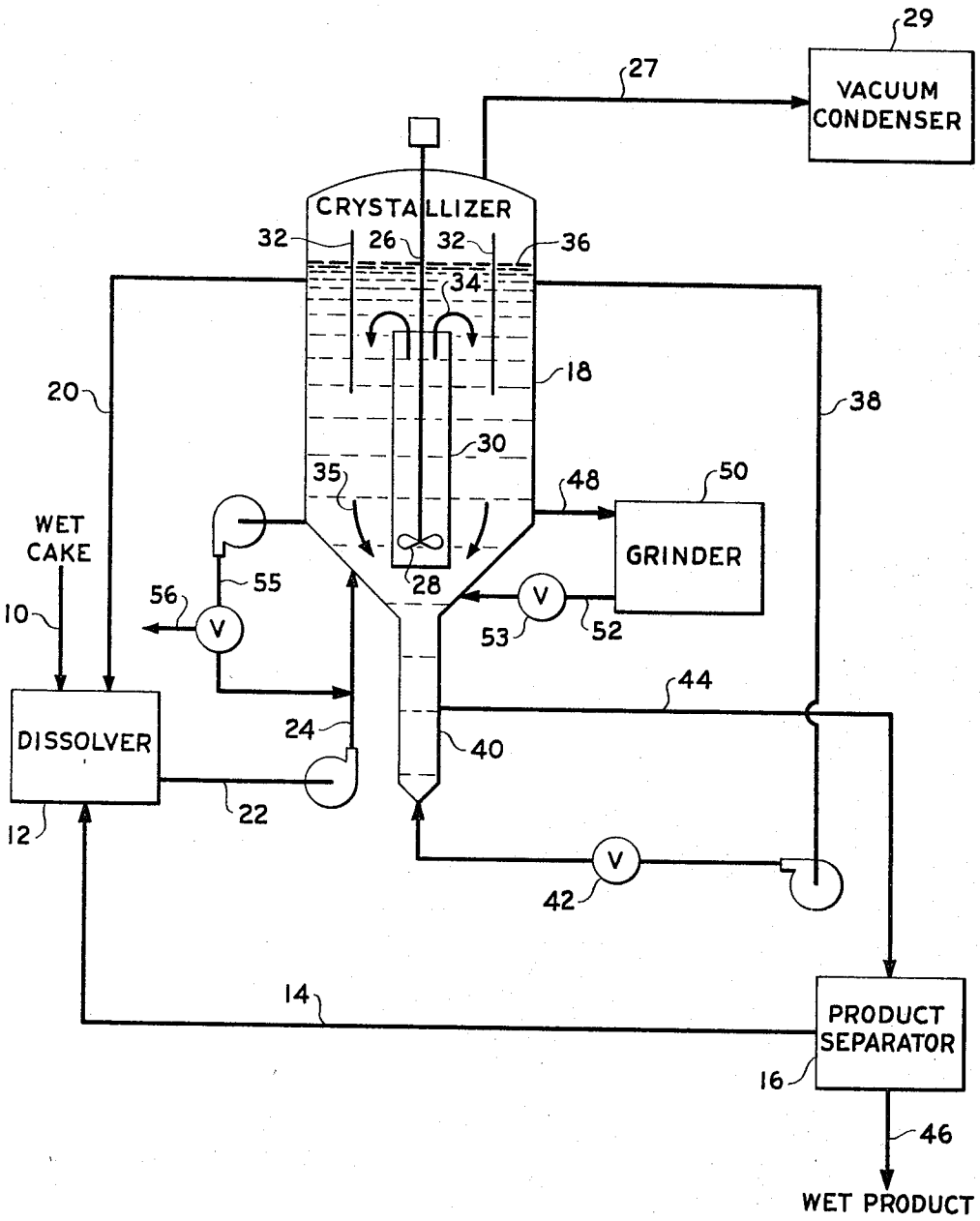
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# CRYSTALLIZATION OF LARGE PARTICLE SIZED AMMONIUM PERCHLORATE

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This invention relates to crystallizing ammonium perchlorate in a large particle size and in a quality suitable for rocket propellant use. More particularly, this invention relates to the crystallization of ammonium perchlorate to effect the production of large size crystals of good crystal structure and low moisture content.

Ammonium perchlorate is used as an ingredient in explosives, in pyrotechnic compositions, as a raw material for the production of perchlorate acid and numerous metallic perchlorates, such as magnesium perchlorate. By far the most predominant use for ammonium perchlorate is as an ingredient in propellant compositions for solid fuel rockets. For this latter use, it is necessary that the ammonium perchlorate meet rigid requirements for chemical purity and physical properties.

The art of crystallizing ammonium perchlorate has developed over years of experience to a point where ammonium perchlorate suitable for most uses is obtained by continuous crystallization from aqueous solutions in the temperature range of about 25 to 45 degrees centigrade. However, ammonium perchlorate has a strong tendency to form discontinuities in the crystal structure, thereby resulting in voids within the crystals. These voids effect an undesirable reduction in both the strength and density of the crystal. In addition, the voids are believed to change the burning rate of rocket motor compositions in comparison with similar size particles having a lesser number and smaller volume of voids. The voids are also disadvantageous because they enclose mother liquor which is not removed by washing and drying operations. Such occluded mother liquor causes an undesirable increase in moisture content and is a source of contamination with sodium chloride and other constituents of the mother liquor. Because ammonium perchlorate used in rocket propellant compositions is preferably of low moisture content, crystallization techniques which result in large amounts of included moisture are unsatisfactory.

Moisture, included within the crystal during crystallization is not readily removed by a drying operation, although such operations are commonly used to remove surface moisture before placing the product in storage. In storage, the included moisture slowly diffuses to the surface of the crystals where it can evaporate. Unless care is exercised to see that this moisture evaporates, and is prevented from accumulating in the air spaces between the crystals, the relative humidity builds up until the crystals fuse or agglomerate, forming undesirable cakes. If adequate precautions are taken to prevent caking, the diffusion process will slowly remove much of the included moisture from the product. By such means, low moisture ammonium perchlorate of normal size was previously obtained in a quality suitable for rocket propellant use.

Previously, most specifications for rocket-grade ammonium perchlorate required an average particle diameter of about 200 microns. Recently, for certain rocket propellant uses, a large size ammonium perchlorate crystal, having the same high quality as that specified for normal sized ammonium perchlorate, has been found to be desirable. Such a desired large size ammonium perchlorate is of an average particle diameter approximately twice the diameter of the normal sized product. Moisture included within these larger crystals is much more slowly



diffused to the surface, so that a significant fraction of the originally included moisture requires an impracticably long period of storage to remove.

To complicate the problem of achieving a sufficiently low moisture content, it is found that when large size crystals are made by conventional crystallizing techniques, the percentage of included moisture is considerably greater than that of normal sized material made by conventional techniques. With the increased moisture content, the number and size of the voids increase proportionally. Because of these difficulties, a practical method for producing large particle size ammonium perchlorate, having the desired low moisture content, was needed.

It is an object of this invention to provide a process for producing large particle size ammonium perchlorate of low moisture and void content at practical rates using conventional equipment. This and other objects will become apparent to those skilled in the art from the description of the invention, which follows.

In accordance with the invention, a process is provided wherein large size ammonium perchlorate crystals are produced comprising maintaining a crystallization zone having therein an aqueous slurry supersaturated with ammonium perchlorate, maintaining said aqueous solution at a temperature of 55 to 110 degrees centigrade, feeding to said crystallization zone, a hot, concentrated, aqueous solution containing ammonium perchlorate, maintaining an evaporating zone within said crystallization zone under subatmospheric pressure and evaporating water from said crystallization zone, maintaining a solid phase content of about 20 to 55 percent by volume of the liquid and solids, feeding finely divided ammonium perchlorate seed particles to said aqueous solution in the crystallization zone to provide growth areas for new crystals, withdrawing mother liquor and crystals from said crystallization zone and separating said crystals from the mother liquor. Normally, the mother liquor is further processed for further recovery of ammonium perchlorate.

By the process of this invention, it is now possible to obtain ammonium perchlorate crystals on a commercial scale of about 5 to 10 times the size by weight of those previously obtained, while maintaining the high quality crystal of low moisture and low void content. Crystals produced are individual crystals similar in shape to small size crystals.

Under previous crystallization techniques, ammonium perchlorate was crystallized in an average particle size of about a U.S. Standard Sieve Series Number 70 to 80. This particle size averages about 170 to 210 microns with a broad range of from about 140 to 250 microns. The crystal size of the large size crystals produced by the present invention have an average particle diameter of about twice that of normal size crystals and have a weight corresponding to about 8 times that of normal size crystals. The large size crystals average about a U.S. Standard Sieve Series Number 40 which corresponds to a diameter of about 400 microns. Also, larger particles can be made. Thus, by the present method, crystals of a diameter ranging from about 200 up to 1000 or more microns are made. The preferred particle diameter averages about 400 microns.

The invention will be described further with reference to the drawing which is a partial schematic diagram and flow sheet illustrating the present invention.

The process of this invention is effected by feeding a source of ammonium perchlorate such as wet cake via line 10 to dissolver 12 wherein the ammonium perchlorate is dissolved in an aqueous solution and heated to an elevated temperature. In addition to using wet cake, which is the undried ammonium perchlorate crystals which may be obtained by other crystallization processes, feed solutions of the reaction mixtures obtained by reacting an

alkali metal perchlorate with ammonium chloride or with ammonia and carbon dioxide, to produce ammonium perchlorate, can be used as the source of ammonium perchlorate. Thus, the solution fed to dissolver 12 can be a relatively pure ammonium perchlorate which is salt free, or an ammonium perchlorate feed stream containing impurities such as an ammonium or alkali metal chloride, perchlorate, carbonate or bicarbonate. However, to produce the highest purity product, a relatively pure ammonium perchlorate wet cake is used.

In dissolver 12, mother liquor and under and oversize ammonium perchlorate crystals from product separator 16 are mixed and heated with the wet cake. Liquor from crystallizer 18 is also passed through dissolver 12 by means of line 20 as a means of maintaining the desired level in crystallizer 18. Sufficient heat, and water, added with the wet cake and other aqueous solutions, is utilized in dissolver 12 to completely dissolve the ammonium perchlorate. The dissolved perchlorate is sent via lines 22 and 24 to crystallizer 18 as a hot, concentrated feed solution maintained at a temperature above saturation to assure complete dissolution of ammonium perchlorate therein. Normally, dissolver 12 effects the heating of the aqueous feed solution to a temperature at least 5 degrees centigrade above the temperature of saturation. Preferably, the feed solution is at a temperature of about 80 degrees centigrade up to the boiling point of the solution which normally is above 105 degrees centigrade. This feed solution contains 20 to about 60 percent by weight of ammonium perchlorate, the preferred range being about 45 to 55 percent by weight of ammonium perchlorate.

Crystallizer 18 is a vacuum crystallizer having means for maintaining a solution temperature of between 55 to 110 degrees centigrade, and preferably between 70 and 90 degrees centigrade, while evaporating large quantities of water. Thus, crystallizer 18 has heating means either external or internal thereto whereby the desired temperatures can be maintained while evaporating water. Often, using an insulated crystallizer and a high circulatory flow through dissolver 12, dissolver 12 may be sufficient as the means for supplying the required heat to the process.

Also contained in crystallizer 18 are agitation means, such as shaft 26 and propeller 28. Such agitation means cause the crystals to remain suspended throughout the crystallizer by producing large circulatory flows within the crystallizer. Draft tube 30 and baffles 32 aid in establishing flow patterns wherein the liquid circulates within the crystallizer growth zone in the direction of arrows 34 and 35. Although the agitation within the crystallizer is sufficient to provide good circulation, such agitation is in a manner such that the abrasion of the crystals within the crystallizer is minimized. Thus, propeller 28 is preferably of large diameter and turns at a moderate to slow speed.

Although the circulation is often effected by means of an agitator, such as propeller 28, other means of establishing circulation within the crystallizer, such as exterior circulating lines and pumps, can be used.

Crystallizer 18 is preferably maintained at liquid level 36 near the top of the crystallizer by continuously withdrawing aqueous solution from crystallizer 18, via line 20. The aqueous liquor withdrawn by means of line 20 is preferably withdrawn from a settling zone in the crystallizer such as that created by baffle 32. Liquor removed via line 20 is returned to dissolver 12 for heating and/or replenishment with additional amounts of ammonium perchlorate.

Liquor withdrawn by means of line 38 is returned to the bottom of crystallizer 18 through elutriating leg 40. The flow through line 38 is regulated by valve 42 so as to enter elutriating leg 40 at a controlled rate. This rate is adjusted so as to effect a fluidization of crystals settling in the elutriating leg 40. Such fluidization results in a classification of the crystals, forcing the smaller crystals back into the main body of the crystallizer.

Attached to elutriating leg 40 is line 44. Crystalline product and mother liquor is withdrawn from the crystallizer by means of line 44 and passed to product separator 16. Product separator 16 removes mother liquor from the crystalline product by filtration, centrifuging or the like liquid-solid separation methods. The separated mother liquor combined with any wash solution is returned via line 14 to dissolver 12 for eventual recycle to the crystallizer.

In the operation of crystallizer 18 in a manner whereby high quality low moisture and low void content crystals are produced, the solution within the crystallizer is maintained in a supersaturated condition below that at which spontaneous crystallization will occur. The liquor in crystallizer 18 is maintained in a supersaturated condition below that at which spontaneous crystallization will occur, by controlled seeding of the crystallizer solution with ammonium perchlorate particles. The seeding provides growth areas on which ammonium perchlorate crystallizes to larger particles.

It has been found that controlled seeding of the crystallizer solution can be conveniently accomplished by withdrawing slurry from crystallizer 18 by means of line 48, passing the slurry through grinder 50 wherein the crystalline product in the withdrawn slurry is ground to a small particle size, and returning the ground ammonium perchlorate particles to crystallizer 18 by means of line 52. Valve 53 on line 52 provides a means for regulating the amount of seed material feed to crystallizer 18. Grinder 50 provides a means for reducing ammonium perchlorate particles to less than half the diameter of the ammonium perchlorate contained in the withdrawn slurry and may reduce the diameter to less than $\frac{1}{100}$ of that of the solids in the withdrawn slurry. Grinder 50 can conveniently be a colloid mill, a gear pump or other grinding and abrasive apparatuses, useful in reducing the particle size of solids contained in aqueous suspensions.

In effecting the crystallization of ammonium perchlorate with in crystallizer 18, a slurry is maintained with a solids content of about 20 to 55 percent by volume. The solid content of the slurry is controlled by the rate at which solids are withdrawn through line 44.

The solids content in the crystallizer is periodically checked by withdrawing a sample of liquor by means of spigot 56 as it is circulated through line 55. The term "solid content" or "volume of solids contained in the crystallizer slurry," means the level to which the solids, in a sample withdrawn from the crystallizer, will settle, when placed in a graduated cylinder. Thus, if a 1000 milliliter sample is withdrawn from spigot 56 into a 1000 milliliter graduated cylinder, and if the solids settled to a level up to the 300 milliliter mark, the solid content is considered to be 30 percent by volume. Although the slurry density can range up to about 55 percent or more by volume, the preferred range of solids is between about 30 and 45 percent by volume.

The following example illustrates certain preferred embodiments of the present invention. Unless otherwise indicated, all parts and percentages used herein are by weight and all temperatures in the example and claims are in degrees centigrade unless otherwise indicated.

## EXAMPLE

The process of this invention was carried out in accordance with the drawing wherein the flow rates, temperatures, crystallization rates, etc., were those obtained as an average of a 48 hour period of continuous operation succeeding several days of continuous operation during which the system was brought into equilibrium from the initial start-up.

The crystallization system was brought into equilibrium by feeding an aqueous solution of ammonium perchlorate to a 9000 gallon operating capacity crystallizer similar to that illustrated in the drawing. The temperature within the crystallizer was maintained at 80 plus or minus one degree centigrade by adjusting the pressure in vacuum

condenser **29** to hold the boiling point of the solution at this temperature while evaporating substantial quantities of water. During the start-up operation, the content of solid ammonium perchlorate crystals in the crystallizer was brought to 30 to 35 percent by volume. The slurry was agitated to maintain the solids in suspension. The average particle size of the crystals in the growth zone was held to a size less than about 200 microns by feeding seed particles of ammonium perchlorate into the growth zone.

The seeding was effected by continuously withdrawing growth zone liquor containing suspended crystalline ammonium perchlorate from the crystallizer, passing it through a colloid mill wherein the crystals were reduced in size by grinding, and returning the effluent to the growth zone. The seeding rate was adjusted so as to maintain the solution in the growth zone at a level of supersaturation below that at which spontaneous crystallization would occur. Under such start-up conditions, small particle size ammonium perchlorate of high quality and low void and moisture content was produced.

During the start-up, as the slurry density approached 20 to 25 percent solids by volume, the seeding was stopped, thereby causing the particles to increase in size.

As the solids content within the growth zone increased to 30 to 35 percent, slurry was commenced to be withdrawn continuously from the elutriating leg of the crystallizer. The rate of withdrawal was adjusted so as to maintain the desired percentage of solids within the growth zone. The withdrawn slurry was passed to the product separator, wherein the particles were separated from the mother liquor. The mother liquor was subsequently returned to the dissolving step for ultimate recycle to the crystallizer. Until there was a significant proportion of product size particles in the product separator, all of the separated solids were returned to the dissolver.

The feed rate to the crystallizer of replenishing quantities of ammonium perchlorate solution was continued at a rate of 300 gallons per minute. The feed liquor contained 65 to 102 pounds of dissolved ammonium perchlorate per 100 pounds of water, such amount being below the saturation point of ammonium perchlorate at the feed temperature of 100 to 105 degrees centigrade. The temperature in the crystallizer was continued to be maintained at 80 plus or minus one degree centigrade by controlling the vacuum.

Samples of crystallizer growth zone liquor were periodically withdrawn to determine the solids content in the growth zone.

Seeding was again commenced when the particle size of solids in the product separator had increased to contain a high proportion of 400 micron average diameter material.

During the crystallization process, liquor was withdrawn from a still zone in the crystallizer. This liquor was returned to the crystallizer as a steady flow of approximately 60 gallons per minute through the elutriating leg of the crystallizer. This flow rate produced a fluidization and classification of crystalline particles causing a predominance of the larger crystals to settle in the elutriating leg.

Also withdrawn from a decantation zone in the crystallizer was a stream of crystallizer mother liquor. This liquor was returned to the dissolving step, wherein additional amounts of ammonium perchlorate were dissolved in the liquor and heated prior to returning the liquor to the crystallizer growth zone. The flow rate of liquor withdrawn from the decantation zone and fed to the dissolver was in an amount of about 250 gallons per minute.

As product size ammonium perchlorate crystals appeared in the product recovery system, they were passed to a drying operation. The dried material was passed through an air classification and screening process wherein the undersized and oversized particles were removed and returned to the dissolver. Thus, in a 48 hour period of continuous operation, 64,000 pounds of large ammonium perchlorate product meeting the following particle size specification were obtained:

| U.S. Standard Sieve Series Number | Particle Size Distribution (Cumulative Weight Percent Retained) | |
|---|---|---|
| | Minimum | Maximum |
| 30 | | 3.0 |
| 40 | 35.0 | 55.0 |
| 50 | 90.0 | 100.0 |
| 70 | 98.0 | 100.0 |

The ammonium perchlorate crystals obtained were of high density and low void and low moisture content, meeting or surpassing the most stringent requirements for rocket propellant use. The moisture content averaged 0.04 percent ranging from 0.03 to 0.05 percent. Such a moisture content was well below the maximum 0.09 percent moisture specified for this particle size material for rocket propellant use.

A particularly significant advantage of the present process is that large quantities of crystalline ammonium perchlorate of large crystal size can be produced continuously, thereby producing an end product of high uniformity and greatly reducing the variation that normally occurs in batch operations. Also, the previously required storage period is eliminated in that low moisture product is obtained directly. Although the crystals produced by the present invention are about eight times the weight of conventionally produced ammonium perchlorate, even larger particles can be made by this process if it is so desired.

Although the described process is particularly useful for producing large size ammonium perchlorate crystals of high quality and low moisture content, normal size crystals can also be produced in this manner by withdrawing crystallizer slurry from the main body of the crystallizer rather than from the elutriating leg. Such normal size crystals are of a much lower moisture content than normal size crystals produced by conventional methods, the low moisture content being directly obtained without a storage period. The directly produced crystals are of a quality satisfying the most rigid rocket propellant specifications.

While there have been described various embodiments of the present invention, the methods described are not intended to be understood as limiting the scope of the invention, as it is realized that changes therein are possible. It is further intended that each element recited in any of the following claims is to be understood as referring to all elements for accomplishing substantially the same results in substantially the same or equivalent manner. It is intended to cover the invention broadly in whatever form its principles may be utilized.

What is claimed is:

**1.** A process for producing high quality ammonium perchlorate crystals comprising maintaining a crystallization zone having therein an aqueous slurry supersaturated with ammonium perchlorate, maintaining said aqueous solution at a temperature of 55 to 110 degrees centigrade, feeding to said crystallization zone, a hot, concentrated, aqueous solution containing ammonium perchlorate, maintaining an evaporating zone within said crystallization zone under subatmospheric pressure, and evaporating water from said crystallization zone, while maintaining a solid phase content of about 20 to 55 percent by volume of the liquid and solids, feeding finely divided ammonium perchlorate seed particles to said aqueous solution in the crystallization zone to provide growth areas for new crystals, withdrawing mother liquor and crystals from said crystallization zone, and separating said crystals from the mother liquor.

**2.** The process of claim **1** wherein the temperature of the aqueous ammonium perchlorate slurry in the crystallizer zone is maintained at a temperature of 70 to 90 degrees centigrade.

3. The process of claim 1 wherein the feed solution of aqueous ammonium perchlorate fed to the crystallization zone is at a temperature of at least 5 degrees centigrade above the saturation temperature of the solution.

4. The process of claim 1 wherein the feed solution of aqueous ammonium perchlorate fed to the crystallization zone contains 20 to 60 percent by weight of ammonium perchlorate and the solution is maintained at a temperature above its saturation point so as to substantially eliminate undissolved ammonium perchlorate therein.

5. The process of claim 1 wherein seed particles are fed to the aqueous slurry in the crystallization zone at a rate sufficient to maintain the crystallization solution in at least a supersaturated condition but below that supersaturation point at which spontaneous crystallization occurs.

6. The process of claim 1 wherein the seed particles fed to the aqueous slurry in the crystallization zone are of an average particle size of about ½ to about 1/100 of the average size of particles in the crystallization zone.

7. A process for producing 200 to 1000 micron size ammonium perchlorate crystals of low moisture content comprising maintaining a crystallization zone having therein an aqueous slurry supersaturated with ammonium perchlorate, maintaining said aqueous solution at a temperature of 70 to 90 degrees centigrade, feeding to said crystallization zone a solution of 20 to 60 percent by weight of ammonium perchlorate maintained at a temperature above its saturation point so as to substantially eliminate undissolved ammonium perchlorate therein, maintaining an evaporating zone within said crystallization zone under subatmospheric pressure, and evaporating water from said crystallization zone while maintaining a solid phase content in the crystallization zone of about 20 to 55 percent by volume of liquid and solids, feeding finely divided ammonium perchlorate seed particles to said crystallization zone to provide growth areas for new crystals, withdrawing mother liquor and crystals from said crystallization zone, separating said crystals from the mother liquor and returning the mother liquor for further processing.

8. The process of claim 7 wherein the crystals separated from the mother liquor are classified and the undersize and oversize crystals are returned for recrystallization.

9. A process for producing 200 to 1000 micron size ammonium perchlorate crystals comprising maintaining a crystallization zone having therein an aqueous slurry supersaturated with ammonium perchlorate maintaining said solution at a temperature of 70 to 90 degrees centigrade, feeding to said crystallization zone a 20 to 60 percent by weight ammonium perchlorate solution maintained at a temperature at least 5 degrees centigrade above its saturation temperature, maintaining an evaporating zone within said crystallization zone under subatmospheric pressure and evaporating water from said crystallization zone, while maintaining a solid phase content in the crystallization zone of about 20 to 55 percent by volume of the liquid and solids, feeding seed particles to the liquid in the crystallization zone at a rate sufficient to limit the supersaturation in the crystallization zone below that at which spontaneous crystallization occurs, said seed particles having an average diameter of ½ to 1/100 of the solid particles in the crystallization zone, withdrawing mother liquor and crystals from said crystallization zone, separating said crystals from the mother liquor and returning the mother liquor for further processing.



10. A process for producing low moisture and low void content ammonium perchlorate in a particle size of about 400 to 500 microns comprising maintaining a crystallization zone having therein an aqueous slurry supersaturated with ammonium perchlorate, maintaining said solution at a temperature of 70 to 90 degrees centigrade, feeding to said crystallization zone a 45 to 55 percent by weight ammonium perchlorate solution maintained at a temperature at least 5 degrees centigrade above its saturation temperature, maintaining an evaporating zone within said crystallization zone under subatmospheric pressure and evaporating water from said crystallization zone while maintaining a solid phase content in the crystallization zone of about 30 to 45 percent by volume of the liquid and solids, feeding seed particles to the liquid in the crystallization zone at a rate sufficient to limit the supersaturation in the crystallization zone below that at which spontaneous crystallization occurs, withdrawing mother liquor and crystals from said crystallization zone, separating said crystals from the mother liquor, drying the crystals, classifying the dried crystals to retain the 400 to 500 micron size particles and returning the mother liquor, undersize and oversize particles for further processing.


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