United States Patent [19]

Kirwin et al.

[11] **3,782,546**

[45] **Jan. 1, 1974**

[54] **CATIONIC CONDITIONING AGENTS FOR POTASH FLOTATION**

[75] Inventors: **Roscoe Conklin Kirwin,** Midland, Tex.; **William Lewis Hart,** Pittsburgh; **Joseph Michael Antonetti,** Burgettstown, both of Pa.

[73] Assignee: **Calgon Corporation,** Pittsburgh, Pa.

[22] Filed: **Dec. 3, 1971**

[21] Appl. No.: **204,647**

[52] **U.S. Cl.** **209/166,** 209/5

[51] **Int. Cl.** **B03d 1/02**

[58] **Field of Search** 209/166, 5; 210/53, 210/54

[56] **References Cited**

UNITED STATES PATENTS

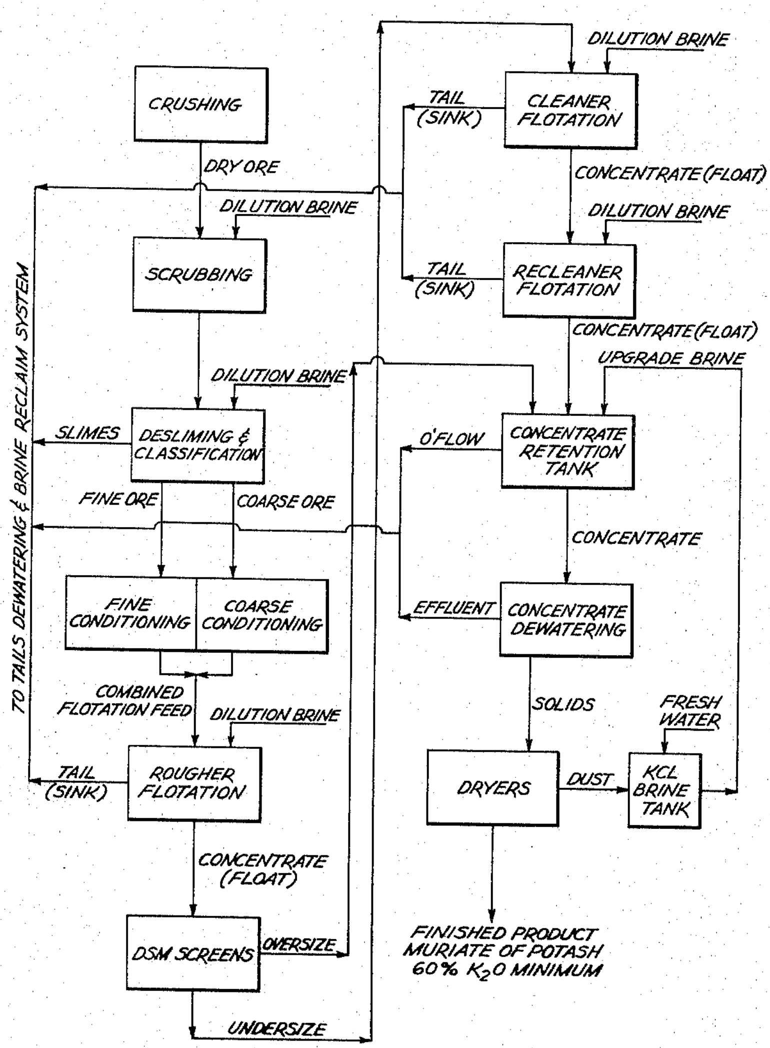
2,923,408	2/1960	Williams	209/166
3,165,465	11/1965	Ray	209/5 X
3,259,237	7/1966	Schoeld	209/166 X
3,321,649	5/1967	De Benedictis	209/166 X
3,408,292	10/1968	Da Jani	210/54 X
3,452,867	7/1969	Bishop	209/166

Primary Examiner—Robert Halper
Attorney—Martin L. Katz et al.

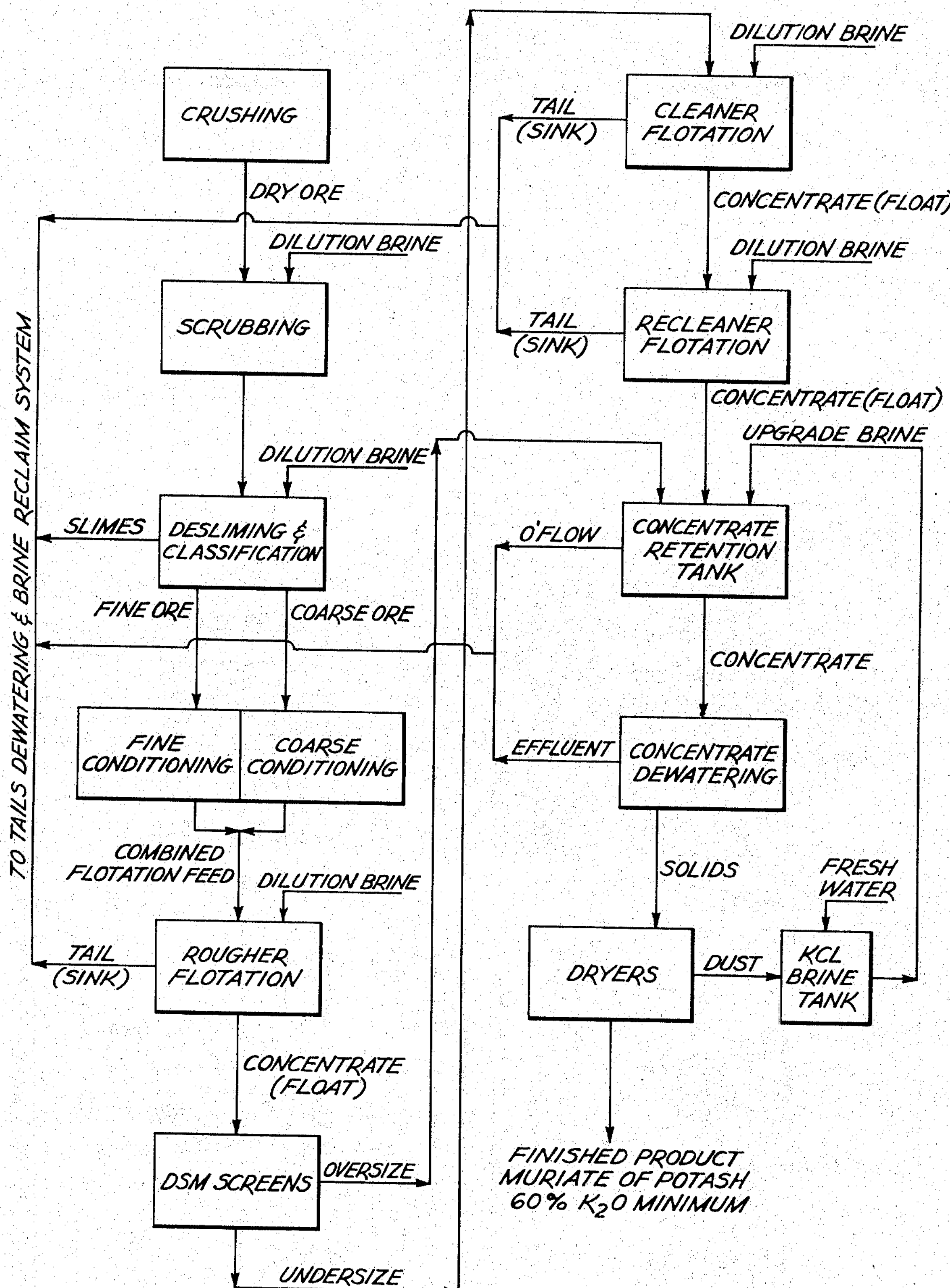
[57] **ABSTRACT**

An improved froth flotation process for separating sylvite from a pulp containing sylvite using a water-soluble, high molecular weight, diallyl dialkyl quaternary ammonium polymer as a slime conditioning agent is disclosed.

3 Claims, 1 Drawing Figure



POTASH FLOTATION FLOW DIAGRAM



POTASH FLOTATION FLOW DIAGRAM

CATIONIC CONDITIONING AGENTS FOR POTASH FLOTATION

BACKGROUND OF THE INVENTION

This invention is directed to the use of high molecular weight, water-soluble, diallyl dialkyl quaternary ammonium polymers as slime modifying agents to improve the concentrate purity and yield of sylvite in the potash froth flotation process.

Potash froth flotation is the most commonly employed process for separating potash values from pulps containing potash. Potash ores mined in the United States and Canada generally contain from about 5 to 50 percent sylvite (KCl) with the balance being primarily halite (NaCl) and the remainder gangue materials. Generally, the gangue minerals found with sylvite/halite ore are clays such as montmorillonite and gypsum along with minor amounts of iron, manganese oxides and other minerals. These ores are the primary source of potash chemicals for agriculture and industry.

In order to concentrate and recover the sylvite from the other constituents of the ore, a froth flotation process is utilized. Essentially, the potash flotation process comprises the following general steps. First, the sylvite-containing ore is crushed and ground in a saturated brine until the ore particles are from 8 to 20 mesh in size. Saturated brine solution is used throughout the potash flotation process since sylvite is soluble in water and any unsaturated water used in the process would dissolve the ore and result in a loss. The ore pulp is then diluted with additional brine until a consistence of about 20 to 40 percent by weight ore solids is obtained. After dilution, the various conditioning agents, collecting agents, and frothing agents are added to the ore slurry. The pulp is then aerated to produce a froth at the pulp surface. The potash values are concentrated in the froth and the remainder of the ore consisting essentially of halite and gangue remains in the aqueous pulp phase. The potash-bearing froth is then separated from the residual pulp and further processed to obtain the desired metal. The residual liquid pulp generally referred to as the flotation tailings is then further subjected to additional frothing steps if it contains a sufficiently high concentration of potash. If not, the tailings are discarded. It is safe to say that the majority of potash flotation processes follow the above sequence. However, it should be noted that many additional but optional steps such as scrubbing, desliming and classifying are commonly employed and many variations of the above-described general process have found wide acceptance in the art.

In the potash flotation process, it is desirable to recover as much of the potash value from the ore as possible, yet doing so in a selective manner. That is, it is the object of the flotation process to recover as much of the potash from the ore as possible without carrying over the halite and gangue with the potash or without leaving high concentrations of the potash compounds in the gangue tailings. In order to accomplish this selectivity, many collecting, frothing, and conditioning agents have been employed.

A collecting agent for the potash flotation process is one which preferentially adheres to the sylvite but not to the halite thereby producing a water repellent coating on the potash particles. The air bubbles will then cling to the potash particles and concentrate them in the froth. The most commonly employed collecting

agents for potash flotation are the fatty amines, especially the amine salts such as octylamine hydrochloride and octadecylamine acetate.

Frothing agents are compounds which dissolve in the pulp solution and have both a polar and nonpolar group in the molecule. These compounds change the air-pulp solution interface tension thereby helping to produce a voluminous body of bubbles at or above the surface of the flotation pulp and also helping to prolong the life of the bubbles so produced. The most commonly employed frothing agents for the potash flotation process are the C_8 to C_{12} aliphatic alcohols.

In addition to the collecting agent and frothing agent, a conditioning agent is usually employed. Both the collecting agent and frothing agent have a tendency to be consumed by the gangue, especially clay. Therefore, as much of the gangue is removed by mechanical means that is practicable. Thereafter, it is necessary to add a conditioning agent which decreases the attraction of the gangue for the collecting and frothing agents. This type of conditioning agent is commonly called a slime blinder or slime depressant. The most commonly used deslimers used in potash flotation processes are starch and other carbohydrate polymers. For example, see Fast et al, U.S. Pat. No. 3,456,790. Recently, high molecular weight polymers have been utilized as slime blinders. For example, see Bishop, U. S. Pat. No. 3,452,867.

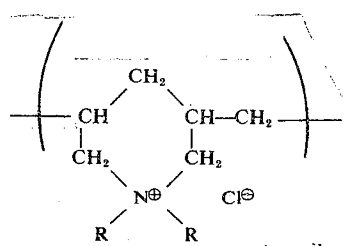
SUMMARY OF THE INVENTION

The present invention is directed to a conditioning agent, particularly to a conditioning agent which increases the potash yield by acting on the gangue (slime). More particularly, the present invention is directed to the use of high molecular weight, water-soluble, diallyl dialkyl quaternary ammonium polymers as conditioning agents for increasing the potash recovery in potash flotation processes.

We have found that high molecular weight, water-soluble, diallyl dialkyl quaternary ammonium polymers increase the efficiency of the potash froth flotation process. The polymers of our invention increase the rate of potash recovery and also yield a higher grade concentrate. While we do not wish to be bound by any theories, it appears that the polymers increase the rate of recovery and the concentrate grade by selective coagulation of the slime. It is undisputed that the presence of slimes is detrimental to most flotation processes. The slimes adsorb large quantities of collecting agents and frothing agents thereby hindering the flotation process. In addition, the slimes entrap the potash particles and are, therefore, a large source of lost mineral values. Finally, the slimes themselves may be carried over in the froth if they have adsorbed the collecting agents. However, by selectively coagulating the slime and reducing the total surface of the slime, the process efficiency is increased. First of all, less amount of collecting agents and frothing agents are adsorbed by the slime. This leads to an increase in efficiency since more of the agents are available for the potash particles and less of the slime is found in the froth. In addition, the coagulated slime does not entrap the potash particles and the coagulated slime is less likely to be found in the froth. Therefore, is appears that the polymers of our invention increase the flotation process by selectively blinding the slime.

As mentioned above, the polymers of our invention are high molecular weight, water-soluble, diallyl dialkyl quaternary ammonium polymers. These polymers are prepared by polymerizing the well known diallyl monomers that readily undergo free radical polymerization.

The high molecular weight, water-soluble polymers of the diallyl dialkyl quaternary ammonium chlorides are represented by the formula:



where R is hydrogen or an alkyl group of 1 to 18 carbon atoms. The preparation and use of this class of compounds is illustrated in Butler U.S. Pat. No. 3,288,770, Boothe U.S. Pat. Nos. 3,461,163 and 3,472,740, Schuller et al U.S. Pat. No. 2,923,701 and Booth et al. U.S. Pat. No. 3,147,218. The preferred diallyl dialkyl polymers are when R is a lower alkyl group of 1 to 4 carbon atoms, preferably methly.

The polymers of our invention may be prepared by polymerizing the cationic monomer using any of the well known solution, emulsion or suspension techniques. We have prepared effective polymers using all three of these methods. Our invention is independent of the method of preparation so long as the resulting polymer is a water-soluble, high molecular weight cationic polymer of diallyl dialkyl quaternary ammonium chlorides.

As mentioned above, the polymers of our invention are prepared by polymerizing the quaternary ammonium monomers. It is also within the scope of our invention to use copolymers of two or more different quaternary ammonium compounds. It is also within the scope of our invention to use polymers containing groups derived from monomers in addition to the cationic monomers. Our invention contemplates the use of copolymers containing up to about 97.5 mole percent of other water-soluble comonomers and up to about 10 mole percent of water-insoluble comonomers. Examples of some of the useful water-soluble comonomers are acrylamide, methacrylamide, diacetone acrylamide and the N-lower alkyl substituted acrylamides and methacrylamides. Examples of some of the water-insoluble comonomers are vinyl acetate, acrylonitrile, vinyl chloride, styrene, and the lower alkyl esters of acrylic and methacrylic acid. Therefore, while the polymers of our invention consist essentially of diallyl dialkyl quaternary ammonium compounds, they may also contain up to about 97.5 mole percent of other water-soluble monomers and up to about 10 mole percent of water-insoluble comonomers and still be within the scope of our invention. The diallyl dialkyl quaternary ammonium polymers of our invention are water-soluble, high molecular weight and contain at least 2.5 percent diallyl dialkyl quaternary ammonium compounds. The preferred polymers of our invention contain at least 5 percent diallyl dialkyl quaternary ammonium compounds and the preferred comonomer is acrylamide.

The molecular weight of the polymers may be as low as 1,000 or as high as 10,000,000 or higher. We have found that generally the higher molecular weight polymers are somewhat better than low molecular weight polymers. There is no reason to believe that there is a critical minimum molecular weight which must be achieved in order to show an improved flotation process. However, for all practical purposes, a minimum molecular weight of about 10,000 is necessary for economic results.

Similarly, there is no critical minimum concentration that is necessary. A small amount will show a slight effect when compared to a larger amount. However, for all practical purposes, we have found that concentrations less than 0.001 pounds per ton based on the weight of the dry ore, will seldom be used. Likewise, concentrations greater than 1.0 pounds per ton will seldom be used. The preferred concentration range will differ depending on which ore is being processed. However, in the majority of cases, the concentration of cationic polymer will be from about 0.001 to about 0.01 pounds per ton.

The polymers of our invention are added to the flotation process just prior to the flotation step. They are added at the conditioning stages immediately prior to flotation. In a typical potash flotation plant, there are several flotation steps. The polymers of our invention may be added at the conditioning stages prior to any of these flotation steps. FIG. I is a flow diagram of a typical potash flotation process. With reference to FIG. I, it can be seen that the process has three different flotation steps where the potash is separated from the undesirable by-products. In FIG. I, these steps are labeled rougher flotation, cleaner flotation, and recleaner flotation. The polymers of our invention may be added prior to any of these flotation steps in order to increase the efficiency of that particular flotation step. We have found that the use of the polymer in the rougher flotation is most beneficial and essential. However, the use of the polymers in the other flotation steps is optional and will depend on the grade of ore being refined and the efficiency of the rougher flotation step in removing the slime.

Since the cationic polymers of our invention work on the gangue, they are effective in processing other soluble salts which may be refined by froth flotation. For example, they may be used in the flotation of halite from sylvite, langbeinite from halite, sodium bicarbonate from halite and many others.

We have performed numerous experiments which demonstrate the effectiveness of our invention. The following experiments illustrate our invention but should not be considered to limit the same.

A series of experiments were performed in the laboratory to demonstrate the effectiveness of cationic polymers in the recovery of potash values via froth flotation. The experiments were performed in a modified five-liter laboratory Denver flotation cell in the laboratory of Southwest Potash Company's Carlsbad, N.M. plant. The ore sample was taken directly from the plant processing stream. The following procedure was followed in running the experiments. A bucket of the ore from the plant was run through a proportioner three times. The proportioner divided the sample in halves each time through with one half being recycled and the other half discarded. The sample from the proportioner weighed about 2,000 grams and was approximately one eighth of the original bucket. Saturated brine was then added to the 2,000 grams of ore so that the total weight was about 3,380 grams. This ore slurry was stirred for about 20 minutes and subjected to three desliming operations. The first desliming step had a settling time of 1 and a half minutes, the second had a settling time of 1 minute and the final desliming step had a settling time of a half minute. After the desliming steps, a slime blinder was added to the ore pulp and mixed for about 2 minutes. Then the collecting and frothing agents were added and the pulp mixed vigorously for an additional minute. The pulp was then added to the flotation cell and the level of the cell adjusted to just below the lip with saturated brine. The cell was turned on and the pulp was floated for 3 minutes or slightly longer (until done). The concentrate and tails were then collected, filtered, dried, cooled and weighed. They were then pulverized and analyzed spectrometrically for K_2O.

Table I gives the results of the laboratory tests performed on the ore samples taken during a one day period. The ore was −8 mesh. The slime blinders tested were guar gum (Guar), a high molecular weight, slightly hydrolyzed polyacrylamide (PAM) and a higher molecular weight homopolymer of dimethyl diallyl ammonium chloride (DMDAAC). The other agents employed for collecting and frothing were an amine collector, methoxy propylene glycol and methyl isobutyl carbinol.

TABLE I

Blinder in lbs. /Ton	Percent K_2O in Feed	Percent K_2O in Concentration	Percent K_2O in Tails	Percent K_2O Recovered
Guar				
0.08	17.37	56.77	1.18	95.10
0.08	17.78	57.48	1.90	92.13
0.08	17.89	56.37	1.50	90.80
PAM				
0.02	17.50	56.52	0.85	96.38
0.03	17.51	55.64	0.85	96.55
0.04	17.27	56.31	0.82	96.57
DMDAAC				
0.006	17.54	56.55	0.77	96.82
0.0095	17.67	57.65	0.82	96.62
0.012	17.73	56.49	0.92	96.29
0.02	17.36	55.32	0.56	97.73

Table I clearly illustrates the effectiveness of diallyl dialkyl quaternary ammonium polymers, especially DMDAAC, as slime blinders in the potash flotation process. The cationic polymer was more effective at lower concentrations than guar gum or polyacrylamide.

Table II gives the results of the laboratory tests performed on a series of ore samples taken during a one day period. The ore was −6 mesh and the agents employed are the same as mentioned for Table I above.

TABLE II

Blinder in lbs. /Ton	Percent K_2O in Feed	Percent K_2O in Concentration	Percent K_2O in Tails	Percent K_2O Recovered
Guar				
0.06	17.67	57.76	2.14	90.86
0.07	17.10	56.49	1.98	91.47
0.08	17.44	57.26	1.88	92.16
0.08	17.30	56.38	1.88	91.96
PAM				
0.01	17.64	57.26	1.89	92.03
0.02	17.45	55.91	1.62	93.20
0.03	17.56	55.91	1.62	93.77
DMDAAC				
0.008	17.81	56.69	1.58	93.46
0.009	17.31	56.83	1.19	94.97
0.01	17.38	55.86	1.25	94.78

Table II also illustrates that the cationic polymers are more effective at lower concentrations that the heretofore employed slime blinders. In the above tables, the additional mineral recovery caused by the use of the cationic polymer is in the neighborhood of about 1 percent. However, this small improvement is of great economic importance since many commercial operations process 50,000 tons or more of ore daily. With this very high throughput rate, relatively small improvements in the percent potash recovery yields many additional tons of product. In addition, the lower dosages of additives needed give a considerable savings when one considers the high throughput rate.

Table III gives the results of laboratory tests performed on a series of three ore samples. The ore was −8 mesh and the agents employed are the same as for Table I above. In these tests, the guar and polyacrylamide were used together.

TABLE III

Blinder in Pounds/Ton		Percent K_2O in Concentration	Percent K_2O in Tails	Percent K_2O Recovered
Guar	PAM			
.06	.02	57.72	1.57	94.87
DMDAAC				
0.009		58.12	1.29	95.63
0.015		57.35	0.98	96.74

Table IV gives the results of laboratory tests which were performed the same as for Table III.

TABLE IV

Blinder in Pounds/Ton		Percent K_2O in Concentration	Percent K_2O in Tails	Percent K_2O Recovered
Guar	PAM			
.06	.02	56.12	1.45	95.09
DMDAAC				
0.01		56.85	1.36	95.33
0.015		56.42	1.26	95.65

The results in Tables III and IV illustrate that the cationic polymers of our invention are more effective at lower dosages than a combination of both guar and polyacrylamide.

We have performed many additional experiments using various other cationic polymers. The results of these experiments clearly indicate that high molecular weight, diallyl dialkyl quaternary ammonium polymers are effective slime blinders in the potash flotation process.

We claim:

1. An improved potash froth flotation process comprising grinding the potash ore, mixing the ground ore with water to form an ore pulp, aerating the pulp to form a froth and collecting and processing the froth wherein the improvement comprises adding to the ore pulp during said flotation process, but prior to frothing, a water-soluble, high molecular weight, diallyl dialkyl quaternary ammonium polymer consisting essentially of dimethyl diallyl ammonium chloride as a conditioning agent.

2. An improved potash froth flotation process comprising grinding the potash ore, mixing the ground ore with water to form an ore pulp, aerating the pulp to form a froth and collecting and processing the froth wherein the improvement comprises adding to the ore pulp during said flotation process, but prior to frothing, from about 0.001 to about 0.01 pounds per ton based on the weight of the dry ore of a water-soluble, high molecular weight, polymer consisting essentially of dimethyl diallyl ammonium chloride as a conditioning agent, said polymer having a molecular weight of at least about 10,000.

3. An improved process as in claim **2** wherein the potash ore is sylvite.

* * * * *