefore less costly than those heretofore proposed.

With this and other objects in view the invention consists in the novel steps and combinations of steps constituting the process, all as will be more fully hereinafter disclosed and particularly pointed out in the claims.

In order that the precise invention may be the more clearly understood it is said:—It is well known that in selecting flotation agents for concentrating sulphide ores it has been customary to use greater or less percentages of the "tar acids" or aromatic hydroxy acids, of the mon-acid phenol type, chiefly in the form of a cresol such as $CH_3.C_6H_4OH$.

It is also well known that flotation oils consisting largely of pine oil, coal tar creosote, eucalyptus oil, crude coal tar and kindred substances have found their way into use to a greater or less extent, but no one prior to this invention seems to have discovered the real compounds upon which depend the efficiencies for flotation purposes of these various substances.

I have discovered on the other hand, that the active principle upon which an efficient flotation depends occurs naturally in these oils or tars in more or less minute and accidental quantities.

I have further discovered that if the acid, basic and neutral constituents of said oils and tars are separated out, the frothing and selective portions of said oils and tars will always accompany said acid or basic, or acid and basic constituents, but never the neutral portions. By basic constituents I mean those portions that are extracted by dilute mineral acids, by acid constituents I mean those portions that are extracted by dilute alkalis, and by neutral constituents I mean the residue after treatment with an acid and an alkali.

I have further discovered that effective frothing flotation agents are relatively more soluble in water than are those neutral oils and substances which are not frothing flotation agents.

I have also found in the actual milling of porphyritic ore, containing chalcocite and chalcopyrite, while the pulp is going through its successive stages of grinding, classification, etc., that in some cases the resultant feed to the flotation is sometimes acid, sometimes neutral, and at other times alkaline or basic. The difference in the character of the reaction of the pulp may be explained by slight changes in the ore as mined, by the varying quantity of mineral alkali and acid purposely added, by the oxidizing action of the air, or by the type of mill water used, which is influenced by the fact that in general practice it is customary to reclaim the mill water and use it again.

I have also discovered that if an acid ore is thus fed to the flotation apparatus, a soluble compound of the general chemical type $R(OH)x$ where R represents a carbocyclic hydrocarbon, will be effective in making an efficient and well mineralized froth. This result is obtained notwithstanding the fact that these carbocyclic hydrocarbons are not so soluble in dilute mineral acid solutions as they are in neutral solutions or in slightly alkaline solutions.

These said carbocyclic hydrocarbons represented by R, as is well known, often have side chains other than those composed of OH.

I have still further discovered when the ore fed to the flotation machine is basic, that compounds of a heterocyclic type, contain-

ing nitrogen members are effective. These last mentioned heterocyclic compounds are all basic in character, pyridine is one of them, and they are not so soluble in dilute mineral alkali solutions, as they are in neutral, or slightly acid solutions.

Now, by carrying on experiments to determine more efficient reagents for the flotative separation of copper and other ores, I found that the erratic nature of the flotation results found in practice are caused more or less by the difference of the reaction (whether acid or basic) of the flotation feed; and that the action can be made more or less uniform by the purposeful addition of either a mineral acid or an alkali, depending, as the case may be, upon the general type of the flotation oil used, the amount being based on the preponderance of the acid or the basic substances present in the said oil substance.

Following the above discoveries, I further found that if a flotation agent is made to contain a substantial amount of, or is composed of what I will call an "acid substance of the aromatic hydroxy type" mixed with a basic substance of a "nitrogen heterocyclic type" in substantially combining proportions, then there results a flotation agent that will work about equally well on ores fed to the flotation machine, whether said ores are slightly acid or are slightly basic.

As an example of said mixtures or flotation agents that are of value I may mention pyridine and phenol mixed in molecular proportions; quinoline and phenol mixed in molecular proportions; pyridine and cresol in molecular proportions; quinoline and cresol in molecular proportions and a number of others that will be obvious to chemists, in view of what has been said above, such for example as pine oils, pine tars and coal tar oils, mixed with basic substances as pyridine but not separately with acid hydroxy compounds. In such case we have a mixture of an hydroxy acid substance and a nitrogen membered base substance.

The use of these flotation mixtures result in a much cleaner concentrate and a better recovery, than does the use of straight aromatic hydroxy acid compounds, or of the straight nitrogen members of the heterocyclic bases. Further, the use of these flotation mixtures results in higher efficiencies when pure than when mixed with neutral oils.

In carrying out this invention I may take a small amount of a mixture in molecular proportion or substantially combining proportions of an aromatic hydroxy acid such as cresol and a nitrogen membered heterocyclic base such as a pyridine and add the same to a pulp whether it be slightly acid or slightly basic. This pulp is then subjected to a mechanical agitation, or to a direct aeration without agitation, as by passing air, or other gas, thereinto through a porous medium, as in the well known bubbles column process. If the pulp is acid the basic or pyridine portion of the flotation agent will be absorbed by the mineral or other acid present, that is, it will form a true salt of the base and mineral acid and go into solution with the water of the pulp, and it will therefore act more or less as a frothing agent. At the same time, the acid portion of the frothing mixture, or agent, will be set free and it will accomplish the selection of the mineral matter over the gangue. If the pulp is basic, the acid portion of the agent is absorbed by the alkali present and acts as a frothing agent, while at the same time, the basic portion is set free and determines the selection of mineral matter over the gangue. The amount of the flotation agents used will vary somewhat with different ores, and have been found by me in practice to be between 0.15 pounds to 0.75 pounds per ton of dry ore.

It will now be clear that in proceeding in general according to my invention I may take one of several courses:— (*a*) I may first determine whether the ore is acid or basic, and if basic, I may concentrate the same with a basic frothing agent of a heterocyclic type containing a nitrogen member. These compounds are chemically known under the name of nitrogen-cyclo-compounds and fall under the subtitles of azines, diazines, triazines, tetra-azines, interlocked rings, etc., pyridine and quinoline being well known examples.

(*b*) If the ore is acid I may concentrate the same with an acid frothing agent of an aromatic hydroxy acid type of which the cresols are examples, and which are found in varying quantities in pine oil, coal tar oil, etc.

(*c*) I may mix an aromatic hydroxy acid compound with a heterocyclic compound containing a nitrogen member, in substantially neutralizing proportions, and thus produce a frothing mixture, or agent, which will be substantially neutral, and I may concentrate the ores with this agent whether they be acid or neutral.

(*d*) If an ore is basic I may treat it with a waste acid solution until it becomes acid, and then froth it with an acid aromatic hydroxy compound; or if the ore is acid, I may treat it with a waste basic solution until it becomes basic, whereupon I may froth it with a basic nitrogen-cyclo-compound. But I prefer in most cases to employ the substantially neutral frothing agent mentioned under paragraph (*c*) above.

(*e*) Since said neutral agent or compound will be effective on either acid or basic ores, it is evident that a preponderance of acid or basic substances mixed with said neutral agent can also be used; and especially when

said additional substances will have the effect of reducing an excessively strong basicity, or acidity in the ore.

It follows from the foregoing that my invention broadly comprises the frothing of basic pulps with basic nitrogen-cyclo-compounds, the frothing of acid pulps with hydroxy acid compounds, or the frothing of either acid and basic pulps with a mixture of acid and basic compounds. In all cases the compounds employed must be of the cyclic or benzene ring type in order to secure a true frothing action. Any suitable means may be employed to recover the values separated from the gangue by the frothing action.

I would call especial attention to the fact not now recognized in flotation practice, that a successful flotation would not be possible with the usually small amounts of so called flotative agents employed, were it not for the presence of the dissolved mineral salts or substances that are found either in the mill water, or are derived from the soluble constituents of the ore. Stated in other language, a well washed pulp using distilled water will give a negative frothing value with any organic frothing agent when used in the quantities usually employed in practice, but will yield a positive frothing value if to the same well washed pulp and distilled water there is added almost any soluble mineral substance such as the sulphates of calcium, sodium, magnesium, etc., or the oxides, chlorides, etc., of these metals. It therefore follows that some non-frothing ores can be converted into frothing ores by the suitable addition of soluble mineral matters.

It is obvious that those skilled in the art may vary the details of the process without departing from the spirit of the invention, and therefore, I do not wish to be limited to the above disclosure except as may be required by the claims.

What I claim is:—

1. The process of concentrating ores that are amenable to flotation processes which consists in subjecting the pulp of said ores whether acid or basic to the frothing action of a substantially neutral flotation agent consisting of a hydroxy acid compound and a nitrogen-cyclo-compound in substantially neutralizing proportions; and recovering the values thus separated from the gangue, substantially as described.

2. The process of concentrating ores that are amenable to flotation processes which consists in subjecting the pulp of said ores, whether acid or basic to the frothing action of a substantially neutral flotation agent consisting of a hydroxy acid compound and a nitrogen-cyclo-compound in substantially neutralizing proportions and to which have been added additional compounds of a non-neutral nature; and recovering the values thus separated from the gangue, substantially as described.

3. The process of concentrating ores which consists of subjecting a pulp of said ores to the action of less than one per cent of a mixture of an aromatic hydroxy acid and an nitrogen-membered heterocyclic base in substantially neutralizing proportions and recovering the values thus separated.

4. The process of concentrating ores which consists of subjecting a pulp of said ores to the action of less than one per cent of a mixture of an aromatic hydroxy acid and an nitrogen-membered heterocyclic base in proportions sufficient to alter the base character of the nitrogen cyclo compound, and recovering the values thus separated.

In testimony whereof I affix my signature.

HUGO EDWARD JAMES FREDRICK.