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## TREATMENT OF SYLVINITE ORES

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6 Claims

### ABSTRACT OF THE DISCLOSURE

The present invention relates to an improvement in the process of separating KCl from sylvinitic ores with the aid of a mineral collector, the ore containing slime-forming clay with interferes with the function of the mineral collector. The improvement comprises carrying out the separation in the presence of an acrylamide-beta methacryloyloxyethyltrimethylammonium methyl sulfate copolymer which copolymer serves to minimize the adverse effect of the clay on the mineral collector.

The present invention relates to a process of treating sylvinitic ores, and more particularly to a flotation process of recovering sylvite (KCl) from sylvinitic ores.

Sylvinitic ores contain various amounts of KCl and NaCl (halite). Typical of such sylvinitic ores are those in the Carlsbad district of New Mexico. Sylvinitic ores also contain small amounts, usually on the order of up

are not intended to limit the present invention beyond the scope of the appended claims.

### Examples 1-6

5 These runs were carried out in order to determine the effect of various slime inhibitors and the recovery of KCl from ores containing same.

A sample of minus 10 mesh sylvinitic ore from the Carlsbad district of New Mexico was scrubbed in a saturated brine solution of the ore and then screened to remove the minus 30 mesh fraction. This removed a portion of the original clay slimes from the ore. Then the partially deslimed ore, at about 50% solids in the saturated brine solution, was thoroughly mixed for two minutes with the slime inhibitor along with 0.11 pound Carbowax 550 (methoxyl polyethylene glycol of approximately 550 molecular weight). The amounts of materials used in these runs were per ton of the partially deslimed ore on a dry weight basis. Then 0.5 pound coal tar creosote (Barrett No. 634) was added and the mixing continued for 5 minutes. At this point amine collector (distilled hydrogenated tallow amine acetate, commercially available as Armac HTD) was added and the mixing continued for 2 minutes. The resulting ore pulp was then transferred to a flotation cell, and 0.07 pound methylisobutyl carbinol added prior to floating. The KCl concentrate in the froth that formed was removed from the surface of the pulp liquor.

Further details appear in table hereinafter.

TABLE

Ex. No.	Slime inhibitor		Percent KCl in—		Percent KCl recovery
	Name <sup>1</sup>	Amount <sup>2</sup>	Concentrate	Tailings	
1.....	None.....	None	91.3	23.7	41.2
2.....	Commercial slime inhibitor.....	0.11	94.3	3.1	94.3
3.....	94% acrylamide, 6% MTMMS.....	0.11	94.4	0.9	98.2
4.....	83% acrylamide, 17% MTMMS.....	1.10	95.6	0.6	98.3
5.....	do.....	0.05	94.8	2.6	93.8
6.....	do.....	0.25	94.5	2.5	95.0

<sup>1</sup> Example 2 used an acrylamide-based anionic slime inhibitor available commercially as "SEPARAN NP-10."

<sup>2</sup> Lbs. per ton dry weight basis by weight of total amount of partially deslimed ore treated, added as a 0.1% aqueous solution.

to about 5% or 6%, water-insoluble clay which forms a slime that interferes with separating KCl from the ore.

Froth flotation processes are used commercially to recover KCl from the ores by flotating the KCl from the NaCl. In this process finely ground ore is mixed with a saturated solution of the soluble constituents (usually insoluble constituents such as e.g. clays are also present) of the ore and various flotation (collection) and auxiliary agents are added. The collection agent causes the separation of the KCl from the ore. The clay adsorbs a substantial amount of the mineral collector and thus seriously interferes with the separation process. Although it is conventional practice to employ a mechanical desliming step, still enough clay remains to substantially hinder the separation process.

In accordance with the present invention it has been found that the addition to sylvinitic ores of a small amount of a certain acrylamide-beta methacryloyloxyethyltrimethylammonium methyl sulfate (acrylamide-MTMMS) copolymer substantially increases the KCl recovery from the ores. Apparently the copolymer acts as a blocking agent or a blinding agent to adsorption by the clay of the KCl collector.

The following examples wherein percent and parts are by weight unless otherwise indicated illustrate various embodiments of the present invention. These examples

From the foregoing examples it is readily apparent that the particular copolymer of the present invention, as compared with prior art polymers, enables the recovery of a substantially higher percentage of KCl from sylvinitic ores and therefore is a significantly superior slime inhibitor. Very small amounts of copolymer of the present invention give substantially increased KCl recovery. Usually the amounts will be about 0.01-0.5, preferably about 0.05-0.20 pound per ton dry weight basis by weight of the total amount of ore treated.

Although the terms "clay" and "slime-forming clay" have been used herein and in the prior art, the present invention is not limited thereto but includes any materials which interfere with the performance of the mineral collector, which interference the copolymer of the present invention lessens. These objectionable slime-forming materials are sometimes referred to in the art as insoluble clay-like minerals.

Although, for the sake of ease of understanding, the present invention is described herein for the most part with reference to a flotation process of concentrating KCl in sylvinitic ores, the invention is not limited thereto. More specifically the present invention is applicable to KCl concentrating processes in general including e.g. those often referred to in the art as flotation, settling, and dissolution processes in general.

The copolymer slime inhibitor of the present invention consists by weight thereof essentially of 99%–20% acrylamide and 1%–80% MTMMS, preferably about 97%–50% acrylamide and 3%–50% MTMMS, about 95%–60% acrylamide and 5%–40% MTMMS being specifically preferred.

Preparation of the particular copolymer employed in the present invention is not claimed herein nor is it per se a part of the present invention. However, the preparation of said copolymer is quite important. In fact, applicant knows of only one process which will produce a product having the properties of the particular copolymer applicable in the present invention. For the sake of completeness this process will now be disclosed. It may be referred to as precipitation polymerization.

The precipitation process broadly comprises polymerizing butanol, aqueous acetone or aqueous tertiary butanol-acetone in the substantial absence of air while agitating the solution to give a copolymer product that can be isolated by filtration, the aqueous tertiary butanol and aqueous acetone being solvents for the monomers but non-solvents for the copolymer product.

Several of the conditions of this precipitation polymerization process are critical, and these conditions will now be discussed.

The solvent for the monomers must be aqueous tertiary butanol, aqueous acetone or aqueous tertiary butanol-acetone (i.e. mixtures of water with tertiary butanol or acetone alone or with both). The concentrations of water in said mixtures must be 30%–65%, preferably 45%–60%, by weight of said mixtures.

The polymerization reaction temperature must be 0° C.–60° C., preferably 0° C.–40° C.

The polymerization may be carried out either in the presence or absence of a polymerization catalyst (initiator), but preferably a polymerization initiator will be used. Both the types and amounts of free radical initiator applicable are well known in this art. Peroxygen compounds are quite suitable, including e.g. ammonium persulfate, potassium persulfate and hydrogen peroxide. Other free radical initiators include e.g.  $\alpha,\alpha'$ -axo-bis-isobutyronitrile. The peroxygen initiators may be used alone or in combination with activators (also well known in this art) including e.g. sodium bisulfite, sodium thiosulfate, tetramethylenediamine, thiourea and ferrous chloride, said combination forming a redox system. The amount of initiator usually will not exceed 0.5%, preferably is 0.05%–0.2%, 0.05% being specifically preferred, by weight of the combined weight of monomers.

Although not necessary, preferably the precipitation polymerization is carried out in the presence of a salt dissolved in the polymerization reaction mixture. By polymerizing in the presence of a salt, or a buffer system comprising one or more salts in combination with another material to complete the buffer system, recovery of the copolymer product is substantially facilitated. These salts and buffer systems include, e.g., (1) alkali metal and ammonium acetates, carbonates, bicarbonates, chlorides, phosphates, sulfates, bisulfates, borates; (2) buffer systems comprising (a) mixtures of weak acid or weak base and their salts including (b) phthalates, citrates, borates, phosphates, acetates, ammonium hydroxide, ammonium acetate, ammonium chloride, (c) specific combinations including mixtures of boric acid-borax, citric acid-sodium acid phosphate, sodium carbonate-sodium bicarbonate, ammonium chloride-ammonium hydroxide, ammonium acetate-ammonium hydroxide; or (3) any combination of (1), and (2).

The amount of salt which may be used is about 0.1%–2.0% preferably about 0.2%–0.7%, by weight of the reaction mixture. If the amount of salt exceeds about 2.0%, usually there is a tendency for the granules of the polymeric product to agglomerate in the polymerization reaction mixture. The manner of adding the salt and the point at which it is added are not critical.

The following is a specific example wherein the precipitation process was used in preparing the particular copolymer applicable in the present invention.

To a glass reactor were charged 116 parts of distilled water, 104 parts of acrylamide, 129 parts of tertiary butanol, 3.9 parts of Tergitol NP-14 (nonylphenyl polyethylene glycol ether), 92.4 parts of a 23% aqueous solution of MTMMS, and 0.05 part of potassium persulfate. The pH was adjusted to 5.3 by addition of  $\text{NH}_4\text{OH}$ . The solution was heated to 45° C. The atmosphere and dissolved air were replaced with nitrogen by a series of evacuations and repressurizations. The pressure was then adjusted to 148 mm. to maintain reflux at 45° C. Then 6.26 parts of a 1% aqueous solution of tetramethylethylenediamine was added at a uniform rate during 1.5 hours. Refluxing the reaction mixture was continued for an additional 1.5 hours. Polymerization occurred and the copolymer precipitated during this 3-hour period. The copolymer was washed with acetone and dried in a vacuum oven at 50° C. There was obtained 130 parts of copolymer containing 93.5% solids. It contained 19 weight percent MTMMS and 81 weight percent acrylamide (dry basis).

Although the copolymer slime inhibitor in accordance with the present invention may be added in dry form to the ore being treated, it is preferred to add it as an aqueous solution in order to get faster and more complete dispersion thereof throughout the ore.

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

1. In a process of separating KCl from sylvinitic ores containing KCl and objectionable slime-forming clay by a KCl concentration process wherein said separation is carried out with the aid of a mineral collector added to the ore, the improvement which comprises adding to the ore before addition thereto of the mineral collector a water soluble acrylamide-beta methacryloxyethyltrimethylammonium methyl sulfate copolymer as a slime inhibitor.

2. In a process of separating KCl from sylvinitic ores containing KCl and objectionable slime-forming clay by a froth flotation process wherein a mineral collector and other auxiliary agents are added to the ore slurried in water substantially saturated with the soluble constituents of the ore and the resulting slurry subjected to a froth flotation process, the improvement which comprises adding to the ore before addition thereto of the mineral collector a water soluble acrylamide-beta methacryloxyethyltrimethylammonium methyl sulfate copolymer as a slime inhibitor.

3. Process of claim 2 wherein the amount of said acrylamide-beta methacryloxyethyltrimethylammonium methyl sulfate copolymer employed is about 0.01–0.30 pound per ton of ore treated on a dry weight basis.

4. Process of claim 2 wherein the copolymer consists by weight thereof essentially of 99%–20% acrylamide and 1%–80% beta methacryloxyethyltrimethylammonium methyl sulfate.

5. Process of claim 2 wherein the copolymer consists by weight thereof essentially of 97%–50% acrylamide and 30%–50% beta methacryloxyethyltrimethylammonium methyl sulfate.

6. Process of claim 2 wherein the copolymer consists by weight thereof essentially of 95%–60% acrylamide and 5%–40% beta methacryloxyethyltrimethylammonium methyl sulfate.

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U.S. Cl. X.R.

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,452,867 Dated July 1, 1969

Inventor(s) William T. Bishop (Case 11)

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 15, "with" should read --which--

Column 1, line 50, "flotating" should read --floating--

Column 2, Table - opposite example 4 under column Amt. (b),  
"1.10" should read --0.10--

Column 3, following line 16 after "polymerizing" insert  
--a solution of acrylamide and MTMMS monomers in aqueous  
tertiary--

Column 3, line 41, "axo" should read --azo--

Column 4, line 42, Claim 2, "constituents" should read  
--constituents--

Column 4, line 58, Claim 5, "30%-50%" should read --3%-50%--

SIGNED AND  
SEALED

MAR 24 1970

(SEAL)

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