This invention relates to the beneficiation of ores containing garnet as a major mineral value substantially free from zircon and titanium oxide.

The practical recovery of garnet from ores is quite a serious problem because the commercial uses of garnet which are mainly in the abrasive field require a high grade material. This has greatly reduced the available garnet deposits and many ores have been considered unsuitable for commercial exploitation because the beneficiation problem up to now has proven unsurmountable. Certain flotation processes have been employed with zircon ores containing garnet as an impurity associated with titanium oxide. Examples of such ores are Egyptian black sands. When these ores are subjected to froth flotation with a sulfonated glycercide oil in acid medium, the zircon is preferentially floated and garnet will be found largely in the tailing associated with gangue minerals. It is not practical to obtain high grade garnet concentrates from such ores by froth flotation procedures using sulfonated glycercide oils. The obtaining of high grade garnet concentrates is an important practical matter when the garnet is the principal mineral value in an ore or at least a major value. Low grade garnet concentrates are not particularly useful, for a fairly high grade such as, for example, more than 80% and preferably more than 90% is normally required for the main industrial uses of garnet such as abrasives.

According to the present invention we have found that with garnet ores of a different type in which the garnet is associated with silicate gangues such as, for example, hornblende, serpentine, and the like without any considerable amounts of zircon or titanium dioxide such as rutile, it is possible by the use of sulfonated fatty acids and their glycercides as promoters to obtain high grade garnet concentrates when certain definite operating procedures are followed. Throughout the specification and claims such garnet ores will be referred to as “substantially free from zircon and titanium dioxide.” It should be understood that small traces of these minerals which may be present as impurities do not alter the flotation characteristics of the ore.

The procedure of the present invention consists in a pretreatment at high solids, for example, 60 to 85%, with an acid having a dissociation constant of at least $10^{-7}$ together with a sulfonated fatty acid or sulfonated glycercide oil. Concentrates are obtainable on froth flotation of the diluted pulp which is high in garnet and these high grade concentrates are associated with good recoveries rendering the process economically satisfactory.

The action of the conditioning treatment with the strong acid appears to alter the surfaces of the garnet particles and perhaps also the gangue. The exact chemical change of the surface is, of course, not capable of determination. The result, however, is quite different from that which would be expected because it is well known that in the flotation of garnet by means of unsulfonated fatty acids or soaps the presence of strong acid depresses the garnet. This is described, for example, by Coghill and Clemmer, Transactions of the American Institute of Mining and Metallurgical Engineers, volume 112 (1934), page 458.

The flotation process of the present invention also is unexpected in another direction. It is well known that sulfonated fatty acids such as sulfonated tallow under the flotation conditions described above is a strong promoter for iron minerals. This process is described in the Booth and Herkenhoff Patent No. 2,417,714. It would therefore naturally be assumed that the use of sulfonated fatty acids and glycercides would tend to float preferentially minerals containing iron. We have found, however, that in the case of the garnets it is apparently the particular silicate type which is floated in preference to other silicate types. Thus, for example, a garnet can be floated away from iron containing gangue such as hornblende or tremolite. The reason for this peculiar behavior of sulfonated fatty acids and glycercide oils in the flotation of the particular garnet ores substantially free from zircon and titanium dioxide, to which the present invention relates, has not been determined fully. However, it would appear that the action may be bound up with the silicate structure of the garnet minerals. Otherwise it would be highly unlikely that silicates of such radically different chemical constitution should float in the same manner. The present invention is, therefore, not limited to any theory of the peculiar operation of the process of the present invention.

In many cases it is desirable to associate the sulfonated fatty acids or glycercide oils with an unsulfonated oil such as fuel oil. This appears to be desirable in many cases but its action has not been definitely determined. It may act primarily to disperse or spread the sulfonated fatty acids and oils over the ore particles or it may act as a froth modifying agent. Without wishing to limit the invention to a particular theory of action we believe that probably both of these functions are performed. This conclusion ap-
pears most likely from the behavior in actual flotation. The composition of the unsulfonated oil is not critical. Ordinary fuel oil such as 20° Bé. fuel oil or other hydrocarbon oils is preferable on economic grounds because it combines excellent results with low cost and ready availability. Other unsulfonated oils such as glyceride oils may be used.

It is an advantage of the present invention that the choice of acids to be used in treating the ore is quite wide. Practically any acid stronger than those having a dissociation constant of 10\(^{-7}\) may be used. Sulfuric acid gives excellent results and because of its cheapness constitutes the preferred acid. Strongly acid salts may also be used.

Where garnets are to be floated from silicious gangue such as hornblende, quartz and the like, the pH of the flotation circuit is not very critical; however, the circuit should be distinctly acid, having a pH below 5. This is a further advantage of the present invention. It is preferable to operate in an acid circuit, but the exact acidity may vary over fairly wide ranges. When this is associated with the garnet very readily floatable material such as, for example, certain iron minerals like ilmenite, the separation is somewhat more difficult and requires careful control of pH.

The preferred embodiment of the present invention in which the ore is treated with an acid in addition to the sulfonated reagent is necessary where garnet concentrates of commercial grade are desired in reasonable recovery. There are certain special conditions, however, where it is necessary to remove garnet as an impurity in other ores and where the grade of the concentrate is not of importance. In such cases good recoveries of a low grade concentrate are obtainable by omission of the acid treatment using the sulfonated fatty acid or glyceride oil alone. Where the acid treatment can be dispensed with, the added advantage is obtained that equipment need not be made of acid resistant material.

The present invention is not limited to particular sulfonated fatty acids or glyceride oils. They are generally usable although with a given garnet ore there will be differences in effectiveness between different sulfonated fatty acids and glycerides. It is also not necessary that the reagent be at all pure. In general, they will be mixtures, sometimes quite crude mixtures, such as sulfonated organic residues from the refining of glyceride oils and fatty acids. These residues, while not quite as effective as some of the best reagents, are very cheap and represent a desirable economic compromise.

The acids used in conditioning may be almost any of the strong mineral acids, sulfuric acid being preferred because it combines excellent results with great cheapness. It is also possible to use other acids such as hydrochloric, hydrofluoric and strong organic acids. Strongly acid salts such as sodium silicofluoride, sodium chlorosulfonate, or sodium or potassium bisulfate may also be used. The amount of the acid salts required is much larger when the acid alone is used and may be of the order of about 5 to 15 lbs. per ton in the case of rougher flotation as opposed to from 2 to 5 lbs. per ton which is used with strong acids. In general, the amount of acid should be sufficient to produce a pH in the rougher float of from 2 to about 4 1/2. Best conditions usually require a pH between 2 and 3.

The flotation procedure of the present invention behaves normally with respect to slime; that is to say, in common with many anionic flocculations it is desirable to decline, but slime is not as critical as in silica flotation operations employing cationic flotation reagents.

The invention will be described in greater detail in conjunction with the following specific examples.

**Example 1**

Screen underside from garnet ore from northeastern United States containing approximately 28% garnet principally in the form of almandite associated with a gangue containing hornblende as a principal constituent, with smaller amounts of feldspar and a minor amount of quartz, was ground at 97% solids to approximately the following screen analyses:

<table>
<thead>
<tr>
<th>Mesh</th>
<th>Per Cent Weight Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>2.25</td>
</tr>
<tr>
<td>45</td>
<td>15.21</td>
</tr>
<tr>
<td>60</td>
<td>24.12</td>
</tr>
<tr>
<td>80</td>
<td>17.60</td>
</tr>
<tr>
<td>100</td>
<td>11.17</td>
</tr>
<tr>
<td>120</td>
<td>9.00</td>
</tr>
<tr>
<td>150</td>
<td>6.68</td>
</tr>
<tr>
<td>180</td>
<td>4.00</td>
</tr>
<tr>
<td>200</td>
<td>2.77</td>
</tr>
<tr>
<td>250</td>
<td>2.50</td>
</tr>
</tbody>
</table>

The ground ore was then deslimed and then conditioned at 80-85% solids with 5 lbs. per ton of sulfuric acid, 1.0 lbs. per ton sulfonated oil, and 1.5 lbs. per ton 22° Bé. fuel oil. The pulp was diluted to froth flotation density and subjected to froth flotation in Pagergren type flotation machines. A rougher concentrate was obtained which was then conditioned for a short time with an additional 0.5 lb. per ton of sulfuric acid and cleaned once. The metallurgical results follow:

<table>
<thead>
<tr>
<th>Assay Per Cent Garnet</th>
<th>Per Cent Recovery Garnet in Final Conc.</th>
<th>Sulfonated Oil Tested 1.0 Lb./ton in each test</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rough Tail</td>
<td>Final Conc.</td>
<td>Sulfonated Castor Oil...</td>
<td>Sulfonated Peanut Oil...</td>
</tr>
<tr>
<td>11.5</td>
<td>94</td>
<td>2.65</td>
<td>2.1</td>
</tr>
<tr>
<td>10</td>
<td>96</td>
<td>65.73</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Conditioning with hydrofluoric acid instead of sulfuric acid resulted in a slightly higher grade but substantially smaller recovery. Hydrochloric acid gave about the same lowered recovery but not quite as high grade, the grade being about 50%. Strong organic acids used in the same amounts gave the same grade as sulfuric acid but a recovery intermediate between that obtained with sulfuric acid and hydrochloric or hydrofluoric acid.

**Example 2**

The procedure of Example 1 was followed on the same ore but various sulfonated fatty acids and other acids were used together with varying amounts of fuel oil as a modifying agent. In each case the rougher concentrate which was obtained was cleaned once, and in each case optimum amounts of fuel oil were used with the
A different garnet ore from that employed in Example 1 but having a similar gangue and assaying about 12% garnet was used in a series of tests with various sulfonated oils.

The ore was ground to minus 48 mesh in the presence of about 1.0 lb./ton NaOH, deslimed, conditioned at high solids for 10 minutes with 5.0 lb./ton sulfuric acid and then for 10 minutes longer with 1.0-2.0 lb./ton sulfonated oil and 1.0-1.5 lb./ton fuel oil, diluted to flotation density and floated in a Fagergren flotation machine for 15 minutes in a rougher float. The rougher concentrate was cleaned twice by reflostation in the presence of 0.5 lb./ton sulfuric acid and 0.1-0.15 lb./ton sulfonated oil. The results obtained in this series of tests follow:

### Example 4

The ore employed in Example 3 was used in a series of flotation tests on sulfonated fatty acids. The testing procedure was the same as that outlined in Example 3, using sulfuric acid and fuel oil, as indicated, along with the sulfonated fatty acid as promoter. Two cleaning steps were employed. The results obtained in this series of tests follow:

### Example 5

A series of flotation tests was run with sulfonated organic residues from glyceride oil and fatty acid refining. The ore and testing method were the same as in Example 3. The results obtained in this series of tests follow:
is obtained relatively rich in garnet and a tailing relatively poor in garnet.

4. A method of beneficiating a garnet ore substantially free from zircon and titanium dioxide which comprises subjecting the ore to froth flotation in the presence of a collector containing as its effective constituent sulfonated gyceride oils and an amount of sulfuric acid, the amount of the sulfuric acid being sufficient to produce a flotation circuit having a pH less than 5 and to modify the flotation characteristics of the garnet particles, whereby a froth concentrate is obtained relatively rich in garnet and a tailing relatively poor in garnet.

5. A method of beneficiating a garnet ore substantially free from zircon and titanium dioxide which comprises subjecting the ore to froth flotation in the presence of a collector containing as its effective constituent a sulfonated fatty acid and an amount of an acid substance, the anion of which is capable of forming an acid having a dissociation constant greater than \(10^{-7}\), and the amount of the acid substance being sufficient to produce a flotation circuit having a pH less than 5 and to modify the flotation characteristics of the garnet particles, whereby a froth concentrate is obtained relatively rich in garnet and a tailing relatively poor in garnet.

6. A method of beneficiating a garnet ore substantially free from zircon and titanium dioxide which comprises subjecting the ore to froth flotation in the presence of a collector containing as its effective constituent sulfonated fatty acids and an amount of sulfuric acid, the amount of the sulfuric acid being sufficient to produce a flotation circuit having a pH less than 5 and to modify the flotation characteristics of the garnet particles, whereby a froth concentrate is obtained relatively rich in garnet and a tailing relatively poor in garnet.

7. A method according to claim 1 in which the ore is conditioned with the collector and acid substance at high solids and the pulp then diluted to froth flotation density.

8. A method according to claim 7 in which the conditioning is effected in the presence of an unsulfonated oil.

9. A method according to claim 2 in which the ore is conditioned with the collector and acid substance at high solids and the pulp then diluted to froth flotation density.

10. A method according to claim 9 in which the conditioning is effected in the presence of an unsulfonated oil.

11. A method according to claim 4 in which the ore is conditioned with the sulfonated gyceride oil and sulfuric acid at high solids and the pulp then diluted to froth flotation density.

12. A method according to claim 11 in which the conditioning is effected in the presence of an unsulfonated oil.

13. A method according to claim 6 in which the ore is conditioned with the sulfonated fatty acid collector and sulfuric acid at high solids and the pulp then diluted to froth flotation density.

14. A method according to claim 13 in which the conditioning is effected in the presence of an unsulfonated oil.

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


Milling Methods, 1934, page 458, AIMME.