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AMMONIUM NITRATE EXPLOSIVE AND PROCESS FOR PRODUCING SAME

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ABSTRACT OF THE DISCLOSURE

A process of producing explosive grade ammonium nitrate prills, comprising heating ammonium nitrate above its melting point, reducing the moisture content to not over about 1.0% by weight, mixing uniformly therewith at least 0.2% by weight of a nucleating agent, prilling the molten mixture in a low prill tower, and subjecting the solidified prills to a plurality of heating and cooling cycles through the 32.1° C. phase transition temperature. Preferably at least 0.1% by weight of an inorganic salt soluble in molten ammonium nitrate is also mixed uniformly with the molten mixture before prilling. The low density prills have a crystalline form and oil retention capacity suitable for use as an explosive.

The present invention relates to the production of explosive grade ammonium nitrate prills from high density prills by addition of small percentages of stabilizers to the molten ammonium nitrate prior to the prilling operation and adjustment of the moisture content of the prills, followed by thermal cycling of the prills through the phase transition occurring at about 32.1° C. More particularly, this invention relates to the production of ammonium nitrate prills, containing from about 0.20% to about 5% of additives which decrease the tendency of the prills to crumble into powder as a result of thermal cycling through the aforesaid phase transition and from about 0.2% to about 1.0% water before cycling, which prills after thermal cycling will have low density, acceptable mechanical strength and a sufficiently high oil absorption or retention capacity for use as explosive grade ammonium nitrate.

As is well known in the art, explosive grade ammonium prills are low density prills, which are ordinarily shipped to the user in uncoated form. These are mixed with a prescribed amount of organic material, usually fuel oil or diesel oil, which is absorbed by the prills. This mixture may then be detonated in the same manner as dynamite. Since the ammonium nitrate prills are non-explosive at any ordinarily encountered temperatures until saturated with oil, the prills can safely be transported and stored without the usual precautions required for dynamite, nitroglycerin, or TNT.

Explosive grade ammonium nitrate prills are conventionally produced by passage of molten ammonium nitrate through a "high" prill tower. The conventional high prill tower is about 100 feet in height, and the low density prills collected at the bottom thereof ordinarily contain several percent of moisture which must be removed by passage through dryers and coolers. The resulting low density prills contain voids and are sufficiently porous to absorb the prescribed amount of oil.

In contrast with this, high density ammonium nitrate prills are conventionally produced in a "low" prill tower

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(from about 30 to 60 feet in height) by passing there-through substantially anhydrous molten ammonium nitrate. Ordinarily no further processing is required. These high density prills generally contain less than about .20% moisture and have non-porous surfaces and relatively few voids. The oil absorption capacity of such conventional high density prills is thus far below the minimum acceptable standard.

It has thus heretofore never been considered possible to make explosive grade ammonium nitrate prills in equipment ordinarily used for production of high density prills, even though the economic advantages in construction and operating costs of equipment for the production of high density prills are apparent. In addition, the high prill towers also require expensive drying and cooling equipment for further processing of the low density prills, as indicated previously. Production of explosive grade ammonium nitrate prills in equipment conventionally used only for production of high density prills, with the addition only of a relatively simple and inexpensive thermal cycling unit for further treatment of the prills, would thus provide a distinct economic advantage in original plant cost and in operating expense.

It is a primary object of the present invention to provide an economical process and apparatus for the production of explosive grade ammonium nitrate prills.

It is a further principal object of the invention to provide explosive grade ammonium nitrate prills at a lower cost than is currently possible.

Another object of the invention is to provide additives for ammonium nitrate prills which will prevent crumbling or caking of the prills upon thermal cycling through the phase transition at about 32.1° C.

It is a further object of the invention to provide a novel process for the production of ammonium nitrate prills in a conventional low prill tower, which prills are then subjected to adjustment of their moisture content and to thermal cycling so as to decrease the density of the prills and increase their oil absorption capacity, while at the same time avoiding an appreciable loss in mechanical or physical strength.

These and other objects of the invention which will be apparent to one skilled in the art upon reading these specifications are accomplished by those novel features and modes of operation, the parts and combinations thereof, as hereinafter described.

Pure ammonium nitrate is capable of existing in five crystalline modifications, the transition from one crystalline phase to another being accompanied by thermal changes. It exists in an orthorhombic pseudo-tetragonal form between -18° and +32.1° C., and in an orthorhombic form between +32.1° and about +84° C. The phase change upon heating up through 32.1° C. is accompanied by an expansion in volume, which is about .02 cubic centimeters per gram, according to published literature. On the other hand, it has been found that upon cooling down from a temperature above 32.1° C., the phase change from orthorhombic back to orthorhombic pseudo-tetragonal is not accompanied by a corresponding contraction in volume. In other words, for each heating and cooling cycle through the 32.1° C. transition point, only one increase in volume occurs with no counteracting decrease in volume upon cooling. It will thus be apparent that ammonium nitrate prills subjected to successive heating and cooling through this transition temperature will

undergo an expansion in volume (and consequent reduction in density) each time the temperature of the material rises from below 32.1° C. (about 90° F.) and passes upwardly to a higher temperature. High density prills stored under these conditions have broken down completely into powder, even if not subjected to moving or handling, within a relatively short time.

Surprisingly, it has been found that the addition of relatively small percentages of certain finely divided materials which are substantially insoluble in molten ammonium nitrate, not only result in a marked increase in oil absorption capacity after thermal cycling of the prills but also maintain the mechanical properties and resistance to crumbling within acceptable limits.

Although not intending to be bound by theory, it is believed that certain finely divided materials having an average particle size not greater than 40 microns, which are substantially insoluble in molten ammonium nitrate, are capable of acting as a nucleating or seeding agent, i.e., the particles act as nuclei in the molten ammonium nitrate around which a relatively large number of small ammonium nitrate crystals form as the drops fall through the prilling tower and solidify in descent. Without these nuclei or seeding agents present, the molten ammonium nitrate apparently forms a relatively small number of large crystals, or even a single crystal, while dropping from the prill head. Such prills are subject to physical disintegration upon thermal cycling because of the thermal stresses created upon cooling and because of the relatively tightly packed crystalline lattice. Thermal cycling of such relatively large crystals apparently results in fractures along crystalline planes which greatly weaken or result in complete breakdown of the prills. In contrast to this, thermal cycling of the small crystals in the prills of the present invention results in minute fractures or voids, and the small crystals remain interlocked in the prills.

Exemplary insoluble materials having an average particle size not greater than about 40 microns which are capable of acting as nucleating agents when thoroughly mixed with molten ammonium nitrate in amounts of from about 0.20% to about 4.0% by weight include kaolin, diatomaceous earth, montmorillonite (an aluminum silicate-containing clay), mineral clays containing magnesium and/or calcium silicate, processed clays containing silica, calcium silicate and the like, and metallic oxides such as magnesium, zinc and copper oxides. Other suitable materials, which will suggest themselves to those skilled in the art, are within the scope of this invention.

While a metallic oxide such as magnesium oxide will react with molten ammonium nitrate to form magnesium nitrate, and while copper oxide will form a copper-ammonia complex in molten ammonium nitrate, these reactions are not instantaneous. Consequently, by maintaining the ammonium nitrate at a temperature only about 20° F. above its melting point and by mixing the metallic oxides therewith just before the prilling step, these undesirable reactions are minimized, and at least a major part of the metallic oxide particles remains unconverted to act as nuclei. Materials which are inert to, as well as insoluble in, molten ammonium nitrate can of course be mixed therewith without special precautions and could, if desired, be added before the ammonium nitrate solution from the nitric acid-ammonia reactor is evaporated, or could even be added to the nitric acid if inert thereto.

It has been found that the moisture content of the prills at the beginning of thermal cycling has an important effect on the physical structure of the crystals and the prills. If the moisture content of the prills before thermal cycling is below about .20% to .25% by weight, prills containing a nucleating agent as the sole additive are very stable, and a relatively large number of thermal cycles is required, generally six or more, in order to obtain the desired decrease in density and increase in oil sorption capacity. On the other hand, with a moisture content between about 0.25% and 1.0% by weight the desired decrease in den-

sity and increase in oil sorption capacity can be achieved with not more than four thermal cycles. It has been found that the preferred moisture content of such prills prior to thermal cycling should be in a range from about 0.3% to 0.6% by weight.

The conditions of the thermal cycling can of course be adjusted in order to remove most of the moisture from the prills and obtain a final product having a crystalline form exhibiting good explosive properties. It should also be understood that lowering of the moisture content to a value below about 0.2% after cycling again stabilizes the prills and permits storage thereof without a coating or parting agent. This is a further advantage of the practice of the invention.

The presence of from about .25% to 1% of moisture in the prills before thermal cycling is believed to increase the spacing between the atoms in the crystals, thereby resulting in a less tightly packed crystalline lattice which has greater freedom to expand when heated up through the 32.1° C. phase transition temperature.

In its broader aspect, the process of the present invention thus involves the addition of from about .20% to about 4.0% by weight of an insoluble material having an average particle size not greater than about 40 microns, and which is capable of acting as a nucleating agent, to molten ammonium nitrate prior to the prilling thereof, thoroughly mixing the insoluble material with the ammonium nitrate, passing the mixture through a prilling head, causing the droplets to fall through a counter-current flow of cooling gases to form solidified prills, adjusting the moisture content of the prills to a range between about 0.20% to about 1.0% by weight, and subjecting the prills to a plurality of heating and cooling cycles through the 32.1° C. transition temperature. In its broader aspect the product of the present invention comprises low density ammonium nitrate prills of commercially acceptable mechanical strength, containing from 0.20% to 4.0% by weight of an insoluble nucleating agent uniformly dispersed therein having an average particle size not greater than about 40 microns, the prills having an oil sorption capacity and crystalline form suitable for use as an explosive.

While the class from which the nucleating agent may be selected is relatively broad, an interrelation exists between the decrease in density resulting from thermal cycling, the crystalline structure, and the mechanical or physical properties of the prills which should be observed for optimum results. Certain additives, or combinations of additives, have proved to be superior in achieving a controlled decrease in density (with consequent increase in oil sorption capacity) and a desired crystalline form with only two to four thermal cycles, while at the same time maintaining within acceptable limits the original mechanical strength and resistance to crumbling and caking of the prills. In the preferred practice of the invention, from about .20% to 3.0% by weight of a salt, such as potassium nitrate, ferric sulfate and zinc nitrate, is added to the molten ammonium nitrate along with the substantially insoluble, finely divided nucleating agent. Such salts are soluble in molten ammonium nitrate at least within the relatively low percentage ranges contemplated by the present invention. These small amounts do not substantially affect the phase transition temperature. When this combination of additives is used, the total will range between about 0.35% and about 5% by weight, of which from about .10% to 3.0% by weight may comprise the soluble salt, while the remainder is the insoluble nucleating agent. The proportions may be varied within these limits although at least about 0.25% by weight of the insoluble nucleating agent is preferred.

While again not intending to be bound by theory, it is believed that these relatively small amounts of soluble salts influence the rate of crystal change or transition when subjected to thermal cycling through the 32.1° C.

transition temperature. According to the published literature, about one hour is required to complete the phase change at the transition point in the case of pure ammonium nitrate. Certain soluble salts apparently are capable of accelerating this rate of change, although the moisture content may also have some relation to this effect. As is the case when using an insoluble nucleating agent alone, the combination of a soluble salt and an insoluble nucleating agent results in prills of very high stability if the moisture content before thermal cycling is not greater than about .20% by weight. Here again, it has been found that a moisture content between about .25% and 0.6% by weight gives good results when using this combination of additives. Optimum results have been obtained with the addition of from .4% to 4.0% by total weight of an insoluble nucleating agent and a soluble salt with the moisture of the prills before thermal cycling adjusted to a value between .25% and 0.4% by weight. Under such conditions only from two to four thermal cycles are required to reach the desired oil sorption capacity. Apparently a minimum of about 0.20% moisture results in maximum expansion of such prills and decreases the temperature differential required between heating and cooling. This in turn makes possible a reduction in the number of cycles required.

In its preferred practice, this invention thus involves adding to molten ammonium nitrate from about 0.25% to about 3.0% by weight of an insoluble material having an average particle size not greater than about 40 microns and which is capable of acting as a nucleating agent, and from about 0.10% to about 3.0% by weight of a soluble salt which is capable of influencing the rate of crystal transition, the total amount of insoluble material and soluble salt not exceeding about 5.0% by weight, thoroughly mixing the insoluble material and the soluble salt with the molten ammonium nitrate prior to the prilling thereof, passing the mixture through prilling orifices, causing the droplets to fall through a counter-current flow of cooling gases to form solidified prills, adjusting the moisture content of the prills to a range between about 0.25% to about 0.4% by weight, and subjecting the prills to not more than four thermal cycles through the 32.1° C. transition temperature.

Thermal cycling tests have been carried out under a wide variety of conditions of which the following are representative:

Test I.—Plenum temperatures 41° F. to 128° F. Prills subjected to heating and cooling cycles at 6.75 minutes per cycle.

Test II.—Plenum temperatures 55° F. to 230° F. Prills subjected to heating and cooling cycles at 4 minutes per cycle.

Test III.—Plenum temperatures 80° F. to 135° F. Each cycle comprised heating to 135° F. for 1.5 minutes, cooling to 80° F. and holding for 1 minute.

Test IV.—Plenum temperatures 88° F. to 150° F. First cycle—prills at 88° F. heated to 150° F. in 3.8 minutes and held above 92° F. for 5 minutes; cooled to 78° F. in 4.3 minutes and held below 88° F. for 2.9 minutes. Second cycle—prills heated to 142° F. in 3.5 minutes and held above 94° F. for 4 minutes; cooled to 80° F. in 1.8 minutes.

It will be understood that each thermal cycle, as the term is used herein and in the appended claims, comprises one heating and one cooling treatment and may include first bringing the prills to a desired temperature below the 32.1° C. transition temperature before the heating treatment.

Prills made in accordance with the preferred practice of the instant invention, when subjected to two thermal cycles as described in Test III, developed 5.2% oil re-

tention capacity, and when subjected to 3 Test III cycles developed 6% oil retention capacity.

A highly satisfactory thermal cycling apparatus was one in which an air stream of controlled temperature and humidity was passed upwardly through a conveyor screen supporting a bed of prills. Using this exemplary equipment, a bed of prills three inches deep was subjected to the thermal cycling conditions of Test IV. The pressure drop across the bed was 3" of water, and the linear velocity of the air in the space above the bed was about 600 feet per minute. The velocity through the bed was estimated to be about 3000 feet per minute. No dust was observed in the air stream above the bed.

In the thermal cycling of Test IV the prills were first treated with air at 88° F. and 75% Relative Humidity for 1.5 minutes. The temperatures and times of this test resulted in a heating rate of approximately 1° F. per 3 seconds and a cooling rate of approximately 1° F. per 2 seconds.

It will be understood that the moisture content of the prills can readily be adjusted to the desired value by passing air of a controlled humidity through the bed of prills before the first heating cycle is started. This affords a convenient and simple way of precisely controlling the moisture content between the required value of about 0.2% to 1.0% before thermal cycling, although preliminary control is also maintained by adjustment of the moisture content of the molten ammonium nitrate before and during the prilling operation. Thus, the amount of change in the moisture content of the prills by treatment with air of controlled humidity is quite small usually on the order of about 0.1% to 0.3%.

From the above data it is apparent that two or three cycles between about 80° F. and about 140° F., with sufficient time at each extreme of temperature to ensure that the prills have reached substantial equilibrium or have at least passed through the transition temperature of about 90° F., can be depended upon to effect the desired expansion and increase in oil absorption capacity of prills made in accordance with the preferred practice of the invention.

Optimum results are obtained by a combination of the following interrelated factors: the nucleating agent and soluble salt used to make the high density prills; the moisture content of the prills before thermal cycling; the number of thermal cycles; and the conditions used in cycling.

The minimum average particle size of the nucleating agents does not constitute a limitation on the invention. Materials having a particle size approaching that of colloidal particles (i.e., on the order of .1 micron or less) are capable of acting as a nucleating agent. On the other hand, the upper limit for the average particle size of materials capable of acting as a nucleating agent appears to be in the neighborhood of about 40 microns.

While a minimum of about 0.2% by weight of the nucleating agent apparently is required to impart the desired stable crystalline structure to the prills, there is no sharply defined upper limit aside from the evident limitation that the amount of foreign material added to the ammonium nitrate should desirably be kept to a minimum and should in any event be kept below an amount which would decrease its explosive capacity, as measured by detonation velocity. Consequently, the maximum of 4% by weight of nucleating agent mentioned throughout these specifications and appended claims has been more or less arbitrarily set as the maximum desirable amount which should be added to ensure optimum detonation velocity of the prills. It is within the scope of the invention to add a greater amount of nucleating agent provided the detonation velocity and other desired properties of the prills are not adversely affected thereby.

Similarly, the minimum amount of soluble salt required in the preferred practice of the invention is apparently about 0.1% by weight, while the maximum

should not exceed an amount which will substantially change the phase transition temperature or eliminate the phase transition by modification of the crystalline structure of the ammonium nitrate. Here again, it is within the scope of the invention to add more than the 3.0% maximum so long as the particular salt selected does not adversely affect the desired properties of the ammonium nitrate prills.

EXAMPLE 1

Commercial grade ammonium nitrate was adjusted to a pH of about 6, heated above its melting point of about 160° C. and evaporated to a moisture content of 0.1%. The temperature was then brought to about 170° C., and 0.25% by weight of magnesium oxide having an average particle size of about 5 microns and 0.25% by weight of "Zeosyl" (a precipitated silica having an average particle size of about .2 micron, sold by J. M. Huber Co.) were added to the molten ammonium nitrate and rapidly and thoroughly intermixed. The mixture was then immediately passed through a prill tube headplate having orifices about .025 inch in diameter and dropped through a prill tower providing a free fall of 40 feet through which was passed counter-current cooling air at ambient temperature at a linear velocity of about 800 feet per minute. The prills were collected and cooled to a temperature of about 80° F. At this stage the moisture content of the prills was less than 0.1%. The prills were then placed on a foraminous conveyor, in a layer 3 inches deep, and air having a relative humidity of 75% to 80% was passed therethrough until the moisture content of the prills reached 0.20% by weight. This required about one and one half minutes. The prills were then subjected to the thermal cycling treatment described in Test III above. The cycling was continued for twelve cycles for test purposes, and the oil retention capacity is set forth in Table I below.

EXAMPLE 2

The process of Example 1 was repeated substituting 1% by weight of kaolin and 1% by weight of potassium nitrate as additives. These were added to the molten ammonium nitrate prior to evaporation. After collection and cooling the prills were adjusted to a moisture content of 0.16% by weight and subjected to the thermal cycling treatment described in Test I above. The oil retention capacity was measured after four cycles and eight cycles and is reported in Table I below.

EXAMPLE 3

The process of Example 1 was repeated substituting 0.5% by weight of "Zeolex" (a silica having an average particle size of about 1 micron) and 0.2% by weight of ferric sulfate as additives. The moisture content of the prills was adjusted to 0.35% by weight, and the prills were then subjected to the thermal cycling treatment described in Test III above. After two cycles the oil retention capacity was slightly over 5%, and after three cycles the oil retention capacity was 6.0% for +12 prill size.

The test method used to measure oil retention capacity for all samples was as follows:

A disc of Whatman No. 1 filter paper is fitted into the bottom of a 25 ml. Gooch crucible. The crucible and disc are then wet with No. 2 fuel oil and centrifuged at 1,000 r.p.m. for 5 minutes. The excess oil is wiped from the crucible and weighed to obtain the tare weight.

Approximately 10 gms. of prills are weighed accurately and placed in the crucible. The crucible is placed in a 50 ml. beaker, and sufficient fuel oil (No. 2) is poured over the prills to keep them covered. Both the fuel oil and prills should be at 25° C.

The prills are allowed to soak in oil for 15 minutes

at 25° C., then the crucible is removed from the breaker and allowed to drain for 5 minutes. The crucible is centrifuged at 1,000 r.p.m. for 5 minutes with the center of the bed of prills 4 inches from the hub of the centrifuge.

Finally excess oil is wiped from the crucible, and it is weighed with the prills to obtain the weight of oil absorbed. The calculation is:

$$\frac{\text{Weight gain}}{\text{Sample weight} + \text{Weight gain}} \times 100 = \text{percent oil retained}$$

For reproducible results it is necessary that the prills and oil be brought to a constant temperature of 25° C. before mixing. Variations as high as 20% result from temperature variations on the order of 10° C.

Table I summarizes data on oil retention tests and thermal cycling for Examples 1-3 and for additional examples prepared by processing steps similar to those of Example 1 but with substitution of different additives. For purposes of comparison, Table I also includes data on oil retention tests performed on commercially available stabilized high density prills (Monsanto E-2) and on unstabilized, uncoated high density prills having average mechanical properties among a representative group of commercially available products.

It will be noted that the stabilized high density prills expanded only slightly, and the increase in oil absorption capacity was almost negligible, the value after 12 cycles being only 1.3% by weight.

Although the unstabilized high density prills did increase substantially in oil retention capacity after 6 thermal cycles, the expansion of the prills cannot be controlled consistently, the prills lose considerable physical strength; and a large percentage fracture and many of the prills break down into powder. A representative uncoated, unstabilized high density prill sample, when subjected to the relatively rapid cycling conditions of Test II, exhibited breakage of more than 30% of the prills and a very high loss in the form of dust. In contrast to this, prills made in accordance with the present invention exhibited breakage of less than 1% and practically no dust under the same cycling conditions.

Although an oil retention capacity of 6% is the commercial standard, it was found by actual detonation velocity tests, as described hereinafter, that prills made in accordance with the present invention having an oil retention capacity between about 4.6% and 5.5%, had detonation velocities substantially equal to a standard ammonium nitrate used by the United States Bureau of Mines for comparison purposes.

Example 2 illustrates the effect of the moisture content of prills prior to cycling on the number of cycles required to attain a satisfactory oil retention capacity. Since the moisture content was somewhat below the preferred minimum of 0.25%, it required eight thermal cycles to obtain an average oil retention capacity of greater than 6%.

Examples 3 and 4 illustrate the preferred practice of the invention. It will be noted that satisfactory oil retention capacities were obtained after only 2 or 3 thermal cycles.

Example 5 may be compared to Example 1 to illustrate the effect of the higher moisture content, when using a nucleating agent alone, in reducing the number of thermal cycles required to reach a satisfactory oil retention capacity.

Example	Additive	Prill size	Percent H ₂ O prior cycling	Number of thermal cycles	Bulk density	Oil retention, percent
1.....	0.25% MgO, 0.25% "Zeosyl"	+12	0.20	0	.91	1.9
		+14	0.20	0	.93	6.2
		+12	-----	12	.68	-----
		+14	-----	12	.70	-----
2.....	1% kaolin, 1% KNO ₃	+10	0.16	0	.91	1.3
		+12	0.16	0	.93	1.5
		+14	0.16	0	.95	1.4
		+10	-----	4	-----	3.9
		+12	-----	4	-----	4.2
		+14	-----	4	-----	2.9
		+10	-----	8	.69	5.4
		+12	-----	8	.70	7.6
		+14	-----	8	.72	7.1
3.....	0.5% "Zeolex," 0.2% Fe ₂ (SO ₄) ₃	+12	0.35	0	.92	-----
		+12	-----	2	.83	5.2
		+12	-----	3	-----	6.0
4.....	1% Pikes Peak Clay, 1% KNO ₃	+10	0.26	0	.92	1.0
		+12	0.26	0	.93	1.0
		+10	0.09	2	.79	4.2
		+12	0.09	2	.79	4.7
		+10	0.04	3	.78	4.7
		+12	0.04	3	.78	4.9
5.....	2% Pikes Peak Clay	+12	0.40	0	.91	3.6
		+12	-----	4	.80	6.7
Monsanto E-2.....		+12	.20	0	.93	1.2
		+12	-----	12	.91	1.3
Central Nitrogen.....		+12	.20	0	.93	2.0
		+14	.20	0	.93	2.2
		+12	.12	6	.84	4.4
		+14	.14	6	.83	4.6
Chevron Chemical.....		+12	.26	0	.92	2.3
		+14	.26	0	.92	2.5
		+12	.09	6	.83	5.8
		+14	.09	6	.83	6.1

The nucleating agent of Examples 4 and 5 viz, Pikes Peak clay, is a montmorillonitic clay having an average particle size of not greater than about 40 microns.

Example 4 was subjected to the thermal cycling treatment described in Test II above, while Example 5 was subjected to the thermal cycling treatment described in Test IV above, with the third and fourth cycles being identical to the second cycle of that test.

Table II summarizes the results of tests made to determine the physical strength or toughness of the individual prills, and the resistance of the prills to crumbling, both before and after thermal cycling. In these tests all samples were subjected to twelve thermal cycles, the time for each cycle being three hours. In Examples 1 and 2 the cycling temperatures were from 75° F. to 120° F. In Examples 3 through 5 and the commercial samples the cycling temperatures were from 36° F. to 130° F.

The physical strength of individual prills was tested on a Shore "durometer" which showed the relative strength of prills on an empirical scale of from 0 to 100.

A glass bead test was devised in order to simulate the crushing of prills as a result of handling. 50 grams of prills (—10 +12, or —12 +14 mesh size) were placed in a sixteen ounce widemouth sample jar with an 88 mm. cap size together with 125 grams of No. 5 boro-silicate glass beads (without holes). The sample jar was placed on a ball mill roller having two-inch rollers and was rotated for thirty minutes at 400 r.p.m. plus or minus 5. The contents of the jar were then screened through a 6 mesh screen to remove the glass beads. Next the material was screened (on a 12 mesh screen for —10 +12 mesh size, or on a 14 mesh screen for —12 +14 mesh size) with a pan beneath for five minutes on a Ro-Tap machine. The material passing the screen and caught in the pan was calculated as the percent crushable.

Ex.	Additive	Durometer Crushing Test		Glass Bead Crushing Test, percent		Percent H ₂ O	Bulk Density	
		—12+12	—12+14	—10+12	—12+14		—10+12	—12+14
1.....	0.25% MgO, 0.25% "Zeosyl":							
	Precycled.....	62.5	57.5	0.8	12.3	0.20	.91	.93
	Cycled.....	31.5	39.0	12.9	13.5	.09	.68	.70
2.....	1% kaolin, 1% KNO ₃ :							
	Precycled.....	63.0	52.5	1.0	1.3	-----	.93	.95
	Cycled.....	46.5	49.0	1.8	1.0	-----	.81	.81
							—12+16	
3.....	0.5% "Zeolex," 0.2% Fe ₂ (SO ₄) ₃ :							
	Precycled.....	73.0	68.0	0.3	0	.16	.93	
	Cycled.....	63.0	56.0	10	18	.08	.77	
4.....	1% Pikes Peak Clay, 1% KNO ₃ :							
	Precycled.....	97.0	86.0	1.0	1.3	.07	.95	
	Cycled.....	59.0	46.0	19	53	.06	.82	
5.....	2% Pikes Peak Clay:							
	Precycled.....	97.0	89.0	0.8	0.2	.16	.93	
	Cycled.....	73.0	71.0	1.6	0.9	.10	.83	
	Commercial Low Density Prills						—10+12	—12+14
Atlas:								
	Precycled.....	84.0	76.0	0.5	1.0	.08	.79	.80
	Cycled.....	40.5	38.0	46.5	18.5	.03	.68	.70
Brea:								
	Precycled.....	67.0	60.0	0.5	4.0	.08	.77	.77
	Cycled.....	35.5	35.0	5.5	7.0	-----	.72	.74
Hawkeye:								
	Precycled.....	75.5	58.5	1.0	1.0	.08	.79	.80
	Cycled.....	54.0	20.5	50.0	100.0	.04	.79	.60
Hercomix:								
	Precycled.....	63.5	62.5	2.0	1.0	.07	.82	.80
	Cycled.....	22.5	43.0	96.0	95.0	.06	.65	.66
Carolina Nitrogen:								
	Precycled.....	64.0	62.0	1.5	1.0	.11	.80	.81
	Cycled.....	80.0	70.5	2.5	2.5	.05	.68	.71

Wide variations in mechanical properties of commercially available low density prills will be noted from inspection of the data of Table II, particularly after thermal cycling. In general it may be considered that a percent crushable of 20% or less after 12 thermal cycles would be acceptable commercially. Of twelve commercially available products tested under these conditions only three had less than 20% crushable after thermal cycling. Two of these (Brea and Carolina nitrogen) are reported in Table II. By contrast, it will be noted that only the -12 +14 fraction of Example 3 had a percent crushable of greater than 20%.

It should also be recognized that the prills of Examples 1, 2, 3 and 5 were not reduced to a moisture content of about 0.1% before the thermal cycling tests and hence were not compared under the most favorable conditions with the commercially available products, all of which had moisture contents of about 0.1% before thermal cycling.

Moreover, it was found that there was little consistency in mechanical properties between different samples from the same commercial sources, made by the conventional high prilling tower procedure. By contrast, the process of the instant invention is easily controllable to give a uniform and consistently reproducible product which has high stability after the moisture content is reduced below the critical level. When coupled with the facts that the yield is exceptionally high (less than 1% fractured prills during processing) and that the thermal cycling equipment is less expensive to install and more rapid in operation than the coolers and dryers required for conventional high prill towers, the advantages of the invention will be readily apparent.

Detonation velocity tests were run by the Bureau of Mines of the U.S. Department of the Interior on prills made in accordance with the present invention. One test was made on prills of Example 3 except that the prills were subjected to 4 thermal cycles and had an oil retention capacity of 6.8% by weight. Another test was made on prills made in accordance with Example 1 but containing 1.5% Pikes Peak clay and 0.13% zinc oxide (having an average particle size of about 5 microns) as the nucleating agent, and subjected to 2 thermal cycles as described in Test II above. The results are set forth in Table III below together with comparative results on a commercially available product (Hawkeye) and a standard ammonium nitrate explosive used by the Bureau of Mines.

TABLE III.—DETONATION VELOCITY
Ammonium nitrate prills and fuel oil

Identification	Oil Retention, percent	Average Velocity, Meters/Sec.
Example 3 (4 cycles).....	6.8	3,025
1.5% Pikes Peak Clay and 0.13% ZnO (2 cycles).....	4.8	2,966
Hawkeye.....	7.3	3,200
Bureau of Mines Standard.....		3,150

It will be noted that Example 3 was about 4% lower in velocity rating than the Bureau of Mines standard sample, while the sample containing 1.5% Pikes Peak clay and 0.13% ZnO was about 6% lower than the standard, despite the low oil retention capacity. The detonation velocities of these samples was within the commercially acceptable range.

From the data of Table III, it appears that oil retention is not the sole criterion for determining detonation velocity. The crystalline structure of the ammonium nitrate prills appears to have a very important effect, and the crystalline structure of the prills of the present invention is such as to produce substantially standard detonation velocity even though the oil retention capacity may be somewhat below the standard of 6%.

Modifications may be made in this invention without departing from its scope and spirit. For example, it is considered within the scope of the invention to form

the soluble salt in situ during the reaction of ammonium with nitric acid to form the ammonium nitrate. Accordingly, while various specific embodiments of the invention have been described, no limitation is to be inferred except insofar as set forth in the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Ammonium nitrate prills within the size range of -10 +16 mesh having a bulk density not greater than about 0.83 gram per milliliter and having commercially acceptable mechanical strength, containing uniformly dispersed therethrough at least 0.2% by weight of a nucleating agent having an average particle size not greater than about 40 microns, said nucleating agent being substantially insoluble in molten ammonium nitrate, said prills having an oil retention capacity and a crystalline form suitable for use as an explosive.

2. Explosive grade ammonium nitrate prills having commercially acceptable mechanical strength, containing uniformly dispersed therethrough from 0.25% to 4.0% by weight of a substantially insoluble nucleating agent having an average particle size not greater than about 40 microns chosen from the class consisting of aluminum silicate-containing clays, magnesium silicate-containing clays, silica, calcium silicate, magnesium oxide, zinc oxide, copper oxide and mixtures thereof, said prills having a bulk density not greater than about 0.83 gram per milliliter when within a size range of -10 +16 mesh.

3. Explosive grade ammonium nitrate prills having an oil retention capacity of at least 6.0% by weight and commercially acceptable mechanical strength, said prills containing uniformly dispersed therewithin from 0.2% to 4.0% by weight of a nucleating agent having an average particle size not greater than about 40 microns, said nucleating agent being insoluble in molten ammonium nitrate and capable of causing formation of small unstressed crystals of ammonium nitrate, and containing from 0.1% to 3.0% by weight of a dissolved salt capable of influencing the rate of crystal transition of ammonium nitrate, the total amount of said nucleating agent and said dissolved salt not exceeding about 5.0% by weight.

4. Explosive grade ammonium nitrate prills having commercially acceptable mechanical strength, containing uniformly dispersed therethrough from 0.25% to 4.0% by weight of a nucleating agent having an average particle size not greater than about 40 microns chosen from the class consisting of aluminum silicate-containing clays, magnesium silicate-containing clays, silica, calcium silicate, magnesium oxide, zinc oxide, copper oxide, and mixtures thereof, and containing from 0.2% to 3.0% by weight of a dissolved salt chosen from the class consisting of potassium nitrate, zinc nitrate, ferric sulfate, and mixtures thereof, the total amount of said nucleating agent and said dissolved salt not exceeding about 5.0% by weight.

5. In a process of producing ammonium nitrate prills having commercially acceptable mechanical strength and an oil retention capacity suitable for use as an explosive which includes the steps of providing ammonium nitrate heating the ammonium nitrate to a temperature above its melting point, passing the molten ammonium nitrate through prilling orifices in the form of spherical droplets, and causing the droplets to fall through a counter-current flow of cooling gases to form solidified prills, the improvement which comprises reducing the moisture content of said ammonium nitrate to not more than 1% by weight, mixing uniformly with the molten ammonium nitrate prior to passage through said prilling orifices at least 0.20% by weight of a nucleating agent having an average particle size not greater than about 40 microns, said nucleating agent being insoluble in molten ammonium nitrate, adjusting the moisture content of the solidified prills to a range between 0.20% and 1.0% by weight, and

effecting a controlled expansion of said prills by repeated thermal cycling through the 32.1° C. phase transition point of ammonium nitrate, said phase transition involving a change in crystalline form and consequent increase in volume.

6. The process claimed in claim 5, wherein from about 0.25% to about 4.0% by weight of said nucleating agent is uniformly mixed with said molten ammonium nitrate.

7. The process claimed in claim 5 wherein the moisture content of said high density prills as formed is not greater than about 0.2% by weight and wherein the moisture content is adjusted to a range between about 0.30% and about 0.6% by weight by treating the prills with air of high relative humidity.

8. The process claimed in claim 5 wherein the moisture content of the prills is reduced to not more than about 0.20% by weight as a result of said thermal cycling.

9. In a process of producing low density ammonium nitrate prills suitable for use as an explosive, which includes the steps of providing ammonium nitrate, heating the ammonium nitrate to a temperature above its melting point, passing the molten ammonium nitrate through prilling orifices, and causing the drops to fall through a countercurrent flow of cooling gases to form solidified prills, the improvement which comprises reducing the moisture content of said molten ammonium nitrate to not more than 1% by weight, dissolving in said molten ammonium nitrate prior to the prilling step at least about 0.10% by weight of a soluble salt chosen from the class consisting of potassium nitrate, zinc nitrate, ferric sulfate, and mixtures thereof, mixing uniformly with the molten mixture at least 0.20% by weight of a nucleating agent having an average particle size not greater than about 40 microns, adjusting the moisture content of the prills to a range between about 0.25% and about 0.6% by weight, and subjecting the prills to not more than four heating and cooling cycles through the 32.1° C. phase transition temperature of ammonium nitrate whereby to effect a controlled expansion of said prills as a result of the increase in volume which accompanies said phase transition.

10. The process claimed in claim 9, wherein from about 0.10% to about 3.0% by weight of said soluble salt is dissolved in the molten ammonium nitrate, and wherein from about 0.25% to about 4.0% by weight of said nucleating agent is uniformly mixed with said molten ammonium nitrate, the total amount of soluble salt and nucleating agent not exceeding about 5.0% by weight.

11. The process claimed in claim 9, wherein the moisture content of said high density prills as formed is not greater than about 0.2% by weight, and wherein the moisture content is adjusted to a range between about 0.25% and about 0.4% by weight before thermal cycling.

12. The process claimed in claim 11, wherein the moisture content of the low density prills is reduced to not more than 0.2% by weight as a result of said thermal cycling.

13. The process claimed in claim 10, wherein said nucleating agent is chosen from the class consisting of

aluminum silicate-containing clays, magnesium silicate-containing clays, silica, calcium silicate, magnesium oxide, zinc oxide, copper oxide, and mixtures thereof.

14. The process claimed in claim 13, wherein said prills are subjected to not more than three heating and cooling cycles between the temperatures of about 80° F. and about 140° F.

15. A process of producing low density ammonium nitrate prills suitable for use as an explosive, comprising the steps of providing ammonium nitrate, heating the ammonium nitrate to a temperature above its melting point, evaporating moisture therefrom to a moisture content not greater than 1.0% by weight, mixing uniformly therewith from about 0.25% to 3.0% by weight of a nucleating agent having an average particle size not greater than about 40 microns, said nucleating agent being insoluble in and inert to molten ammonium nitrate, said evaporating and mixing steps being practiced in indiffernt order, passing the molten mixture through prilling orifices, subjecting the drops to a free fall of about 60 feet through a countercurrent flow of cooling gases at ambient temperature to form solidified high density prills having a moisture content not greater than about 0.2% by weight, collecting and cooling said prills, adjusting the moisture content thereof to a range between about 0.25% and 0.6% by weight by treatment with air of high humidity, subjecting the prills to not more than four heating and cooling cycles between the temperatures of 80° F. and 140° F. with at least one minute holding time at each extreme of temperature, whereby to decrease the density of the prills and obtain an oil retention capacity suitable for use as an explosive.

16. The process claimed in claim 15, including the step of dissolving in said ammonium nitrate, prior to the prilling thereof, from about 0.2% to about 3.0% by weight of a soluble salt chosen from the class consisting of potassium nitrate, zinc nitrate, ferric sulfate, and mixtures thereof, the total amount of said nucleating agent and said soluble salt not exceeding about 5.0% by weight, wherein the moisture content of said prills is adjusted to a range of about 0.25% to 0.4% by weight prior to said heating and cooling cycles, and wherein said prills are subjected to not more than three said heating and cooling cycles.

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