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## FROTH FLOTATION PROCESS

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8 Claims. (Cl. 209—166)

This invention relates to a process for concentrating minerals and more particularly to a froth flotation process for concentrating non-metallic minerals.

Heretofore, fatty acids, soaps, or analogous surface active reagents have been utilized as froth flotation agents for non-metallic minerals. These reagents generally were quite unsatisfactory because the siliceous mineral could not be readily floated and large quantities of flotation reagent were required. The resulting concentrates had a low yield and, due to ineffective separation of undesirable materials, were of inferior quality. Also, the reagents were unsatisfactory as the desired selectivity of materials to be separated could not be obtained and the pH and reagent concentrations had to be maintained within relatively narrow limits.

Recently attempts have been made to float non-sulfide minerals by using complex nitrogen derivatives such as quaternary ammonia compounds. However, the high cost of these compounds mitigates against their use as flotation agents, particularly for use in floating low price minerals.

An object of this invention is to provide an improved froth flotation process for concentrating non-metallic minerals.

Another object is to provide a froth flotation product for concentrating non-metallic minerals from ores containing non-metallic and/or sulfide minerals.

Another object is to provide a froth flotation process which is economical and efficient in operation.

Another object is to provide a froth flotation process for producing high concentrations of non-metallic minerals which formerly could not be separated or could be concentrated only with great difficulty.

Another object is to provide a froth flotation process wherein relatively small amounts of flotation reagents are employed and the pH of the circuit may vary over a relatively wide range.

A further object is to provide an improved flotation process wherein a comparatively inexpensive, readily available froth flotation reagent is employed.

Other and further objects will be obvious upon an understanding of the illustrative embodiment about to be described, or will be indicated in the appended claims, and various advantages not referred to herein will occur to one skilled in the art upon employment of the invention in practice.

These objects are accomplished by frothing an aqueous suspension of non-metallic minerals in the presence of a reaction product of a chlorinated hydrocarbon of the paraffin series and ammonia. These reaction products contain a positively charged surface active ion and are adapted to concentrate non-sulfide minerals. The froth flotation process preferably is carried out with the aid of a frothing agent or frother, and a dispersing agent.

In accordance with the invention, I have found that a frother known to the trade as Du Pont's B-23, which is a mixture of aliphatic alcohols and a dispersing agent known to the trade as American Cyanamid's No. 610, which is a lignin sulfonate, can be advantageously utilized in conjunction with the chlorinated hydrocarbon-ammonia reaction products. If desired pine oil may be used as a frother and Goulac, a product of waste sulfite liquors may be used as a dispersing agent.

The chlorinated hydrocarbon-ammonia reaction products which I employ, may be prepared from hydrocarbons containing between about eight and about thirty carbon atoms but preferably are prepared from paraffin wax or similar hydrocarbon compounds of the paraffin series containing between twenty-two and twenty-eight carbon atoms and designated by the formulas, $C_{22}H_{46}$, $C_{23}H_{48}$, $C_{24}H_{50}$, $C_{25}H_{52}$, $C_{26}H_{54}$, $C_{27}H_{56}$, and $C_{28}H_{58}$. These products are prepared by chlorinating paraffin wax or other suitable hydrocarbons in any well-known manner to contain from 10 to 70% chlorine and preferably from 20 to 55% chlorine; and then reacting the chlorinated product with ammonia. Such products contain a positively charged surface active ion and are very effective in concentrating, floating, and collecting non-metallic minerals, particularly such minerals which are free from sulfides.

I have found that the following products can be made economically in a simple manner:

| Products | Composition |
|---|---|
| A | A 52% chlorinated paraffin-ammonia reaction product containing 7.1% nitrogen and 14.0% chlorine. |
| B | A 30% chlorinated paraffin-ammonia reaction product containing 6.0% nitrogen and 12.3% chlorine. |
| B—HCl | Like B with amines converted to hydrochlorides. |
| $B_1$ | A product similar to B which is heated for three hours at 200° C. |
| C | A 21% chlorinated paraffin-ammonia reaction product containing 4.5% nitrogen and 8.0% chlorine. |
| C—HCl | Like C with amines converted to hydrochlorides. |

To determine the effectiveness of the foregoing described products, 200 g. of −65 +200 mesh deslimed quartz and water were placed in a flota-

tion cell and were agitated. The frother and product under test were added in the amounts shown in the following table and air was passed therethrough and the pH of the circuit was maintained as designated.

*Flotation of quartz with chlorinated paraffin-ammonia reaction products*

| Product | Lbs./ton quartz | pH | Frother lbs./ton quartz | Recovery |
|---|---|---|---|---|
| | | | | *Precent* |
| A | 0.10 | 6.2 | 0.10 | 100 |
| A | 0.10 | 8.0 | 0.07 | 100 |
| B | 0.10 | 6.2 | ---------- | 100 |
| B | 0.10 | 8.0 | ---------- | 100 |
| B | 0.12 | 9.5 | 0.12 | 100 |
| $B_1$ | 0.10 | 6.2 | ---------- | 100 |
| C | 0.10 | 8.0 | ---------- | 100 |
| C | 0.10 | 9.3 | ---------- | 100 |

These tests indicated that satisfactory quartz collectors can be produced by reacting ammonia with chlorinated paraffins which contain from 21 to 52% chlorine. The reaction products may contain from 4.5 to 7.1% nitrogen and from 8.0 to 14.0% chlorine and can be used efficiently in the presence of a frother at concentrations between .07 and .12 lb./ton while maintaining a pH varying over a wide range, for example, between 6.2 and 9.5, and maintaining reagent concentrations between .10 to .12 lb./ton. The products also are efficient when used without a frother at reagent concentrations of about .10 to .12 lbs./ton and a pH between 6.2 and 8.0. The collecting properties of the product $B_1$ were not changed by heating three hours at 200° C. thus indicating that the product is very stable.

In another test 200 g. of −65 +200 mesh deslimed feldspar was used instead of quartz and the foregoing described procedure was followed using product B in an amount corresponding to .40 lb./ton of feldspar at a pH of 6 with .06 lb./ton of B–23 frother. A 100% recovery was obtained.

The foregoing tests illustrate the collecting properties of the products on non-sulfide minerals namely, quartz and feldspar.

As demonstrated by the following examples, the products are suitable for separating silicates from carbonates in siliceous limestone slurry where the problem is to readjust the relative proportions of the calcareous and siliceous materials. The slurry contains on an average 70% calcite (including a small amount of dolomite), 15% mica, and quartz and feldspar equal to about 15%. Removal of some of the last three mentioned constituents is necessary to prepare a suitable cement mix.

To accomplish this, the slurry was first deslimed and the more granular part of the material was froth flotated in the presence of a chlorinated paraffin-ammonia reaction product. The resulting concentrate was rich in silicates and left a tailing containing a high percentage of calcite corresponding to a good recovery. By floating the silicates, which constitute a minor proportion of the slurry, the carbonates and silicates are more quickly separated and without using a relatively large quantity of flotation agents. This greatly increases plant capacity and decreases the cost of the flotation process.

### *Example I*

First 1,000 cc. of cement rock slurry, prepared from a rock containing 68.19% $CaCO_3$ and 23.79% insoluble, was diluted to about 15 liters with tap water. The slurry was well mixed and then 1¾ minutes were allowed for settling. The slimes were siphoned off down to a volume of about 4 liters. This operation was carried out for two additional times. The deslimed material was then transferred to a 1,000 gram flotation cell for the actual test. Thereafter 5 cc. of a 1% solution of a 30% chlorinated paraffin-ammonia reaction product in the form of hydrochloride, product B—HCl, was added, and a concentrate was taken off for about 3 minutes. Then a second concentrate was collected for the same time by the addition of 2.5 cc. of product B—HCl solution at 0.095 lb./ton. The following metallurgical results were obtained:

| | Weight | Percent | $CaCO_3$ | Insoluble | Recovery | |
|---|---|---|---|---|---|---|
| | | | | | $CaCO_3$ | Insoluble |
| | *Grams* | | *Percent* | *Percent* | *Percent* | *Percent* |
| Concentrate No. 1 | 59.0 | 10.2 | 31.83 | 56.81 | 4.7 | 24.3 |
| Concentrate No. 2 | 107 | 20.3 | 26.40 | 64.06 | 7.9 | 54.6 |
| Tail | 362 | 69.5 | 85.73 | 7.20 | 87.4 | 21.1 |

### *Example II*

About 900 cc. of cement rock slurry prepared from a rock containing 63.8 to 64.0% $CaCO_3$ and 26.1 to 26.2% insoluble materials was diluted to about 15 liters with tap water. To this was added 1 gram of a dispersing agent, No. 610 (American Cyanamid), and after being well mixed with the slurry, the slimes were removed as described in Example I. The test was made in a 1,000 gram flotation cell and .06 lb./ton of B–23 alcohol frother was added and then 4 cc. of 1% solution of the hydrochloride of a 30% chlorinated paraffin-ammonia reaction product, corresponding to reaction product B—HCl at .14 lb./ton. A concentrate was collected for 5 minutes. The metallurgical results of which were as follows:

| | Weight | Percent | $CaCO_3$ | Insoluble | Recovery | |
|---|---|---|---|---|---|---|
| | | | | | $CaCO_3$ | Insoluble |
| | | | *Percent* | *Percent* | *Percent* | *Percent* |
| Concentrate | 126 | 22.7 | 17.00 | 72.31 | 6.0 | 62.5 |
| Tail | 429 | 77.3 | 77.78 | 12.72 | 94.0 | 37.5 |

### *Example III*

The method of desliming the cement rock slurry in the presence of 1 gram of a dispersing agent was carried out in the same manner as in Example II. B–23 alcohol frother equal to a .12 lb./ton concentration was added and 2 cc. of 1% solution of a 30% chlorinated paraffin-ammonia reaction product, product B, was introduced and concentrate No. 1 was collected for 3 minutes. Then 1 cc. more of the same solution (product B) was added and concentrate No. 2 was taken off for 3 minutes. The metallurgical results were as follows:

| | Weight | Percent | $CaCO_3$ | Insoluble | Recovery | |
|---|---|---|---|---|---|---|
| | | | | | $CaCO_3$ | Insoluble |
| | | | *Percent* | *Percent* | *Percent* | *Percent* |
| Concentrate No. 1 | 77.0 | 18.4 | 18.48 | 69.16 | 15.4 | 48.4 |
| Concentrate No. 2 | 79.0 | 18.8 | 35.02 | 53.36 | 10.4 | 38.2 |
| Tail | 263.0 | 62.8 | 85.02 | 5.59 | 84.2 | 13.4 |

### *Example IV*

Two 900 cc. portions of cement rock slurry prepared from a rock containing about 64.3% $CaCO_3$

and about 24.2% insoluble were deslimed separately in the presence of 1 gram of dispersing agent No. 610 by following the same procedure in each case as given under Example II. The total deslimed material from both portions was transferred to the 1,000 gram Denver Sub A flotation cell and the separation made. 0.06 lb./ton of B–23 alcohol frother was added. Then 2 cc. of 1% solution of 30% chlorinated paraffin-ammonia reaction product (0.04 lb./ton) was introduced which gave concentrate No. 1, collected for 3 minutes. Concentrate No. 2, collected for 2 minutes, was produced by an additional 1 cc. of the same reagent (0.02 lb./ton). Likewise concentrate No. 3, collected for 2 minutes, resulted from an additional 1 cc. of the reagent at 0.02 lb./ton, (total for test 0.08 lb./ton). Metallurgical results were as follows:

| | Weight | Percent | $CaCO_3$ | Insoluble | Recovery | |
|---|---|---|---|---|---|---|
| | | | | | $CaCO_3$ | Insoluble |
| | | | *Percent* | *Percent* | *Percent* | *Percent* |
| Concentrate No. 1 | 55.09 | 5.7 | 14.51 | 68.41 | 1.3 | 16.1 |
| Concentrate No. 2 | 73 | 7.7 | 14.86 | 72.41 | 1.8 | 23.1 |
| Concentrate No. 3 | 106 | 11.0 | 22.93 | 65.22 | 3.9 | 29.7 |
| Tail | 729 | 75.6 | 79.09 | 9.93 | 93.0 | 31.1 |

*Example V*

About 1,000 cc. of cement rock slurry, prepared from a rock containing 65.8% $CaCO_3$ and 23.9% insoluble, was deslimed in the same manner as given under Example II, except Goulac, a product from waste sulfite liquors, probably a lignin sulfonate, was used instead of the dispersion agent No. 610. This test was made on the deslimed material in a 1,000 g. flotation cell and a quantity of B–23 alcohol frother equal to a .06 lb./ton concentration was added. Then 2 cc. of 1% solution of 30% chlorinated paraffin-ammonia reaction product (product B) equal to 0.08 lb./ton was added providing concentrate No. 1, which was collected for 3 minutes. A second concentrate, collected for 3 minutes, was produced by the addition of 2 cc. more of the same solution of reagent (0.08 lb./ton). The metallurgical results were as follows:

| | Weight | Percent | $CaCO_3$ | Insoluble | Recovery | |
|---|---|---|---|---|---|---|
| | | | | | $CaCO_3$ | Insoluble |
| | *Grams* | | *Percent* | *Percent* | *Percent* | *Percent* |
| Concentrate No. 1 | 14 | 2.8 | 12.93 | 71.78 | 0.5 | 8.4 |
| Concentrate No. 2 | 87 | 17.3 | 18.05 | 69.87 | 4.8 | 50.6 |
| Tail | 401 | 79.9 | 77.97 | 12.26 | 94.7 | 41.0 |

The problem in connection with the above examples on cement rock, is the preparation of high grade lime product. The above examples show that chlorinated paraffin-ammonia reaction products collect the siliceous material and leave behind a high grade calcite tailing containing from 78 to 85% $CaCO_3$. The reagent is very efficient and as little as .10 to 0.15 lb./ton of rock is required. The reagent has a high selectivity for the silica as well. As illustrated by the fact that the amount of calcite in the tailing corresponds to 84 to 95% recovery.

*Example VI*

Under proper controlled conditions it is possible to separate other non-metallic minerals from quartz and silicate with chlorinated paraffin-ammonia reaction products. This is shown by the following tests. Here the material worked with is a kyanite tailing containing about 6% kyanite ($Al_2SiO_5$), the balance being quartz, black mica and garnet (dark purple). While limiting the amount of the reagent to 0.4 to 0.5 lb./ton, it is possible to separate the mica and garnet from the quartz and kyanite. The quartz does not float along with the other two. Because of the differences in color of the mica and garnet, the separation could be readily observed. The tailing was practically white with a little rose-colored quartz mixed in. The kyanite contents were determined, which is a check on the selectivity of the product.

Two hundred g. of 48-mesh kyanite tailings and distilled water were placed in the flotation cell and while agitated, pine oil to the extent of 0.07 lb./ton was added. Then 0.50 lb./ton of the 30% chlorinated paraffin-ammonia reaction product was introduced. Air was then passed through and a concentrate was taken off for 5 minutes. The dark colored mica and garnet readily flocculated and floated. The tailing was 21.5% of the total and analyzed 21.8% kyanite, which corresponds to 95.5% kyanite recovery.

Another test carried out in exactly the same manner with 0.04 lb./ton of the same product gave a tailing equal to 37.2% of the total and analyzed 15.7% kyanite which corresponds to a 96.8% recovery.

Numerous other sulfide or non-sulfide ores might be substituted in place of the ores floated in the foregoing mentioned examples. While this invention relates particularly to the flotation of negatively charged minerals, it is to be understood that it is not limited thereto and may frequently be used to float positively charged minerals. It may be applied to both sulfide and non-sulfide ores. When applied to the former, the flotation agents described herein may be used along with the customary flotation agents for sulfide ores such as collectors, frothers, conditioners, depressants, dispersing agents, etc. When applied to non-sulfide ores which contain a positive charge, the flotation agents described herein may be mixed with soap, soap-like products, sulfonated products, etc., and other flotation agents. The proportions of the individual components in such admixtures may vary within wide limits.

From the foregoing description and examples, it will be seen that the present invention provides a simple, rapid, and inexpensive process for collecting non-sulfide, non-metallic minerals. The yield attained by the process is highly satisfactory and can be attained at a very low cost. The products employed as collectors are relatively inexpensive and are readily available. Due to their low cost, they can be used for froth flotation of low price minerals which do not allow the use of the high price materials used heretofore as collectors. Also relatively small amounts of flotation reagents are used and the pH of the circuit may vary over a wide range.

It will be understood that the details and examples hereinbefore set forth are illustrative only and that the invention as broadly described and claimed is in no way limited thereby.

What I claim and desire to protect by Letters Patent is:

1. A process for the froth flotation of negatively charged minerals which comprises frothing an aqueous suspension of the minerals in the presence of a reaction product of chlorinated

paraffin-hydrocarbons having between twenty-two and thirty carbon atoms and ammonia, said product having a positively charged surface active ion.

2. A process for the froth flotation of non-sulfide, non-metallic, negatively charged minerals which comprises frothing an aqueous suspension of the minerals in the presence of a reaction product of chlorinated paraffin-hydrocarbons having between twenty-two and thirty carbon atoms and ammonia, said product having a positively charged surface active ion.

3. A process for the froth flotation of non-metallic minerals which comprises frothing an aqueous suspension of the minerals in the presence of a reaction product of a chlorinated wax-like paraffin-hydrocarbon and ammonia containing 4 to 8% nitrogen and 8 to 14% chlorine.

4. A process for the froth flotation of non-metallic minerals which comprises frothing an aqueous suspension of minerals in the presence of a reaction product of a chlorinated wax-like paraffin-hydrocarbon, which contains from 21 to 52% chlorine, with ammonia.

5. A process for the froth flotation of non-metallic minerals which comprises frothing an aqueous suspension of minerals in the presence of a reaction product of wax-like paraffin-hydrocarbons and ammonia, maintaining the reaction product concentration between .10 and .12 lb./ton and maintaining a pH between 6.2 and 9.5.

6. A process for the froth flotation of non-metallic minerals which comprises frothing an aqueous suspension of minerals in the presence of a reaction product of wax-like paraffin-hydrocarbons and ammonia, maintaining the reaction product concentration between .10 and .12 lb./ton and maintaining a pH between 6.2 and 9.5, and adding a frother in amounts to provide concentrations of between .07 and .12 lb./ton.

7. A process for the froth flotation of non-metallic minerals which comprises frothing an aqueous suspension of the minerals in the presence of a reaction product of a chlorinated wax-like paraffin-hydrocarbon and ammonia, and an added flotation agent.

8. A process for the froth flotation of non-metallic minerals which comprises frothing an aqueous suspension of the minerals in the presence of a reaction product of a chlorinated wax-like paraffin-hydrocarbon and ammonia, a dispersing agent, and a frother.

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