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FLOTATION OF CALCIUM CARBONATE ORES

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This invention relates to the separation by froth flotation of calcium carbonate minerals from pulps containing them, and is especially concerned with rendering calcium carbonate ores more suitable for use in the manufacture of cement, lime and like materials.

In floating calcium carbonate particles from pulps containing such particles one or more flotation agents are added to the pulp to collect the calcium carbonate in the froth. In some cases collecting agents (preferably emulsified or saponified fatty acids) and frothing agents are added separately, while in other cases a single substance will act both as collecting and frothing agent, as is the case with saponified tall oil. In actual fact this agent, the use of which in flotation is described in my prior U. S. Patent No. 2,165,268, contains both fatty acid soaps which act as collectors and resin acid soaps which act as frothers. Now while in the flotation the calcium carbonate minerals are for the most part removed from the siliceous and other impurities, a perfect separation of the calcium carbonate from the other substances is virtually impossible, and a certain quantity of the siliceous minerals appears in the concentrate and a certain quantity of calcium carbonate in the reject. A concentrate containing a high calcium carbonate content is referred to as a "clean" concentrate, and the higher the calcium carbonate content the "cleaner" is said to be the concentrate.

It has now been found that better results, especially as regards the cleanness of the concentrate, are obtained when using resinate frothing agents if an adequate quantity of a mineral acid (e. g. sulphuric acid, hydrochloric acid, nitric acid or phosphoric acid) or of a soluble salt of an alkaline earth metal which forms a resinate of relatively low solubility is incorporated in the pulp, and if the pulp on flotation has a pH value of from 6 to 9, and preferably below 8. It appears probable that the mineral acid or metal salt reacts in the pulp and causes some degree of precipitation of the resinate frothing agent, either as resin acid or as the resinate of the metal present in the metal salt, and thereby modifies the frothing action. By such precipitation the concentration of the resinate dissolved in the pulp is decreased, regardless of whether it is the insoluble hydrogen resinate or resin acid, or an alkaline earth metal resinate salt which is precipitated. Furthermore, the mineral acids and the metal salts in many cases increase the selectivity of the fatty acid soap and similar collecting agents used in floating calcium carbonate minerals. This is due to a certain degree to flocculation which takes place of the unsaponifiable matter invariably present in the collecting agents; this matter, which is generally present in soap solutions as a colloidal suspension, otherwise often reduces the selectivity of the fatty acid soaps.

The invention is of especial value when using saponified tall oil (which as indicated above contains resinate frothing agent) as flotation agent.

The metal salt employed is often preferably a calcium salt, but salts of other metals, e. g. of barium and magnesium, may be used. The salts which are appropriate for use in the process of my invention I have referred to herein and in the claims as the "alkaline earth metal salts" and it is to be understood that in using this designation I intend to include within its scope salts of magnesium. Where it is stated above that the metal salt is "soluble," it is meant not that the salt is necessarily highly soluble, but that it is sufficiently soluble in the pulp to give the desired effect on the flotation. That is, the solubility should be in excess of that of the corresponding resinate salt. Thus calcium sulphate, which has in point of fact only a relatively low solubility, is sufficiently soluble to be used; other examples of suitable salts are calcium chloride and calcium bicarbonate. It might be added that calcium carbonate itself is for practical purposes insoluble in water.

It is of advantage, especially when adding saponified tall oil as flotation agent, to use a pulp from which the bulk of the particles below 10 microns in size have been removed, for example by centrifuging. Furthermore, it is also of advantage to add the saponified tall oil or other flotation agents (or the greater part thereof) to the pulp while the latter is in a concentrated or dense condition (it may be just fluid) and to dilute the pulp before flotation, the mineral acid or metal salt being then added during or after the dilution. Thus the mineral acid or metal salt can conveniently be dissolved in the dilution water.

In some cases, where an alkaline earth metal salt is being used, it may be possible to incorporate sufficient of the salt in the pulp by forming the pulp from a natural hard water containing for instance calcium bicarbonate or sulphate, or part of the necessary metal salt may be introduced in this way.

The water obtained when dewatering the concentrate from the flotation and also that obtained from dewatering the slimes (where these

are separated out before flotation) can be used again in the grinding or elsewhere in the process, in which case the process can be carried out in such a way that the make-up water required, which normally is introduced in the mills, classifiers or thickeners, is instead all added as dilution water before the flotation step. The supply of mineral acid or metal salt required to support the process can then be introduced in this make-up water.

The process of the invention is especially useful in treating relatively coarse pulps of coarse-grained ores.

The mineral acid or metal salt need not be added before the flotation (although this is usual) but may be added during flotation, or it may be added in stages. Thus part may be added before flotation and part during flotation, or portions may be added at different stages during the flotation. The acid or salt may be introduced between two consecutive flotation cells. The modifying agent may thus be added at any of a number of points prior to the completion of flotation.

Example

A series of tests was made with a slurry of a ground low-grade limestone containing 43.8% of calcium carbonate, using saponified tall oil as flotation agent and carrying out the flotation in a Fagergren cell with rougher flotation followed by cleaner flotation of the concentrate without the addition of further reagents.

In the first test no mineral acid or metal salt was added, and comparative tests were then carried out adding various of the mineral acid or metal salt modifying agents to the pulp after addition of the saponified tall oil. The results are shown in the following table:

Modifying agent	$CaCO_3$ in cleaned concentrate	$CaCO_3$ in reject
	Percent	*Percent*
None	71.0	4.6
$CaCl_2$	84.8	12.2
$Ca(HCO_3)_2$	84.3	1.5
$CaSO_4$	80.8	18.0
H_2SO_4	84.5	9.3

I claim:

1. In the separation of calcium carbonate particles from a pulp containing such particles, the pulp having an alkalinity equivalent to a pH value of 6 to 9, the process which comprises improving the cleanness of the concentrate by subjecting the pulp to froth flotation in the presence of a collecting agent capable of floating the calcium carbonate and a resinate frothing agent, and prior to the completion of flotation decreasing the concentration of resinate dissolved in the pulp by incorporating in the pulp an inorganic compound capable of forming a resinate of low solubility selected from the class consisting of mineral acids and alkaline earth metal salts which have a solubility in excess of that of the corresponding resinate salt.

2. In the separation of calcium carbonate particles from a pulp containing such particles, the pulp having an alkalinity equivalent to a pH value of 6 to 9, the process which comprises improving the cleanness of the concentrate by removing from the pulp the bulk of the particles originally in the pulp below 10 microns in size, and thereafter subjecting the pulp to froth flotation in the presence of a collecting agent capable of floating the calcium carbonate and a resinate frothing agent, and prior to the completion of flotation decreasing the concentration of resinate dissolved in the pulp by incorporating in the pulp an inorganic compound capable of forming a resinate of low solubility selected from the class consisting of mineral acids and alkaline earth metal salts which have a solubility in excess of that of the corresponding resinate salt.

3. In the separation of calcium carbonate particles from a pulp containing such particles, the pulp having an alkalinity equivalent to a pH value of 6 to 9, the process which comprises improving the cleanness of the concentrate by adding to the pulp while in a concentrated form a collecting agent capable of floating the calcium carbonate and a resinate frothing agent, diluting the pulp, subjecting the diluted pulp to froth flotation, and prior to the completion of flotation decreasing the concentration of resinate dissolved in the pulp by incorporating in the pulp an inorganic compound capable of forming a resinate of low solubility selected from the class consisting of mineral acids and alkaline earth metal salts which have a solubility in excess of that of the corresponding resinate salt.

4. In the separation of calcium carbonate particles from a pulp containing such particles, the pulp having an alkalinity equivalent to a pH value of 6 to 9, the process which comprises improving the cleanness of the concentrate by adding to the pulp while in a concentrated form a collecting agent capable of floating the calcium carbonate and a resinate frothing agent, diluting the pulp, decreasing the concentration of resinate dissolved in the diluted pulp by incorporating therein an inorganic compound capable of forming a resinate of low solubility selected from the class consisting of mineral acids and alkaline earth metal salts which have a solubility in excess of that of the corresponding resinate salt, and thereafter subjecting the diluted pulp to froth flotation.

5. In the separation of calcium carbonate particles from a pulp containing such particles, the pulp having an alkalinity equivalent to a pH value of 6 to 9, the process which comprises improving the cleanness of the concentrate by adding to the pulp while in a concentrated form a collecting agent capable of floating the calcium carbonate and a resinate frothing agent, diluting the pulp, subjecting the diluted pulp to froth flotation, and prior to the completion of flotation decreasing the concentration of resinate dissolved in the pulp by incorporating in the pulp an inorganic compound capable of forming a resinate of low solubility selected from the class consisting of mineral acids and alkaline earth metal salts which have a solubility in excess of that of the corresponding resinate salt, at least a part of said compound being added to the pulp while dissolved in the dilution water.

6. In the separation of calcium carbonate particles from a pulp containing such particles, the pulp having an alkalinity equivalent to a pH value of 6 to 9, the process which comprises improving the cleanness of the concentrate by adding to the pulp while in a concentrated form a collecting agent capable of floating the calcium carbonate and a resinate frothing agent, diluting the pulp with a natural hard water, subjecting the diluted pulp to froth flotation, and prior to the completion of flotation decreasing the concentration of resinate dissolved in the pulp by incorporating in the pulp an alkaline earth metal salt capable of forming a resinate of lower solu-

bility at least a part of which is added to the pulp dissolved in the said natural hard water.

7. In the separation of calcium carbonate particles from a pulp containing such particles, the pulp having an alkalinity equivalent to a pH value of 6 to 9, the process which comprises improving the cleanness of the concentrate by subjecting the pulp to froth flotation in the presence of a collecting agent capable of floating the calcium carbonate and a resinate frothing agent, and prior to the completion of flotation decreasing the concentration of resinate dissolved in the pulp by incorporating in the pulp an inorganic acid thereby to form a resin acid of low solubility.

8. In the separation of calcium carbonate particles from a pulp containing such particles, the pulp having an alkalinity equivalent to a pH value of 6 to 9, the process which comprises improving the cleanness of the concentrate by subjecting the pulp to froth flotation in the presence of a collecting agent capable of floating the calcium carbonate and a resinate frothing agent, and prior to the completion of flotation decreasing the concentration of resinate dissolved in the pulp by incorporating in the pulp a minor proportion of sulphuric acid.

9. In the separation of calcium carbonate particles from a pulp containing such particles, the pulp having an alkalinity equivalent to a pH value of 6 to 9, the process which comprises improving the cleanness of the concentrate by subjecting the pulp to froth flotation in the presence of a collecting agent capable of floating the calcium carbonate and a resinate frothing agent, and prior to the completion of flotation decreasing the concentration of resinate dissolved in the pulp by incorporating in the pulp an alkaline earth metal salt capable of forming a resinate having a solubility less than that of the alkaline earth metal salt.

10. In the separation of calcium carbonate particles from a pulp containing such particles, the pulp having an alkalinity equivalent to a pH value of 6 to 9, the process which comprises improving the cleanness of the concentrate by subjecting the pulp to froth flotation in the presence of a collecting agent capable of floating the calcium carbonate and a resinate frothing agent, and prior to the completion of flotation decreasing the concentration of resinate dissolved in the pulp by incorporating in the pulp a minor proportion of a calcium salt capable of forming a resinate having a solubility less than that of the calcium salt.

11. In the separation of calcium carbonate particles from a pulp containing such particles, the pulp having an alkalinity equivalent to a pH value of 6 to 9, the process which comprises improving the cleanness of the concentrate by subjecting the pulp to froth flotation in the presence of a collecting agent capable of floating the calcium carbonate and a resinate frothing agent, and prior to the completion of flotation decreasing the concentration of resinate dissolved in the pulp by incorporating in the pulp a minor proportion of calcium chloride.

12. In the separation of calcium carbonate particles from a pulp containing such particles, the pulp having an alkalinity equivalent to a pH value of 6 to 9, the process which comprises improving the cleanness of the concentrate by subjecting the pulp to froth flotation in the presence of a collecting agent capable of floating the calcium carbonate and a resinate frothing agent, and prior to the completion of flotation decreasing the concentration of resinate dissolved in the pulp by incorporating in the pulp a minor proportion of calcium bicarbonate.

13. In the separation of calcium carbonate particles from a pulp containing such particles, the pulp having an alkalinity equivalent to a pH value of 6 to 9, the process which comprises improving the cleanness of the concentrate by subjecting the pulp to froth flotation in the presence of tall oil acting both as collecting and frothing agent, and prior to the completion of flotation decreasing the concentration of resinate dissolved in the pulp by incorporating in the pulp an inorganic compound capable of forming a resinate of low solubility selected from the class consisting of mineral acids and alkaline earth metal salts which have a solubility in excess of that of the corresponding resinate salt.

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