This invention relates to the concentration of oxidized zinc ores, and provides an improved process for producing a zinc concentrate from an oxidized zinc ore by froth flotation. In particular, the invention provides for concentrating oxidized zinc ores by froth flotation in the presence of a soluble sulphide and a soluble salt of certain aliphatic amines.

Oxidized zinc ores are not readily amenable to concentration by heretofore known flotation processes. Zinc is often found in association with lead in mixed lead-zinc ores, which may be sulphiide, or oxidized, or both. The flotation process has provided an important tool for economically separating the lead from the zinc in the course of recovering these two valuable metals from mixed sulphide ores as it has been possible, by means of flotation, to produce sulphide concentrates of both lead and zinc. The flotation process also has been useful in separating lead from zinc in the treatment of oxidized lead-zinc ores, but here the process has been less successful, because recovery of a high percentage of the zinc in a concentrate of good grade has not heretofore been accomplished on a commercial scale. Generally in the treatment of such ores, a lead concentrate is prepared by flotation, and the tailing containing both the zinc and the gangue, has constituted the product treated for the recovery of zinc. While some flotation processes for the concentration of the zinc in this product have been proposed, they have not proven successful commercially.

We have found that oxidized zinc ores in general, and the oxidized zinc-bearing tailing resulting from flotation concentration of the lead present in mixed lead-zinc oxidized ores in particular, may be concentrated by flotation in the presence of a soluble sulphide and a soluble compound of an aliphatic amine containing from 8 to 18 carbon atoms. Sodium sulphide is an inexpensive and advantageous soluble sulphide to employ in the new process, and the hydrochlorides are convenient and readily prepared water-soluble compounds of the amines that may be used. Laurylamine hydrochloride, for example, has proven very effective in the new process.

In carrying out our process, the oxidized zinc ore is finely ground (preferably 75% minus 200 mesh) to liberate the metal values from each other and from the gangue. Of course, the fineness to which the grinding operation must be carried depends entirely on how finely the zinc is disseminated through the ore, and with some ores a considerably coarser grind may be satisfactory. The ore is incorporated in an aqueous pulp, preferably during the course of the grinding operation.

The pulp of ground ore is prepared for flotation by incorporating the necessary flotation reagents. We have found that flotation proceeds most effectively in a slightly alkaline pulp, and accordingly it is advantageous to add a small amount (say about two to ten pounds per ton of ore) of an alkaline modifying reagent, such as sodium carbonate, sodium bicarbonate, sodium hydroxide, sodium silicate, or milk of lime. Of these compounds, the sodium carbonate seems to be the most satisfactory. We have found that milk of lime does not always give as good results as other inexpensive alkaline modifying agents.

The reagents necessary for flotation of the zinc concentrates are the soluble sulphide and the soluble amine compound. Any water-soluble sulphide may be employed. Sodium sulphide is inexpensive and very satisfactory, but other soluble sulphides, such as barium sulphide and ammonium sulphide, may be employed with success. The amount of soluble sulphide employed generally is in the range of 6 to 12 pounds per ton of ore in the pulp. The amount added preparatory to floating the zinc concentrate may depend upon what prior treatment has been given to the pulp. If no soluble sulphide has previously been added, then an amount in the upper portion of the above stated range preferably is added at this stage. If, however, the pulp has already been subjected to previous flotation treatment or to some other operation in the course of which a soluble sulphide has been added to it, then only enough soluble sulphide need be added at this stage in order to bring the total amount added to within the above range, and preferably to within the upper half of the range. For example, if a previous flotation operation has involved adding say five pounds of sodium sulphide per ton of ore to the pulp, then a further addition of say four or five pounds per ton preparatory to floating the zinc concentrate ordinarily will be sufficient.

The soluble amine reagent may be any soluble compound of an aliphatic amine (preferably a primary amine) containing 8 to 18 carbon atoms. The most common soluble compounds of such amines are the acetates and the hydrochlorides. A hydrochloride of the chosen amine is generally very readily prepared and gives excellent results. It is not essential that the soluble amine reagent consist solely of a single compound. It may instead be a mixture of soluble compounds of sev-
eral aliphatic (straight chain, branch chain, or both) amines containing 8 to 18 carbon atoms. A reagent of this character that has given very satisfactory results is laurylamine hydrochloride, prepared by reacting commercial laurylamine with hydrochloric acid. The resulting product contains chiefly the hydrochloride of laurylamine, but commercially it may also contain appreciable quantities of deacylamine hydrochloride, tetra-decylamine hydrochloride, etc.

Only a very small amount of the amine reagent is required. Generally from 0.1 pound to 0.5 pound of this reagent per ton of ore in the pulp is a satisfactory amount.

All of the sodium sulphide and all of the amine reagent may be added to the pulp at one time prior to subjecting the pulp to flotation, or alternatively, the sulphide and the amine reagent may be added separately at different times. In some instances it may be advantageous to add only a portion of either one (or both) of these reagents at one time, and to add a further portion (or portions) at a later time (or times). Usually it is best (but it is not always essential) to add at least a portion of each reagent shortly prior to the zinc flotation operation, and to agitate the pulp for a short while after these reagents have been added but before the pulp is subjected to flotation. This conditioning period, during which the pulp is agitated with the reagents, should be conducted so as to insure effective dissemination of the reagent through the pulp, and permit whatever surface reaction may occur between the ore particles and the added reagents.

A frothing agent advantageously (but not necessarily) is incorporated in the pulp, as is common practice in flotation operations. Any suitable frothing agent such as pine oil, methyl amyl alcohol, or the like, may be employed. If the ore has been subjected to a previous flotation operation, it may contain sufficient residual frothing agent so that none need be added to effect flotation of the zinc concentrate.

Following addition of the reagents and conditioning of the pulp, it is subjected to a froth flotation operation in the usual manner and in any suitable flotation cell. In the course of the flotation operation, the oxidized zinc constituents of the ore collect in the froth that floats to the surface of the pulp, and may be skimmed therefrom as a zinc concentrate. The siliceous and other gangue materials of the pulp are withdrawn as a tailing in the underflow from the flotation machine. Intense agitation of the pulp during conditioning and intense agitation and aeration during the actual flotation operation are beneficial in obtaining a high recovery and good grade of zinc concentrate.

Very good recoveries of oxidized zinc minerals in a concentrate of good quality are obtained in accordance with this new flotation method.

The following examples illustrate the results obtained in the treatment of mixed lead-zinc ores for the recovery of a zinc concentrate following removal of a lead concentrate:

Example 1
An aqueous pulp of an oxidized lead-zinc ore having the analysis shown under "Heads" in Table I below was first subjected to a flotation operation to produce a lead concentrate. The reagents employed to produce the lead concentrate were four pounds per ton of sodium silicate, seven pounds per ton of sodium sulphide, and 2.5 pounds per ton of pentasol amyl xanthate (pentasol amyl xanthate is potassium amyl xanthate prepared from crude unfractionated amyl alcohol containing about six amyl alcohol isomers). The reagents were added at intervals in the order named during a conditioning period just prior to the actual flotation operation. The flotation operation was carried out in a Fagergren type sub-aeration flotation cell, and a lead concentrate having the analysis shown in Table I below was produced. The tailing from this flotation operation, containing most of the zinc present in the original ore, was then agitated with five pounds per ton of sodium bicarbonate, 0.10 pound per ton of sodium sulphide, and 0.27 pound per ton of laurylamine hydrochloride, added at intervals in the order named. The thus-treated pulp was subjected to a second flotation operation in a Fagersren type cell, resulting in the production of a zinc concentrate having the analysis shown in Table I.

<table>
<thead>
<tr>
<th>Heads</th>
<th>Pb Conc.</th>
<th>Zn Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Per cent Pb</td>
<td>8.7</td>
<td>55.4</td>
</tr>
<tr>
<td>Per cent Zn</td>
<td>12.4</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Example 2
An oxidized lead-zinc ore containing some lead sulphide was ground in a pulp with water, and was subjected to a first flotation operation to recover a sulphide lead concentrate. The tailing from this flotation operation was subjected to a second flotation operation to recover an oxide-lead concentrate. The tailing from the second flotation operation was subjected to third and fourth flotation operations each designed to produce an oxide-zinc concentrate. The reagents used were as follows: 0.36 pound per ton of potassium ethyl xanthate and 0.25 pound per ton of pentasol amyl xanthate were incorporated in the ore pulp during grinding. Just prior to floating the sulphide-lead concentrate, 0.09 pound per ton of "Pentasol No. 25" (crude unrefined amyl alcohol) was added to the pulp as a frothing agent. The sulphide-lead concentrate was floated, and the tailing from this operation was prepared for floating the oxide-lead concentrate by agitating with four pounds per ton of sodium silicate, 0.4 pound per ton of potassium ethyl xanthate, five pounds per ton of sodium sulphide and 2.5 pounds per ton of pentasol amyl xanthate, added in the order named. The thus-treated pulp was subjected to a second flotation operation to recover the oxide-lead concentrate, and the tailing produced, containing most of the zinc, was then conditioned by agitating, in the order named, with five pounds per ton of sodium carbonate, four pounds per ton of sodium sulphide, and 0.13 pound per ton of pentasol amyl xanthate, added in the order named. The thus-treated pulp was then subjected to a third flotation operation, resulting in the production of the first zinc concentrate and a tailing still containing considerable zinc. This tailing was agitated with two pounds per ton of sodium sulphide and was then again subjected to a flotation operation, resulting in the production of a second zinc concentrate and a final tailing. All flotation operations were conducted in a Fahrenwald type sub-aeration flotation machine. The analysis of the "Heads" and of the concentrates produced is given in the following Table II:
EXAMPLE 3

An oxidized zinc ore containing but a small percentage of lead was subjected to a sequence of flotation operations much as described above in Example 1. An oxide-lead concentrate was first produced after conditioning the ore pulp with four pounds per ton of sodium silicate, 3.5 pounds per ton of sodium sulphide, and 2.5 pounds per ton of pentasol amyl xanthate, added in the order named. The tailing from the oxide-lead flotation was treated with seven pounds per ton of sodium carbonate, eight pounds per ton of sodium sulphide, and 0.27 pound per ton of laurylamine hydrochloride, added at intervals, in the order given, while the pulp was being agitated. The thus-treated pulp was subjected to a second flotation operation to produce a zinc concentrate and a final tailing. A Fagergren type flotation cell was used in both flotation operations. Table III gives the analysis of the ore and of the concentrate products:

<table>
<thead>
<tr>
<th>Heads</th>
<th>Sulphide Pb Conc.</th>
<th>Oxide Pb Conc.</th>
<th>1st Zn Conc.</th>
<th>2nd Zn Conc.</th>
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<tbody>
<tr>
<td>Per cent Pb</td>
<td>10.4</td>
<td>72.0</td>
<td>60.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Per cent Zn</td>
<td>8.7</td>
<td>3.8</td>
<td>35.6</td>
<td>40.7</td>
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</table>

Table III

In the treatment described in this example, approximately 84% of the zinc present in the ore was recovered in the zinc concentrate.

EXAMPLE 4

A complex ore containing both sulphide and oxide lead in intimate admixture with oxidized zinc was subjected to a series of three successive flotation operations to produce successively a sulphide-lead concentrate, an oxide-lead concentrate, and an oxide-zinc concentrate. While grinding the ore pulp, 0.36 pound per ton of potassium ethyl xanthate and 0.25 pound per ton of pentasol amyl xanthate were added. Just prior to the first flotation operation to produce the sulphide-lead concentrate, 0.1 pound per ton of methyl amyl alcohol (or frother) was added. The ore pulp was then subjected to the first flotation operation to produce a sulphide-lead concentrate. The tailing from this operation was treated with four pounds per ton of sodium silicate, five pounds per ton of sodium sulphide, and 2.5 pounds per ton of pentasol amyl xanthate. The resulting pulp then was subjected to the second flotation operation, resulting in the production of the oxide-lead concentrate. The tailing from this second flotation operation was treated with five pounds per ton of sodium carbonate, six pounds per ton of sodium sulphide, and 0.2 pound per ton of laurylamine hydrochloride. The pulp then was subjected to the third flotation operation, resulting in the production of a zinc concentrate and a final tailing. The reagents were added in each case in the order named, and all flotation operations were carried out in a Fagergren type flotation cell. The analysis of the initial ore and the concentrate products were as follows:

<table>
<thead>
<tr>
<th>Heads</th>
<th>Sulphide Pb Conc.</th>
<th>Oxide Pb Conc.</th>
<th>Zn Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Per cent Pb</td>
<td>20.0</td>
<td>71.0</td>
<td>62.2</td>
</tr>
<tr>
<td>Per cent Zn</td>
<td>14.8</td>
<td>3.0</td>
<td>3.2</td>
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</table>

Table IV

The zinc concentrate produced in the operation described in this example contained 78.3% of the zinc initially present in the ore.

It is apparent from the foregoing examples that the new process is well adapted for producing a zinc concentrate of good quality from a complex ore by subjecting a pulp of the ore to a considerable number of successive flotation operations designed to recover sulphide and oxide concentrates of all of the valuable minerals present. In treating such complex ores, it is our presently preferred practice to separate the zinc concentrate last, after first producing concentrates of the other metals to be recovered. The new method is equally well adapted to the treatment of oxidized zinc ores in which zinc is the valued component. Such ores may be treated in a single flotation operation to produce a single concentrate, or in successive operations designed to produce two or more separately recovered zinc concentrates, or in conventional rougher and cleaner operations in which the first (rougher) concentrate is retreated in the second (cleaner) operation to improve its grade.

While various proposals have been made heretofore to employ aliphatic amines and aliphatic amine hydrochlorides in flotation operations, such prior proposals have for the most part involved making use of the reagent to float siliceous material away from the valuable mineral component of the ore. Moreover, such prior proposals have not involved the use of a soluble sulphide in conjunction with a soluble compound of the aliphatic amine, as is characteristic of our invention. Experiments have indicated that the sodium sulphide or other soluble sulphide is necessary in combination with the soluble aliphatic amine compound in order to float the oxidized zinc constituents of the ore—the aliphatic amine compound alone has not proven effective for this purpose. Although it has not heretofore been considered possible to sulfidize oxidized zinc minerals and float them with conventional sulphide collecting agents, as has been possible with oxidized lead and copper minerals, it is our belief that in our new process some slight sulphide film must be formed on the surfaces of the oxidized zinc mineral particles, and that this sulphide film is instrumental, in cooperation with the aliphatic amine reagent, to cause flotation of these particles.

We claim:
1. The method of recovering a zinc concentrate from an oxidized zinc ore which comprises subjecting a pulp of the ore to froth flotation in the presence of a soluble compound of an aliphatic amine containing 8 to 18 carbon atoms and about 6 to 12 pounds of a soluble sulphide per ton of ore.
2. The method of recovering a zinc concentrate from an oxidized zinc ore which comprises subjecting a pulp of the ore to froth flotation in the presence of a soluble chloride of an aliphatic amine containing 8 to 18 carbon atoms and about 6 to 12 pounds of a soluble sulphide per ton of ore.
3. The method of recovering a zinc concentrate from an oxidized zinc ore which comprises sub-
jecting a pulp of the ore to froth flotation in the presence of a soluble compound of laurylamine and about 6 to 12 pounds of a soluble sulphide per ton of ore.

4. The method of recovering a zinc concentrate from an oxidized zinc ore which comprises subjecting a pulp of the ore to froth flotation in the presence of laurylamine hydrochloride and about 6 to 12 pounds of a soluble sulphide per ton of ore.

5. The method of recovering a zinc concentrate from an oxidized zinc ore which comprises subjecting a pulp of the ore to froth flotation in the presence of a soluble compound of an aliphatic amine containing 8 to 18 carbon atoms and about 6 to 12 pounds of sodium sulphide per ton of ore.

6. The method of recovering a zinc concentrate from an oxidized zinc ore which comprises subjecting a pulp of the ore to froth flotation in the presence of laurylamine hydrochloride and about 6 to 12 pounds of sodium sulphide per ton of ore.

7. The method of separately recovering lead and zinc concentrates from an oxidized lead-zinc ore which comprises subjecting a pulp of the ore to froth flotation in the presence of a sulphidizing agent and a xanthate collecting agent, thereby producing a concentrate rich in lead and a tailing containing most of the zinc and gangue, and subjecting the tailing to a second froth flotation operation in the presence of a soluble compound of an aliphatic amine containing 8 to 18 carbon atoms and about 6 to 12 pounds of a soluble sulphide per ton of ore, thereby producing a concentrate rich in zinc.

8. The method of separately recovering lead and zinc concentrates from an oxidized lead-zinc ore which comprises subjecting a pulp of the ore to froth flotation in the presence of a sulphidizing agent and a xanthate collecting agent, thereby producing a concentrate rich in lead and a tailing containing most of the zinc and gangue, and subjecting the tailing to a second froth flotation operation in the presence of laurylamine hydrochloride and about 6 to 12 pounds of a soluble sulphide per ton of ore, thereby producing a concentrate rich in zinc.

9. The method of recovering a zinc concentrate from an oxidized zinc ore which comprises subjecting an alkaline pulp of the ore to froth flotation in the presence of a soluble compound of an aliphatic amine containing 8 to 18 carbon atoms and about 6 to 12 pounds of a soluble sulphide per ton of ore.

10. The method of recovering a zinc concentrate from an oxidized zinc ore which comprises subjecting an alkaline pulp of the ore to froth flotation in the presence of laurylamine hydrochloride and about 6 to 12 pounds of a soluble sulphide per ton of ore.

11. In the treatment by froth flotation of a complex ore containing both sulphides and oxidized minerals of lead and an oxidized zinc mineral, the improvement which comprises subjecting a pulp of the ore to a first flotation operation in the presence of a collecting agent for lead sulphides to produce a sulphide lead concentrate, subjecting the tailing from the first flotation operation to a second flotation operation in the presence of a sulphidizing agent and a xanthate collecting agent to produce an oxidized lead concentrate, and subjecting the tailing from the second flotation operation to a third flotation operation in the presence of a soluble compound of an aliphatic amine containing 8 to 18 carbon atoms to produce a zinc concentrate and about 6 to 12 pounds of a soluble sulphide per ton of ore.

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VIRGIL LESSELS.
ERNEST C. PETERSON.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
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<tbody>
<tr>
<td>2,367,307</td>
<td>Ralston</td>
<td>Dec. 23, 1941</td>
</tr>
<tr>
<td>2,410,021</td>
<td>De Vaney</td>
<td>Oct. 29, 1946</td>
</tr>
</tbody>
</table>

OTHER REFERENCES

The Mechanism of Collection of Metals and Metallic Sulphides by Amines and Amine Salts, by Arbiter et al., T.P. 1581; in Mining Technology, May 1942, 10 pages.

Amine Flotation of Sphalerite-Galena Ores, by Kellogg et al., T.P. 1908; in Mining Technology, November 1945, 23 pages.