

Sept. 20, 1960

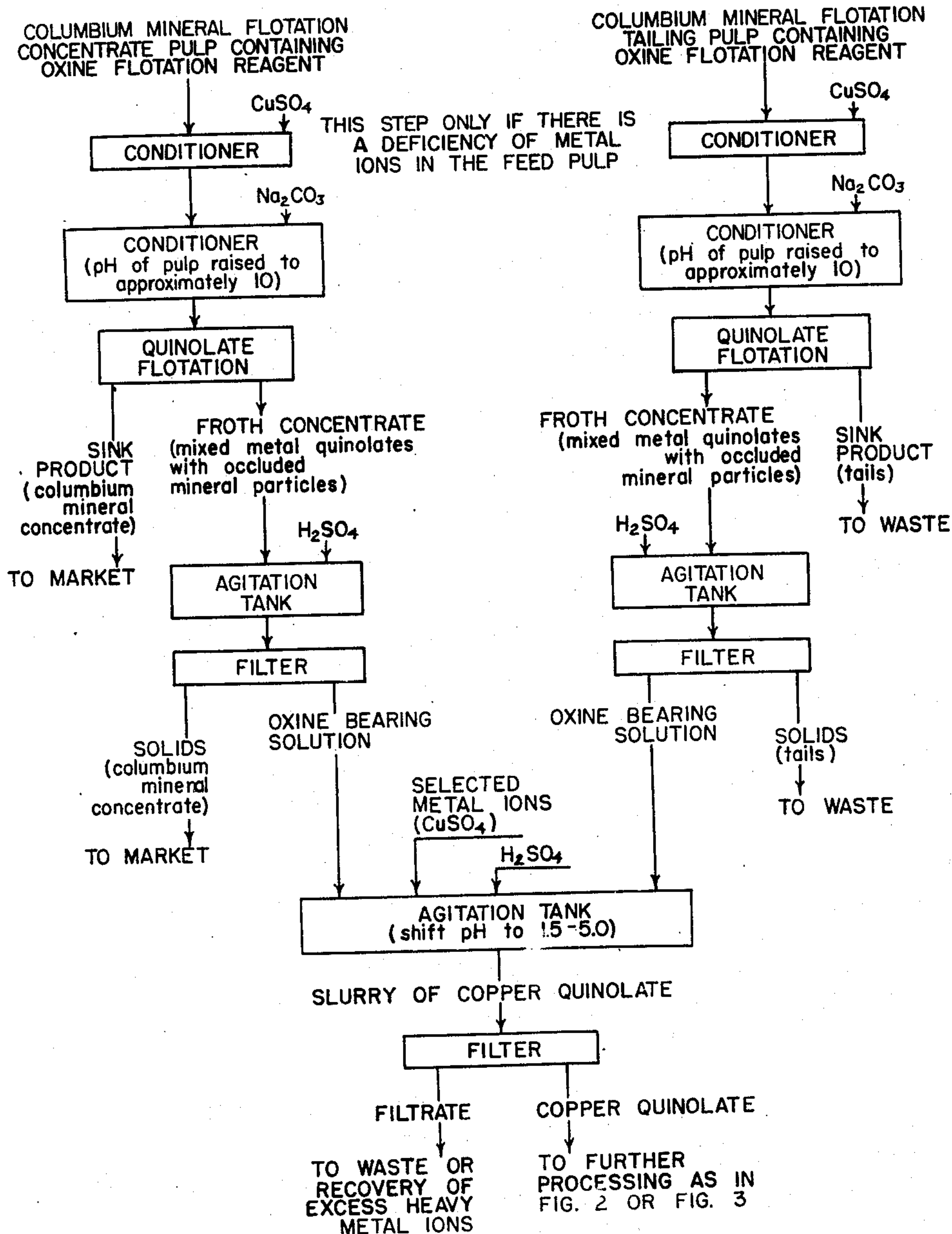
A. W. LAST ET AL  
PROCESS FOR RECLAIMING OXINE FLOTATION  
REAGENT FROM PRODUCTS OF FLOTATION

2,953,569

Filed Feb. 27, 1958

2 Sheets-Sheet 1

FIG. 1.



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2 Sheets-Sheet 2

FIG. 2.

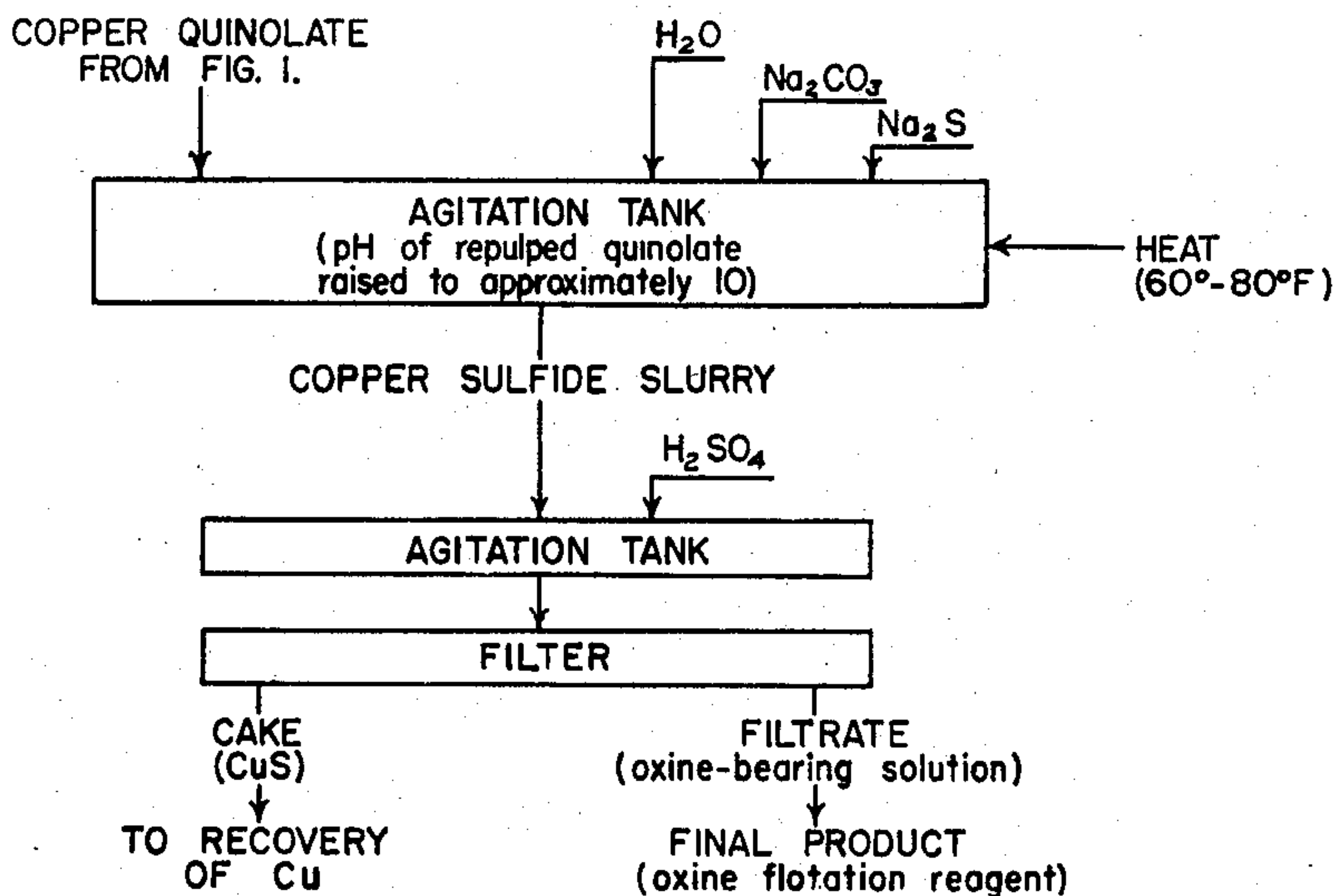


FIG. 3.

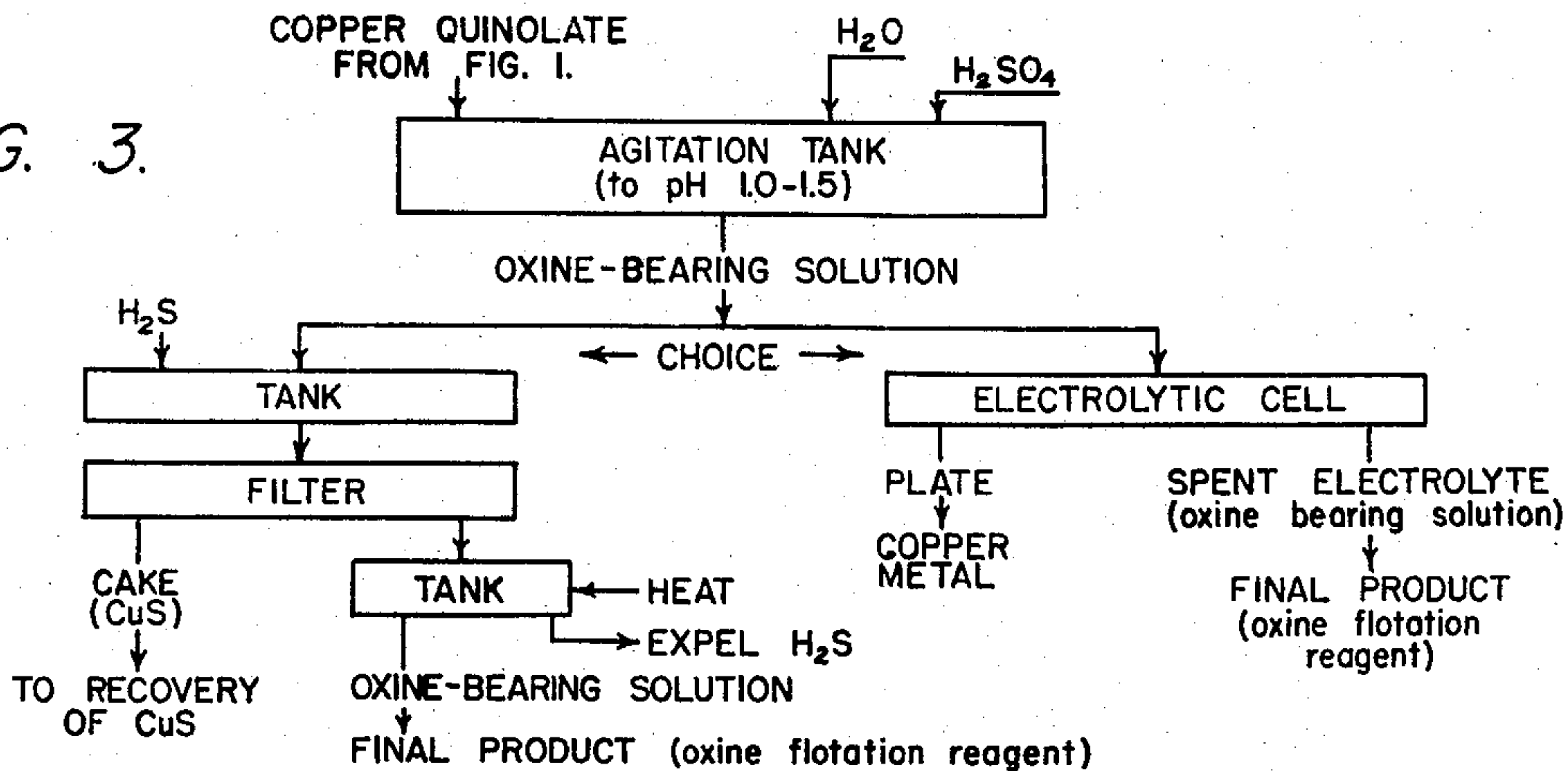
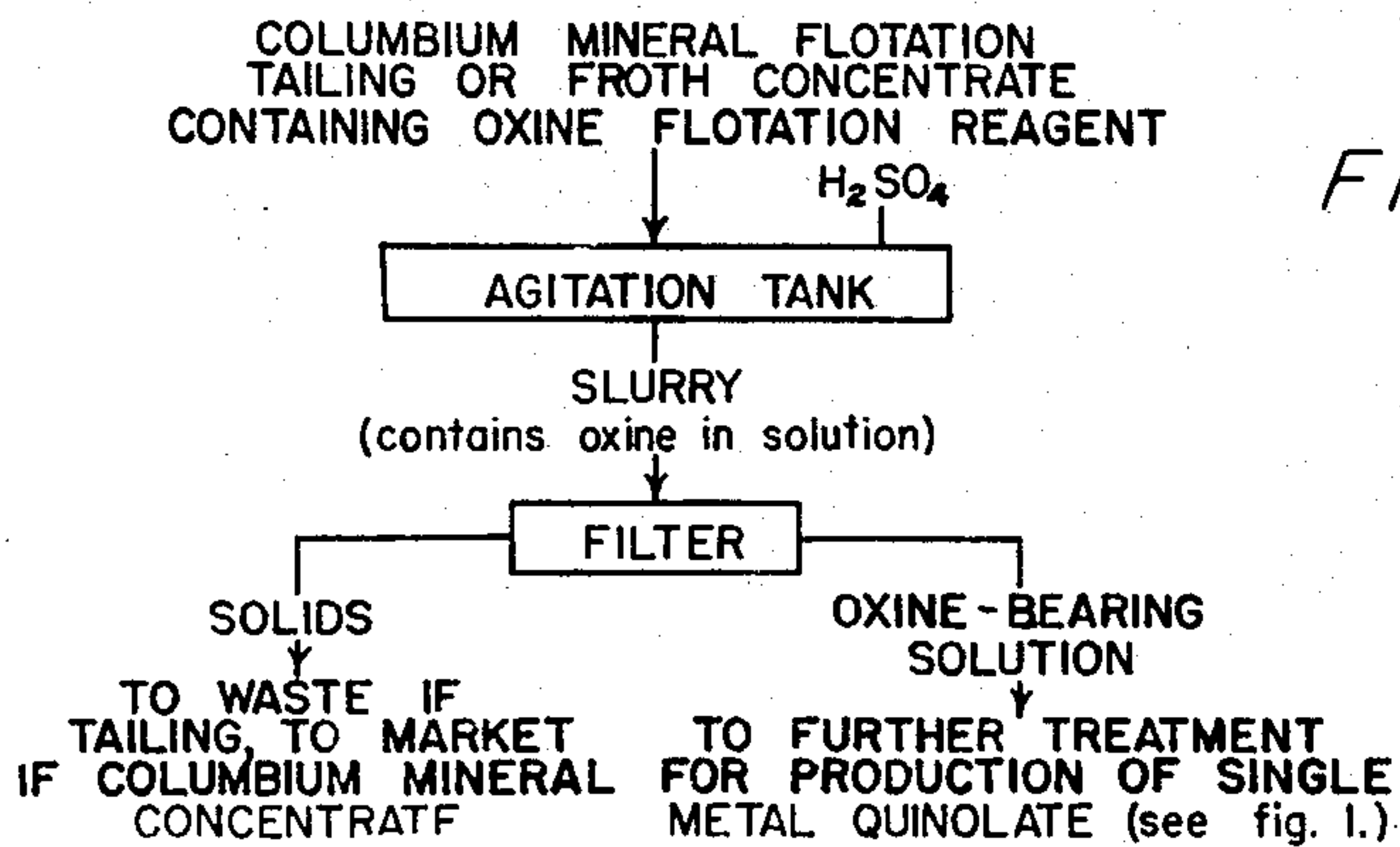


FIG. 4.



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2,953,569

## PROCESS FOR RECLAIMING OXINE FLOTATION REAGENT FROM PRODUCTS OF FLOTATION

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6 Claims. (Cl. 260—270)

This invention relates to the reclaiming of flotation reagents from the froth concentrates and tailings produced by the flotation of metallurgical materials.

In our copending application Serial Number 689,435, filed October 10, 1957, entitled "Process of Concentrating Columbium Minerals by Froth Flotation" (now U.S. Patent No. 2,875,896 granted March 3, 1959), which is a continuation-in-part of our application Serial Number 612,849, filed September 28, 1956 (now abandoned), we have disclosed and claimed a flotation process for the recovery of columbium (niobium) mineral values from ores containing the same by the use of 8-quinolinol ( $C_9H_7NO$ ), commonly called oxine.

While this oxine flotation reagent produces effective results in practice, it is considerably more expensive than reagents customarily used in the flotation art. It is economically feasible as a flotation reagent only because of the present high price of columbium. Under such circumstances, recovery of the expended flotation reagent from the flotation products becomes highly desirable.

In accordance with the present invention, we are able to effectively and economically treat both froth concentrates and tailings produced by oxine flotation of metallurgical pulps, to reclaim the oxine flotation reagent for re-use in further flotation operations.

A principal object of this invention, then, is to provide a process whereby an oxine flotation reagent may be reclaimed for re-use from the products of flotation on a practical, industrial basis.

We have found that the oxine used as a flotation reagent is present in the flotation products as both free oxine and insoluble quinolates, predominantly quinolates of iron, aluminum, calcium, and magnesium, but also including those of other metals, especially heavy metals such as copper and nickel.

Our process takes advantage of this finding by providing, first, for the separation of both the free oxine and the quinolates from the mineral solids of the flotation product pulps, second, changing the mixed metal quinolates and the free oxine to a single quinolate of a heavy metal selected from that group of heavy metals which form highly insoluble sulfides, namely, copper, nickel, cobalt, mercury, and antimony, and third, treating the single metal quinolate to remove the metal ions, whereby an oxine product useful as a reagent in the flotation of additional quantities of mineral is obtained.

An outstanding feature of the invention is the separation of the oxine reagent from the flotation product pulps, namely, the froth concentrate pulp and the tailing pulp, by flotation, resulting in a froth product in which the oxine reagent is concentrated.

We have found that this can be done by raising the pH of such a pulp to an extent insuring the selective flotation of the metal quinolates present. Ordinarily, a large part, if not all, of the oxine in the pulp will be in the form of water-insoluble, metal quinolates, due to the aforementioned metal ions naturally present in the pulps. Any

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free oxine can be put into the form of a water-insoluble metal quinolate by the addition to the pulp of ions of a suitable metal, conveniently a heavy metal, such as copper, in the form of a salt, e.g. copper sulfate.

The metal quinolates recovered by this flotation step are in the form of flocs, which tend to occlude mineral particles. They are dissolved in acid, and the oxine-bearing solution so-obtained is separated from the solids, as by filtering.

Separation of the free oxine and the quinolates from the mineral solids of the pulps obtained from the mineral-concentrating flotation may also be accomplished by adding acid thereto and filtering. The quinolates are dissolved to form free oxine and metal ions, which, together with any free oxine and any metal ions naturally present in the pulps, are recovered in the filtrate. The filtrate corresponds to the oxine-bearing solution derived from the quinolate flotation procedure, and, like it, contains mixed metal ions as well as free oxine.

This procedure is not economic in most instances, however, due to excessive consumption of acid by the usual pulps.

By the addition of ions of a selected metal, preferably copper, to either of these solutions and by adjustment of the pH of the solution, a particular metal quinolate is precipitated.

This precipitate is then treated to remove the ions of the selected metal, leaving an oxine product which is well adapted for use as a flotation reagent in the processing of additional quantities of the columbium ore materials.

There are several possible ways of removing the metal ions from the precipitate. Thus, the precipitate may be treated to produce an oxine-bearing solution containing a sulfide of the metal concerned, followed by removal of such sulfide from the solution by filtration, for example. Again, the precipitate may be dissolved in acid and the resulting solution subjected to electrolysis or to treatment with a precipitant for the oxine present.

Further objects and features of the invention will become apparent from the following detailed description of the particular preferred practices illustrated by way of example in the flow sheets of the accompanying drawings.

In the drawings:

Fig. 1 illustrates, up to the quinolate-treatment stage, a typical application of the process to columbium mineral flotation products, utilizing quinolate flotation for the oxine-separation step;

Fig. 2 shows a preferred way of treating the single metal quinolate to produce the final product;

Fig. 3 presents an alternative way of treating the single metal quinolate; and

Fig. 4 illustrates the way acid is utilized for the oxine-separation step in place of the quinolate flotation step of Fig. 1.

Referring to the drawings:

As indicated in Fig. 1, preferably both the froth concentrate and the tailing pulps derived from a flotation operation applied to a columbium ore and utilizing oxine (8-quinolinol) as a reagent are treated in accordance with the invention. Such a columbium mineral flotation operation is fully set forth in our previously referred to, copending application Serial Number 612,849, now abandoned.

These pulps ordinarily have a pH of about 6.5 to 7.5 and contain both free oxine and precipitated oxine in the form of metal quinolates resulting from combination with certain metal ions naturally present in the pulps. The relative proportion of free and precipitated oxine will depend in each instance upon the quantity of such metal ions in the pulps. As mentioned hereinbefore, heavy



metals, e.g. copper, iron, nickel, cobalt, mercury and antimony, combine with free oxine to form water-insoluble quinolates, as do also certain of the light metals, such as aluminum, calcium, and magnesium.

With particular reference to Fig. 1, if tests show a significant quantity of free oxine in the pulps, metal ions—most suitably heavy metal ions, such as copper—are added by, for example, introducing a heavy metal salt, such as  $\text{CuSO}_4$ , as indicated, and conditioning therewith. Ordinarily, there will be naturally present in the pulps enough iron and other suitable metal ions to make it unnecessary to add much, if any, of the ion-producing salt.

To effect selective flotation of the precipitated metal quinolates, which occur as flocs, it is necessary that the pH of the pulps be raised. We have found that, at approximately pH 10, flotation is selective to the quinolates, and that practically none of the mineral solids are carried over in the froth, except as they are occluded by and within the flocs.

As indicated, the pH of the feed pulps is raised most conveniently by conditioning with sodium carbonate, whereupon the conditioned pulp is passed to rougher flotation cells for flotation treatment. If frothing is insufficient, a little pine oil or other frother may be added; otherwise, flotation of the quinolate flocs is accomplished without the addition of flotation reagents.

The sink product from the mineral tailing flotation is passed to waste. The sink product from the mineral concentrate flotation is, however, the original columbium mineral concentrate. As such, it represents the marketable product from the mineral flotation procedure and is recovered.

The flotation is preferably carried out in rougher and cleaner stages, as is customary in flotation practice, the float product from the rougher flotation being passed to cleaner cells for repeated flotation, and the cleaner tailing being recycled to the rougher cells.

The froth concentrate from the cleaning operation contains the metal quinolate flocs, which are preferably dissolved in acid to release occluded mineral particles and to place the oxine in solution. Any mineral acid is applicable, but sulfuric acid is preferred from an economic standpoint. As indicated, this operation may be conveniently carried out in an agitation tank, the resulting slurry being passed to filtration for separation of the oxine-bearing solution from the solids. Such solids are passed to waste or handled as a marketable product, depending upon whether the feed pulp is tailing or columbium mineral concentrate.

The clear but impure, oxine-bearing, acid solution represents an intermediate product, which, with further processing in accordance with the invention, yields an oxine-bearing solution useful as a reagent in the flotation of additional quantities of columbium minerals from their ores or from which a purified oxine may be obtained.

Such intermediate solution contains ions of various metals, notably calcium, magnesium, aluminum, and iron, the latter being principally in ferric form and the most difficult to eliminate. In order to obtain a solution most suitable for further processing, ions of a metal selected to form highly insoluble sulfides, namely, copper, nickel, cobalt, mercury, and antimony, are first introduced into the solution, whereupon the pH of such solution is carefully raised to precipitate a quinolate of the selected metal.

In practice, it is preferred to run the acid filtrate into an agitation tank, where the selected metal ions (preferably provided by copper sulfate, as indicated) are first added in amount sufficient to insure the precipitation of the quinolate when the pH of the solution is increased. Thereupon, a base is added to shift the pH to a value from about 1.5 to 5.0, depending upon the selected metal ion; in the case of cupric copper the pH should be 2.0

plus or minus. Sodium hydroxide is ordinarily used for the purpose.

The resulting quinolate slurry is passed to filtration, where the quinolate solids are separated from the solution and, incidentally, from any excess metal ions that may be present. The latter may be recovered from the filtrate in some suitable manner if desired.

There are several choices available for the treatment of the quinolate solids to remove the metal ions and yield, as a final product, a solution useful as a flotation reagent.

The presently preferred procedure, indicated as such in the flow sheet of Fig. 2, involves repulping the quinolate solids with water in a suitable agitation tank to a conveniently handled slurry, then adding a carbonate, e.g. sodium carbonate, to raise the pH of the pulp to approximately 10, adding a sulfide, e.g. sodium sulfide, and, finally, heating the pulp (preferably from approximately 60° to 80° F.) to precipitate a sulfide of the selected metal—here copper sulfide. The resulting slurry is treated with acid, advantageously sulfuric, to adjust its pH to approximately 5 to dissolve the oxine; and, is then filtered. Copper sulfide is recovered as a filter cake. The filtrate is an oxine solution free of metal ions capable of forming insoluble sulfides, and is, therefore, useful as a flotation reagent.

Other procedures require that the quinolate of the selected metal be first dissolved by acid, as indicated in the flow sheet of Fig. 3 where a choice of metal-ion-removing procedures is presented.

The oxine-bearing, acid solution may be advantageously treated by what is essentially a known procedure, see "Recovery of Waste 8 Hydroxyquinoline" by S. T. Balyok, Zavodskoga Lab. 5, 878 (1936), cited in Chemical Abstracts 30, 7577<sup>3</sup> (1936). This involves passing  $\text{H}_2\text{S}$  gas through the solution, filtering to remove the resulting metal sulfide (here indicated as  $\text{CuS}$ ), and heating the filtrate to expel retained  $\text{H}_2\text{S}$ . The filtrate solution, without further purification, represents the final product useful as a flotation reagent.

It is also possible, though ordinarily not economic, to treat the oxine-bearing, acid solution by electrolysis to plate out from the solution the ions of the selected metal.

Laboratory tests utilizing the preferred procedures have shown that approximately 75 percent of the oxine used in the flotation of columbium minerals can be recovered for re-use.

The acid leach procedure for separating oxine from the mineral solids of a mineral flotation concentrate and tailing produced with oxine as a flotation reagent is illustrated by the flow sheet of Fig. 4.

Thus, the flotation product pulps are separately agitated with a mineral acid, which, from an economic standpoint, is preferably sulfuric acid. The resulting slurries are passed to filtration, yielding oxine-bearing solutions as the filtrates. Such filtrates are then treated as in the flow sheet of Fig. 1, to form a single metal quinolate.

This procedure is applicable only in instances where the nature of the original columbium ore is such as to not consume acid excessively, for example, where it is essentially silicious, as is the ore found in the Odegi region of Nigeria, Africa.

Various tests performed in the laboratory are reported, as follows:

#### Test No. 1

Oxine (8-quinolinol) was added to a ferric iron solution to form a precipitate of the iron-oxine compound. Acid was then added to bring the solution to pH 1.0, thereby dissolving the complex. Thereafter, cupric copper ion was added, and the solution agitated and carefully neutralized to pH 3.0 by addition of  $\text{NaOH}$ , a flocculant precipitate being formed. This precipitate was removed by filtration, washed, and dissolved in acid



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(0.5N—H<sub>2</sub>SO<sub>4</sub>). H<sub>2</sub>S was then passed through the solution, precipitating CuS. The CuS was removed by filtration and the filtrate boiled to expel excess H<sub>2</sub>S. The resulting solution was made basic by the addition of sodium carbonate to pH of 8–10, producing a precipitate which was recovered by filtration. The precipitate was subjected to X-ray fluorescent analysis, which showed the presence of less than 0.1% iron and the absence of copper.

Of the metal ions encountered in most ore pulps, ferric iron would be the most troublesome in the recovery process because of the tendency of this ion to precipitate as the hydroxide in fairly strong acid solutions. Thus, ions of ferric iron would have the greatest tendency to contaminate the copper-oxine compound, and, since they are not removed by sulfide ions in acid solution, they would contaminate the final oxine product by reaction with oxine.

This test demonstrated that, under extreme conditions insofar as the presence of ferric iron is concerned, it is possible to remove this contaminant completely and produce a high purity oxine product.

## Test No. 2

This test was made to demonstrate the removal of copper from copper quinolate by the preferred procedure of Fig. 1. Five grams of oxine were dissolved in sulfuric acid, 2 grams of copper added to the resulting solution, and the pH of such solution adjusted to 5.5 with caustic. The copper quinolate was removed by filtration and repulped in water. Ten grams of hydrated sodium sulfide were added to the new pulp, which was then digested at a temperature below boiling for 30 minutes. Sulfuric acid was carefully added to the digested slurry until the free oxine was dissolved and only a black precipitate of copper sulfide remained. This copper sulfide was removed by filtration, and sodium carbonate was added to the filtrate to precipitate oxine. Filtration of such filtrate resulted in the recovery of 4.1 grams of pure oxine or 82% of the oxine entering the test.

## Test No. 3

In this test 4500 grams of a columbium ore were treated by flotation to recover a columbium mineral concentrate. A total of 22.5 grams of oxine were employed as the flotation reagent. Both the concentrate and the tailing products of such flotation were treated to recover the oxine.

The mineral concentrate was pulped in a flotation cell, 3 grams of sodium carbonate added, and the oxine and metal quinolates recovered as a froth product. This product was repulped, sulfuric acid added to dissolve the organic salts, and the resulting slurry filtered to remove occluded solids. Two grams of copper as copper sulfate were added to the clarified solution, together with sufficient caustic to raise the pH to 3.4. The copper quinolate was removed by filtration, and was found to weigh 5.2 grams dry.

The rougher tailing of the original mineral flotation was filtered to remove solids, and to the filtrate was added 4 grams of copper as copper sulfate. Caustic was then added to shift the pH to 6.0. Filtration produced a copper quinolate precipitate weighing 18.3 grams dry.

The two samples of copper quinolate were combined and dissolved in dilute sulfuric acid. A small amount of copper was added and the pH adjusted to 2.2. Filtration removed 18.6 grams of purified copper quinolate. Further addition of caustic to the filtrate produced 3 grams of a less pure copper quinolate product, which was not processed further in the test.

The 18.6 grams of copper quinolate were redissolved in sulfuric acid, and hydrogen sulfide gas was introduced to precipitate the copper. The copper sulfide was removed by filtration, and the filtrate boiled to expel any excess hydrogen sulfide. The solution at this point was

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suitable for use as a flotation reagent. However, in this test, it was diluted to 3 liters, and an aliquot thereof was treated with sufficient sodium carbonate to bring the pH to 8.0. The free oxine precipitated, and was recovered by filtration.

Dried, the oxine weighed 3.8 grams and was verified as oxine by infrared spectroscopy. This represented a recovery of 11.4 grams of pure oxine from the 18.6 grams of copper quinolate which entered the final purification stage, or an overall recovery of over 74%.

It should be realized that, since oxine has a slight solubility even at a pH of 8, there will remain in the filtrate some recoverable oxine. Ordinarily, it would not be economic to attempt further recovery. However, in this laboratory test, the filtrate was acidified, copper was added, and the equivalent of an additional 4.8 grams of copper quinolate was recovered. This boosted oxine recovery to over 78%.

## Test No. 4

In this test, 2000 grams of a columbium ore were treated by oxine flotation to produce a columbium mineral concentrate. Ten grams of oxine was used as the flotation reagent.

The procedure was the same as in Test No. 3, except that the oxine recovery from the two mineral flotation products were kept separately. In both instances the mineral flotation product was pulped, sodium carbonate and copper ion added, and the metal quinolates recovered by flotation. This product was then dissolved in acid and filtered to remove occluded mineral solids, and copper quinolate was produced from the filtrate by addition of copper and adjustment of pH. The copper quinolate was dissolved in dilute sulfuric acid, the copper precipitated with hydrogen sulfide, and the oxine recovered by adjusting the pH of the solution to 8.

In this test, 2.4 grams of purified oxine was recovered from the mineral flotation concentrate and 5.6 grams from the mineral flotation tailing for a total recovery of 8 of the 10 grams of oxine employed originally as the flotation reagent. Here, then, the recovery was 80%.

## Test No. 5

This test was made to demonstrate the separation of the oxine reagent from mineral flotation pulps by leaching with acid. A total of 1000 grams of Odegi ore from Nigeria, Africa, was treated by flotation with a total of 10 grams of oxine to recover a mineral concentrate and a tail. These products were filtered and the filtrates combined, so that separate determination of oxine recovery from flotation solution and flotation mineral solids could be made.

The concentrate and tail were combined as a matter of convenience for this test, and were leached with 5 percent H<sub>2</sub>SO<sub>4</sub> for 5 minutes at 40 percent solids. The resulting leach slurry was then filtered, and the solids discarded.

The solution from the leaching step and the solution from the flotation step were each treated as follows: 4 grams of copper were added as copper sulfate, and the pH adjusted to 5.5 with sodium hydroxide. The remaining quinolate slurry was filtered. 2.2 grams of impure copper quinolate were recovered from the flotation solution and 10.8 grams of impure copper quinolate from the leach solution. These two copper quinolates were combined and redissolved in 5 percent H<sub>2</sub>SO<sub>4</sub>, 2 grams of copper ion were added as copper sulfate, and the pH adjusted to 2.3 with NaOH. The resulting purified copper quinolate was filtered, and the filtrate discarded.

The copper quinolate was then digested at low heat for 30 minutes with 2 grams of sodium carbonate, and 25 grams of hydrated sodium sulfide in a water solution of 750 ml. The mixture was carefully acidified with H<sub>2</sub>SO<sub>4</sub> to dissolve the oxine and then filtered.

The filtrate solution contained the oxine in a form suitable for flotation, but, to determine the oxine content, the solution was made alkaline to a pH of 8.5 with sodium



carbonate to precipitate 8.1 grams of pure oxine or 81 percent of the oxine entering the test. This recovered oxine was verified as oxine by infrared spectroscopy and chemical analysis.

While no specific test data is available with respect to the electrolytic treatment of the oxine-bearing solution derived from acid treatment of the single metal quinolate, the metal ions have been successfully plated out of such a solution in the laboratory using stainless steel electrodes, leaving an oxine-bearing solution free of ions which would be detrimental to a mineral flotation operation utilizing such solution as a reagent.

In raising the pH of any solution, pulp, or slurry as called for in the foregoing, a suitable basic material is employed. Inorganic basic materials whose cations will not form water-insoluble quinolates are suitable, for example, alkali metal hydroxides and carbonates.

We have shown in our aforementioned copending application Serial Number 689,435 now U.S. Patent No. 2,875,896 that the homologues of oxine (8-quinolinol) react in substantially the same manner when used as a reagent for the flotation of columbium minerals. It follows that such homologues may also be reclaimed for further use as a flotation reagent by the process of this invention.

Whereas this invention is here illustrated and described with respect to certain preferred procedures, it is to be understood that various changes may be made without departing from the inventive concepts as set forth in the claims that follow.

We claim:

1. A process for reclaiming oxine from a pulp product of mineral flotation in which the oxine was used as a flotation reagent, which pulp product is made up of mineral particles and precipitated metal quinolates in an aqueous medium, said process comprising the steps of adjusting the pH of the pulp to approximately 10; subjecting the so-adjusted pulp to flotation to produce a froth flotation concentrate containing said metal quinolates and a tailing containing said mineral particles; treating said froth concentrate with a mineral acid to dissolve the said metal quinolates, resulting in a solution of oxine and metal ions; introducing into said solution a stoichiometric excess of ions of a heavy metal selected from the group of heavy metals consisting of copper, nickel, cobalt, mercury, and antimony, so as to place said oxine in the form of a single heavy metal quinolate; separating said heavy metal quino-

late from the solution; and removing the metal ions from said single metal quinolate, to yield an oxine solution which is useful as a reagent in further mineral flotation.

2. The process of claim 1, wherein the metal ions are removed from the single heavy metal quinolate by repulping said single metal quinolate with water to form a slurry; raising the pH of the resulting slurry to approximately 10 by the addition of a suitable basic material; adding an alkali metal sulfide to the slurry; digesting said slurry with heat to form a sulfide of the selected heavy metal and to free the oxine therefrom; acidifying said slurry to approximately pH 5 by the addition of a mineral acid thereon; and filtering said acidified slurry to remove the precipitated metal sulfide therefrom.

3. The process of claim 1, wherein the metal ions are removed from the single heavy metal quinolate by dissolving said quinolate in a dilute mineral acid to form an electrolyte; and electroplating the metal ions from said electrolyte.

4. A process for producing an oxine-bearing solution useful as a flotation reagent from a crude quinolate of a heavy metal selected from the group of heavy metals consisting of copper, nickel, cobalt, mercury, and antimony, comprising the steps of pulping said quinolate with water; raising the pH of the pulp to approximately 10; adding an alkali metal sulfide; heating the resulting pulp to produce a sulfide of the particular heavy metal concerned; treating the sulfide pulp with a mineral acid to dissolve the oxine; and separating the metal sulfide from the resulting oxine-bearing solution.

5. The process of claim 1, wherein any free oxine that may be present in the said pulp product from mineral flotation is changed to an insoluble quinolate by adding, to the pulp, ions of a metal which combines with oxine to form an insoluble quinolate.

6. A process for separating an insoluble quinolate from mineral solids in an aqueous pulp containing same, comprising adjusting the pH of said pulp to approximately 10; subjecting the so-adjusted pulp to flotation to form a froth concentrate containing said quinolate; and separating said froth concentrate from the remainder of the flotation pulp.

#### References Cited in the file of this patent

- 45 Hollingshead: Oxine and Its Derivatives, vols. I and II, Butterworths Sci. Publ., 1954, London, pp. 72 and 594-596.