United States Patent Office 3,477,566
Patented Nov. 11, 1969

3,477,566

PROCESS FOR THE ELECTROSTATIC SEPARATION OF THE SYLVITE (KCl) COMPONENT OF A MINERAL

Hans Autenrieth, Hannover-Kirchrode, and Heinrich Wirries, Hannover, Germany, assignors to Kali Forschungs Anstalt GmbH, Hannover, Germany

No Drawing. Filed Dec. 12, 1966, Ser. No. 600,711
Claims priority, application Germany, Mar. 11, 1966, K 58,696
Int. Cl. B03b 1/04
U.S. Cl. 209—9 5 Claims

ABSTRACT OF THE DISCLOSURE

A process for the electrostatic separation of mineral mixtures, and particularly to conditioned particulate crude potassium salts and the electrostatic separation thereof.

In particular embodiments of the present invention crude particulate potassium salt mixtures are treated with inorganic mineral acids or inorganic alkaline reacting substances before, during or after the particulate material is treated with organic conditioning agents, comprising anionic compounds which form negatively charged radicals that split off positive ions and thereby control the electrostatic charging of the particulate material.

CROSS-REFERENCES TO RELATED APPLICATIONS

Applicants claim priority under 35 U.S.C. 119 for application Ser. No. K 58,696 filed Mar. 1, 1966, in the Federal Republic of Germany.

BACKGROUND OF THE INVENTION

It is known that minerals containing crude potassium salts and many other mineral mixtures can be separated into their components electrostatically after being preconditioned, especially by organic compounds which by forming negatively charged radicals split off one or more protons or metal ions. By a suitable choice of conditioning agent, or by a combination of different conditioning agents, the electrostatic charging of the different mineral components can be controlled so that multiple-component systems are separated completely with high yield into individual mineral components of greater purity.

These prior art methods, conditioning agents and starting materials are fully set forth in German Patents 1,056,551, 1,061,713, 1,076,593, and 1,102,663, and the corresponding U.S. Patent 3,217,876, the disclosures of which are incorporated herein.

Autenrieth discloses in U.S. Patent 3,217,876 conditioning agents and the recycling and reconditioning of a portion of the particulate salt mixture.

The conditioning agents disclosed in the prior art patents are suitable for use in the present invention.

It is postulated that the conditioning does not depend, like a flotation process, on a selective application of the conditioning agent to the mineral components. On the contrary, the conditioning for electrostatic separation is made without selectivity. The selective distribution of electric charges to the individual minerals is decisively favored according to the specificity of the particular mineral by the application of the conditioning agent to the surface of the powdered mineral mixture.

The efficiency of the prior art processes is somewhat limited by the presence of claylike components and the selectivity falls off in the smallest particle range of less than 0.1 mm.

DESCRIPTION OF THE INVENTION

It is therefore an object of the present invention to improve efficiency and selectivity in the process of electrostatically separating particulate mineral mixtures.

Another object of the present invention is an improvement in the efficiency and selectivity of the electrostatic separation of crude potassium salts having a particulate size less than 0.1 mm.

Still another object of the present invention is an improvement in the efficiency and selectivity of the electrostatic separation of crude potassium salts containing impurities of clay.

Other objects of the present invention are improved coatings for particulate mixtures of crude potassium salts which facilitate the electrostatic separation thereof.

A particular object of the present invention is a particulate mixture of crude potassium salt having a coating comprising a mixture of an organic conditioning agent and an inorganic acid or base.

Another particular object of the present invention is a particulate mixture of crude potassium salt that is treated with an inorganic acid or base followed by a treatment with an anionic organic conditioning agent.

Still another particular object of the present invention is a particulate mixture of crude potassium salt that is treated with an anionic organic conditioning agent followed by a treatment with an inorganic acid or base.

A further particular object of the present invention is a particulate mixture of crude potassium salt that is treated with an anionic organic conditioning agent followed by treatment with gaseous hydrogen chloride or ammonia.

Upon further study of the specification and claims other objects and advantages of the present invention will become apparent.

According to the present invention it has been found that the specific distribution of electric charges between the minerals to be electrostatically separated is greatly improved when the powdered mixture, either before, during or after treatment with a prior art conditioning agent, is also treated with very small amounts of inorganic mineral acids, or in other cases with inorganic alkaline reacting substances, preferably NaOH, KOH, or NH_4OH. Even with mineral mixtures that are difficult to process, it is possible with the present invention to give them strong and highly selective charges. The unfavorable effect of claylike components, which limited the prior art processes, is to a large extent acoided thereby while at the same time the selectivity in the smallest particle range of less than 0.1 mm. diameter is considerably increased.

The acids or bases which are used as additional reagents are applied advantageously as dilute or concentrated solutions in water, but are also added to the mineral mixture in their gaseous or solid state and thoroughly mixed therewith. The most suitable reagent, its most suitable concentration and the best method of adding it, depend largely on the properties of the mineral mixture to be processed and are easily determined by those skilled in the art.

The electrostatic separation of the present invention is advantageously carried out with ground or pulverized particulate mineral crudes such as sylvinite and hartsalz or mixtures thereof with the separation of salts such as sylvite, kierserite, rock salt and halite.

Representative examples of the organic conditioning agents suitable for conditioning the sylvite containing crude salts or mixtures of those crude salts prior to the separation steps are among others:

(1) Mixtures of fatty acids C_3–C_{22} or of parts thereof, for instance
  (a) Mixtures of fatty acids C_3–C_{10}
  (b) Mixtures of fatty acids C_6–C_{12}
  (c) Mixtures of fatty acids C_{10}–C_{14}
  (d) Mixtures of fatty acids C_{12}–C_{18}
  (e) Mixtures of fatty acids C_{14}–C_{22}
(2) Linseed oil fatty acids;
(3) Benzoic acid;
(4) Phenylacetic acid;
(5) Salicylic acid;
(6) Phthalic acid;
(7) Alpha-nitroso-beta-naphthol, and salts of the above organic acids;
(8) Nonyl sulfate;
(9) Sodium salt of alkylsulfonic acid;
(10) Sodium salt of oxystearic sulfonic acid;
(11) Sodium salt of benzylnaphthalenesulfonic acid;
(12) Sulfonated amides of fatty acids;
(13) Sodium salt of oxystearinsulfonic acid+sodium salt of alkylsulfonic acid 1:1;
(14) Sodium salt of oxystearic sulfonic acid+sodium salt of ricinic acid 1:1;
(15) Beta-nitroso-alpha-naphthol and mixtures of 1 to 15.

Preferred examples of the inorganic acids used in the present invention are HCl in aqueous or gaseous form, H_2SO_4, HNO_3, H_3PO_4 and colloidal silicic acid suspended in water.

The inorganic bases preferably used in the present invention are aqueous or gaseous NH_3, NaOH or KOH.

Combinations of mineral mixtures with a conditioning agent and an inorganic acid which particularly illustrate the new and unexpected results of the invention are hartsalz having in terms of K_2O, 12.9% treated with 6 to 12 carbon atom fatty acid and HCl, H_2SO_4, HNO_3, H_3PO_4 or colloidal silicic acid; and hartsalz having about 12–13% K_2O and 3% clay treated with 3 to 12 carbon atom fatty acid mixture, salicylic acid, phenylacetic acid, phthalic acid, or nitroso-beta-naphthol and HCl, H_2SO_4, HNO_3 or H_3PO_4.

Illustrations of combinations of mineral mixtures with a conditioning agent and an inorganic base showing the new and unexpected results of the present invention include sylvinite having in terms of K_2O, 18.5% and 5% clay treated with 6 to 12 carbon fatty acid and NaOH, KOH, NH_4OH or NH_3; and sylvinite having 15–16% K_2O and about 2% clay with 3 to 12 carbon fatty acid, salicylic acid, benzoic acid or phthalic acid and NaOH, KOH or NH_4OH.

The procedures and conditions for crushing the mineral mixture, applying the conditioning agent and carrying out the electrostatic separation are fully disclosed in U.S. Patents 3,217,876 and 3,225,924.

Before separation in the electrostatic field the preconditioned salts are preferably heated to temperatures between about 30 and 90° C.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the specification and claims in any way whatsoever.

Example 1

Crude material: Hartsalz with a K_2O content of 12.9%.

Conditioning agent: a first run fatty acid mixture having 6–12 C-atoms.

The hartsalz is ground to a fineness of less than 1.0 mm. and is first conditioned and mixed by spraying upon it 0.2 g./kg. of a mixture of, e.g. first run fatty acids having about 6–12 C-atoms and is then warmed to 65° C. by a current of warm air and separated into its components by falling through a potential gradient of 4 kv./cm. in a free-fall electrostatic separator. Instead of the first run fatty acids, other prior art conditioning agents are used, as suggested for example by the German and United States patents disclosed in the Background of the Invention.

TABLE I

Conditioning Agent	Percent K_2O in residue	Percent K_2O in 1st concentrate	Percent K_2O in 2nd concentrate
0.2 g./kg. of first run fatty acid mixture	2.5	25.2	41.0

Further runs were then performed in which the crude salt after being conditioned with the first run fatty acid mixture was then mixed with 0.5 ml. of two normal acids per kg. of crude salt. After this second mixing the salt was warmed to 65° C. and dried by a current of warm air and then separated into its components in the same manner as disclosed above, in a free-fall separator by a potential gradient of 4 kv./cm. The results are given in Table II.

TABLE II

Conditioning Agent	Percent K_2O in residue	Percent K_2O in 1st concentrate	Percent K_2O in 2nd concentrate
0.2 g./kg. first run fatty acid—			
Plus 0.5 ml./kg. 2 N HCl	1.1	40.6	54.0
Plus 0.5 ml./kg. 2 N H_2SO_4	1.1	39.3	51.1
Plus 0.5 ml./kg. HNO_3	1.3	34.2	48.9
Plus 0.5 ml./kg. H_3PO_4	0.9	38.2	50.8
Plus 0.5 ml./kg. 2 N colloidal silicic acid suspended in H_2O	1.6	36.0	51.0

A comparison of the results of the results with and without the subsequent acid treatment shows the extraordinary improvement in the separating process. Whereas without the subsequent treatment with acid solutions the residues contained about 2.5% K_2O, the residues after acid treatment contained only 0.9 to 1.6% K_2O. The improvement is shown even more clearly by the concentrates. After the subsequent acid treatments the K_2O concentrations were 10–15% higher in the first separation stage than without such acid treatment, and in the second separation stage they were also 10–15% higher. After such acid treatment the highest concentrates (by which is meant the end products of concentration after two or more concentrating stages) show an exceptionally high degree of purity. Whereas without acid treatment it is possible in the present case to obtain a maximum concentration of only 52% K_2O yield of 88%, after the acid treatment a maximum concentration of more than 60% K_2O with a total K_2O yield of 92% or more was obtained.

As Table III shows, the selectivity in the fine granular range that is diffcult to process is greatly improved by the acid treatment.

TABLE III

Selectivity of electrostatic separation in granule size ranges up to 0.1 mm.

Conditioning	Granule size ranges 0–0.06 mm.	0.06–0.1 mm.	
0.2 g./kg. first run fatty acid	28.2	44.3	(1)
0.2 g./kg. first run fatty acid plus 0.5 mg./kg. 2 N acid	47.6	57.3	

[1] Percent K_2O in the highest concentrate.

The results listed in Table IV show that the crude salts that were separated as illustrated in Tables II and III may

have the process modified by subjecting the salts to the acid treatment before as well as after their conditioning treatment with the usual conditioning agents, and also in admixture with the conditioning agents.

TABLE IV

Treatment with the acid before, with or after the addition of the first run fatty acids or the like.

	Percent K_2O in residue	Percent K_2O in 1st concentrate
Conditioning with mineral acid:		
Before	1.2	35.1
With	1.3	36.2
After	1.1	39.4

The values given in Table V show that the results depend primarily on the amount of pure acid with which the crude salt is treated, and that the concentration of the acid is of only little importance.

In the separation runs listed in Table V the acid concentrations ranged from 4 N to gaseous, water-free HCl. It is of importance only that the absolute amount of acid is kept at an optimum value, such as can easily be determined by one skilled in the art.

TABLE V

Conditioning Agent	Percent K_2O in residue	Percent K_2O in 1st concentrate	Percent K_2O in 2nd concentrate
0.2 g./kg. first run fatty acid—			
Plus 0.25 ml. 4 N HCl	1.0	41.0	55.1
Plus 0.125 ml. 8 N HCl	1.2	42.3	55.0
Plus 0.99 ml. 12 N HCl	1.1	41.5	54.3

Example 2

As previously set forth in the specification, applicants have found that in some cases the treatment with inorganic bases is preferred to the treatment with inorganic acid.

It is here shown that treatment with alkalies as ancillary conditioning agents results in a desired improvement. As an example of this, the electrostatic processing of a clay-rich sylvinite:

Raw material: Sylvinite with a K_2O content of 18.5% having about 5% clay.

Conditioning agent: First run fatty acid mixture having 6–12 C-atoms.

The crude salt is ground to 1.0 mm. granule size and is first sprayed in with 0.2 g. of a mixture of first run fatty acids having 6–12 C-atoms per kg. of crude salt, and then without subsequent conditioning is warmed to 60° C. by a current of warm air and is then separated by a potential gradient of 4 kv./cm. in a free-fall separator. The separated products are listed in Table VI.

TABLE VI

Conditioning agent	Percent K_2O in residue	Percent K_2O in 1st concentrate	Percent K_2O in 2nd concentrate
0.2 g. first run fatty acid per kg. crude salt	4.7	25.1	30.5

The high K_2O content in the residue and also the meagre enrichment of it in the concentrates show that this is not a good processing method.

TABLE VII

Conditioning Agent	Percent K_2O in residue	Percent K_2O in 1st concentrate	Percent K_2O in 2nd concentrate
0.2 g. first run fatty acid mixture per kg. crude salt—			
Plus 0.5 ml. 2 N NaOH per kg. crude salt	1.9	38	49
Plus 0.5 ml. 2 N KOH per kg. crude salt	1.9	38.8	50.1
Plus 0.5 ml. 2 N NH_4OH per kg. crude salt	1.6	40.5	52.3
Plus 0.017 grams gaseous NH_3 per kg. crude salt added to the drying air	1.5	42.0	54.0

In Table VII are given the results of subsequent treatment with diluted alkalies, aqueous ammonia or gaseous ammonia added to the drying air, of the crude salt that has been preconditioned with the fatty acids. In each case there was a definite improvement in the processing. The K_2O contents of the residues are now only about ⅓ as high as without the use of alkalies as ancillary conditioning agents. The K_2O contents of the concentrates are about 15–25% higher.

Examples 3*a* to 3*e*

Crude material: Hartsalz with a K_2O content of 12–13% and 3% clay.

Separation temperature: 70° C.

TABLE VIII

Organic Conditioning agent	Inorganic acid	Percent K_2O in 2nd concentrate	K_2O yield (content of raw material equals 100%)
(a) Fatty acid mixture of C_3–C_{11} atoms, 0.2 g./kg.		41.0	88
Do	2 ml./kg. 1 N HCl	56.8	94.8
Do	2 ml./kg. 2 N HCl	56.1	95.4
Do	0.5 ml./kg. 2 N HCl	54.0	95.1
Do	0.5 ml./kg. 2 N H_2SO_4	51.1	94.9
Do	0.5 ml./kg. 2 N H_3PO_4	50.8	94.6
(b) salicylic acid, 0.2 g./kg.		45.3	88.2
Do	2 ml./kg. 1 N HCl	53.5	96.5
Do	1 ml./kg. 1 N H_2SO_4	54.1	93.4
(c) Phenylacetic acid, 0.2 g./kg.		46.5	85.5
Do	2 ml./kg. 1 N HCl	55.3	93.3
Do	2 ml./kg. 1 N H_3PO_4	45.7	95.2
(d) Phthalic acid, 0.2 g./kg.		45.1	85.2
Do	2 ml./kg. 1 N HCl	57.8	94.5
Do	2 ml./kg. 1 N HNO_3	55.8	94.1
(e) Nitroso-β-naphthol, 0.2 g./kg.		46.0	83.1
Do	1 ml./kg. 2 N HCl	53.4	95.1
Do	1 ml./kg. 2 N H_2SO_4	52.9	94.8

Examples 4*a*–4*d*

Crude material: Sylvinite with a K_2O content of 15–16% and about 2% clay.

Separation temperature: 45° C.

TABLE IX

Organic Conditioning agent	Inorganic Base	Percent K_2O in 2nd concentrate	Exploited K_2O of the crude salt containing K_2O
(a) Fatty caid mixture of C_3–C_{12}, 0.2 g./kg		30.5	79.7
Do	2 ml./kg.1 N NH_4OH	56.8	95.7
Do	2 ml./kg. 1 N NH_4OH	57.1	96.0
Do	0.5 ml./kg. KOH	50.1	94.1
Do	0.5 ml./kg. NaOH	52.0	94.7
(b) Salicylic acid, 0.2 g./kg		46.7	85.3
Do	2 ml./kg. 1 N NH_4OH	56.3	94.7
Do	0.5 ml./kg. 1 N NH_4OH	55.8	94.0
(c) Benzoic acid, 0.2 g./kg		46.3	86.3
Do	2 ml./kg. 1 N NH_4OH	55.3	95.0
Do	2 ml./kg. 1 N NaOH	55.1	94.8
(d) Phthalic acid, 0.2 g./kg		47.1	85.8
Do	2 ml./kg. 1 N NH_4OH	58.8	93.2
Do	0.5 ml./kg. 1 N NaOH	56.8	94.1

The preceding examples can be repeated with similar success by substituting the generically and specifically described reactants and operating conditions of this invention for those used in the preceding examples.

We claim:

1. In a process for electrostatic separation of sylvite containing crude salt mineral, the improvement comprising: contacting said mineral, after grinding, with a small amount of an agent selected from the group consisting of a small amount of aqueous HCl, aqueous H_2SO_4, aqueous H_3PO_4, aqueous NaOH, aqueous KOH, aqueous NH_4OH, a suspension of silicic acid in water, gaseous NH_3 or gaseous HCl and additionally conditioning said mineral with organic conditioning agents containing an anionic organic radical and warming up said mineral in a stream of hot drying gas and subjecting said mineral to electrostatic separation of its components.

2. The electrostatic separation process of claim 1, wherein said agent is selected from the group consisting of aqueous suspensions and solutions of inorganic hydroxides.

3. The electrostatic separation process of claim 1, wherein said inorganic acids and bases are selected from the group consisting of about 200–2000 ml. of about 1.0 to 4 normal HCl, about 200–2000 ml. of about 1.0 to 4 normal H_2SO_4, about 200–2000 ml. of about 1.0 to 4 normal HNO_3, about 200–2000 ml. of about 1.0 to 4 normal colloidal silicic acid suspended in water, about 200–2000 ml. of about 1.0 to 4 normal NaOH, about 200–2000 ml. of about 1.0 to 4 normal KOH, about 200–2000 ml. of about 1.0 to 4 normal NH_4OH, about 5–25 g. gaseous NH_3 or about 5–25 g. HCl per ton salt mineral.

4. The process according to claim 3, wherein said inorganic agents and said anionic conditioning agents simultaneously or after mixing with said ground salt mineral are warmed up with hot gas at temperatures between about 30–90° C.

5. The electrostatic separation process of claim 3, wherein said inorganic acids and bases are selected from the group consisting of about 500–2000 ml. of about 1–2 normal HCl, about 500–2000 ml. of about 1–2 normal H_2SO_4, about 500 ml. of about 2 normal colloidal silicic acid suspended in water, about 500–2000 ml. of about 1–2 normal NaOH, about 500–2000 ml. of about 1–2 normal KOH, about 500–2000 ml. of about 1–2 normal NH_4OH, about 5–25 g. gaseous NH_3 per ton salt mineral, or about 5–25 g. gaseous HCl per ton salt mineral, and said salt mineral is conditioned with a small quantity of about 200 g. of an organic anionic conditioning agent per ton salt mineral.

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HARRY B. THORNTON, Primary Examiner

R. HALPER, Assistant Examiner

U.S. Cl. X.R.

209—127