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## FLOTATION PROCESS FOR CONCENTRATING CARBONATE MINERALS

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7 Claims. (Cl. 209—166)

This invention relates to an improved process for the concentration of ores to recover carbonate minerals contained therein, more particularly it relates to a flotation process for recovering carbonate minerals from siliceous gangue. Still more particularly it relates to a process for recovering carbonate minerals from siliceous gangue employing salts of amino naphthenes derived from naphthenic acids as collecting or flotation agents. In its preferred embodiment the invention relates to a process for recovering calcium carbonate from accompanying mineral impurities, particularly from siliceous gangues.

This invention has as an object the development of an improved process for the concentration of carbonate minerals. A further object is the development of a flotation process for obtaining calcium carbonate concentrates of high purity. A still further object is the treatment of naturally occurring limestone mineral compositions which will result in a product suitable for the manufacture of Portland cement. Another object is to provide a simple, economical flotation process for concentrating carbonate minerals which does not require the presence of additional agents such as activators, depressants, etc., commonly employed in prior art flotation processes. Other objects will appear hereinafter.

The above and other objects appearing hereinafter are accomplished by the following invention which comprises adding to a pulp containing carbonate minerals a salt of an amino-naphthene derived from naphthenic acids and subjecting the same to a flotation operation. If necessary, an additional frothing agent may be added. The gangue concentrates in the froth layer and leaves the cell as an overflow, while the carbonate values remain in the cell as an underflow or tailing product.

The flotation agents forming a part of this invention are water-soluble and contain a high molecular weight hydrophobic group. When dissolved in water these flotation agents ionize, the hydrophobic group being a part of the positive ion or cation, for this reason we term the reagents of our invention "cation-active flotation agents."

In ordinary froth flotation processes the valuable mineral constituent is lifted into the froth layer by use of suitable flotation reagents and is thereby separated from the refuse or gangue which remains behind in the flotation cell and is thrown away as tailings. The material removed with the froth therefore, constitutes the "concentrate" and is treated by suitable processes such as thickening, filtration, drying, smelting, etc., to separate the desired product in a technically useful and valuable state. The difficulties standing in the way of applying this procedure to some of the non-sulfide minerals such as the carbonates of calcium, magnesium, manganese, iron, etc., are known to those familiar with this art. We have now found that when the gangue present with the carbonate minerals is comprised of quartz and/or one or more of the various silicates such as talc, feldspar, mica, etc., we are able to take advantage of the indifference of the carbonates to the cation-active flotation reagents hereof and remove the siliceous gangue minerals by froth flotation. We have thus effected a reverse flotation, that is, the valuable minerals remain in the flotation cell while the gangue is floated out and discarded.

The invention will be further illustrated but is not intended to be limited by the following example.

### *Example*

A sample of Russian naphthenic acids having an average molecular weight of 174 was converted to the corresponding amide and nitrile by reaction with ammonia followed by dehydration to the nitrile which was then hydrogenated to yield an amino naphthene. Two-tenths of a gram of the amine was suspended in warm water and neutralized to methyl orange by addition of dilute hydrochloric acid. The solution was then diluted to 200 cc. Twenty cubic centimeters of this solution and 0.0086 g. of frothing agent *b* were used in a flotation test carried out by employing a sample of a micaceous limestone used in the production of Portland cement. The mineral composition of said limestone has been described in detail by B. L. Miller and C. H. Breerwood (Am. Inst. Mining Met. Engrs., Tech Pub. No. 606, p. 15, February, 1935). Calcite, mica and quartz constitute the bulk of the rock. Pyrite, limonite, apatite, and amorphous carbon are present in small quantities.

The limestone was crushed in a small jaw crusher and then reduced to minus 40-mesh by means of a Braun disc pulverizer. Slurries for use in flotation experiments were prepared by grinding 1 kg. of the minus 40-mesh ore for 75 minutes in a 1-gallon porcelain jar mill with 1 l. of water and 3 kg. of flint pebbles. The ore particles were then about 84–86% minus 200-mesh. Frothing agent *b* is one of the branched chain, oxygenated organic compounds prepared by the catalytic hydrogenation of carbon oxides described in the U. S. Patents 1,844,129, 1,844,857 and 1,939,708. After five minutes, frothing and collection ceased. An additional 10 cc. portion of

the naphthenylamine hydrochloride solution was then added. Another loaded froth was produced and this was collected separately from the first froth. The products were filtered weighed and analyzed in the customary manner and yielded the following results:

| Product | Weight (g.) | $CaCO_3$ (%) | $CaCO_3$ (g.) | Recovery of $CaCO_3$ (%) |
|---|---|---|---|---|
| Heads | 121.0 | 74.89 | 90.63 | |
| First overflow | 27.9 | 36.35 | 10.14 | 11.2 |
| Second overflow | 12.3 | 37.15 | 4.57 | 5.0 |
| Underflow | 80.8 | 93.96 | 75.92 | 83.8 |

A portion of a ground cement rock slurry prepared as described above and containing about 117 g. of ground rock was placed in a miniature laboratory flotation cell of the type described by Gates and Jacobsen (Engineering and Mining Journal, 119, 19, 771 (1925)). The cell was filled to the pulp level with water, the agitator started and the aforedescribed aminonaphthene solution was added.

The aminonaphthenes, whose water soluble salts are used in the practice of this invention are derived from alicyclic naphthenic acids having an average carbon content of from about 11 to about 19 carbon atoms. Suitable salt forming groups are chlorine, bromine, nitrate, acetate, chloroacetate, etc.

We have found that a number of closely related substances which in some way deviate from the above general formula are entirely ineffective in the separation of quartz and siliceous minerals from calcium carbonate and other carbonates. The following substances are examples of ineffective reagents.

Paratoluidine hydrochloride
n-Amylamine hydrochloride
Dicyclohexylamine hydrochloride
Quinoidine hydrochloride
Ethylpyridinium iodide
Diethyl cyclohexyl benzyl ammonium chloride

The amount of aminonapthene flotation reagents required to produce the above effects varies somewhat with the reagent chosen and the particular rock or ore being treated. In general the amount needed will be between 0.05 pound and 2.0 pounds per ton of ore, but in some cases somewhat smaller or greater quantities may be required. Some of the reagents produce sufficient frothing so that an additional frothing agent is not required, while others have little or no frothing power. When greater frothing power is needed we prefer to use a material such as pine oil, cresylic acid, or one of the oxygenated organic compounds described by Burdick in his U. S. Patent 1,995,913, since these frothers have no adverse effect on the selectivity of the collecting agents. Occasionally we find it advantageous to use mixtures of two or more of the aminonaphthene reagents to produce flotation products of high quality. In carrying out a flotation process according to the teachings of this invention any of the well-known types of flotation cells may be employed. The ratio of pulp solids to water may vary from about 1:1 to 1:6. Ordinarily a neutral pulp is used but in some cases it may be desirable to use an alkaine or acid pulp. We have also found that water glass added in quantity of about 0.5 to about 5.0 pounds per ton of ore is often helpful in giving an increased yield of high quality product. We have also found that certain heavy metal salts such as ferric chloride activate the siliceous minerals to a marked degree and frequently allow better separations to be made.

It will be clear from the above that one of the uses of this invention is the preparation of calcium carbonate content is too low to be of technical value. By means of this process limestone rocks containing from 40 to 70% of calcium carbonate can be purified to such an extent that the product can be used in the manufacture of Portland cement. It is also possible to prepare calcium carbonate concentrates approaching theoretical purity from low-grade limestone by this process. These highly pure concentrates may be used in the manufacture of lime, and in numerous other chemical and technologic processes. The process of this invention also permits the recovery of iron carbonate, manganese carbonate, magnesium carbonate, and other metallic carbonates from ores containing them. Conversely it may be used to prepare talc, mica, or quartz products of high purity and value when the principal impurities are alkaline earth or heavy metal carbonates.

As compared to previously known methods, the present process exhibits several outstanding advantages. First of all, it provides for the first time a process by which quartz and silicate minerals may be lifted into a flotation froth while calcium carbonate and other carbonates are substantially not floated. Secondly, it permits the preparation of calcium carbonate and other metallic carbonate concentrates in a higher state of purity than has been possible with any of the known flotation processes. Thirdly, when the process is used as a method for purifying an ore more than half of which consists of carbonate mineral, the minor constituent of the ore is floated rather than the major constituent, thus effecting savings in reagents, time, and plant capacity.

While we have disclosed the preferred embodiments of our invention, it will be readily apparent to those skilled in the art that many variations and modifications may be made therein without departing from the spirit of the invention. Accordingly, the scope of the invention is to be limited solely by the appended claims constructed as broadly as permissible in view of the prior art.

We claim:

1. A process for concentrating carbonate minerals from pulp mixtures containing the same and siliceous impurities, which comprises adding to the pulp a small amount of a salt of an aminonaphthene derived from naphthenic acids having an average carbon content of from about 11 to 19 carbon atoms, subjecting the mixture to a froth flotation operation, and then removing the carbonate as an underflow.

2. The process of claim 1 in which the carbonate minerals are those of alkiline earth metals.

3. The process of claim 1 wherein the pulp mixture contains calcium carbonate and siliceous impurities.

4. A process as set forth in claim 1 wherein the carbonate mineral is calcite.

5. A process as set forth in claim 1 wherein the carbonate mineral is magnesite.

6. A process as set forth in claim 1 wherein the carbonate mineral is dolomite.

7. The process of claim 1 wherein the salt of the aminonaphthene is the hydrochloride.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 4, after the word "filtered" insert a comma; line 15, beginning with "A portion of" strike out all to and including "added." in line 23 and insert the same on page 1, second column, line 51, before "Frothing"; same page 2, first column, line 70, for "alkaine" read --alkaline--; and second column, line 48-49, for "constructed" read --construed--; line 62, for "alkiline" read --alkaline--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 19th day of November, A. D. 1940.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.