

UNITED STATES PATENT OFFICE

2,657,977

PROCESS FOR PREVENTING THE PHYSICAL DISINTEGRATION OF AMMONIUM NITRATE BY TEMPERATURE FLUCTUATIONS

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No Drawing. Application September 21, 1949, Serial No. 117,062

5 Claims. (Cl. 23-103)

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The present invention relates to a process for preparing an improved ammonium nitrate composition. More particularly it relates to a process for preparing an ammonium nitrate composition which is resistant to temperature induced physical disintegration, by incorporating certain stabilizing agents therewith, as more particularly described hereinafter.

Ammonium nitrate is widely used in agriculture as a fertilizer, and in the chemical industry for explosives and various other purposes. When used for any of these purposes, it is desirable that the ammonium nitrate be in the form of small pellets or crystals of minimum surface area, convenient to handle and of reduced humectant properties. Numerous methods have been devised to produce ammonium nitrate in suitable pellet form, including the processes described in our co-pending application, U. S. Serial No. 75,852.

While the preparation of ammonium nitrate in pellet form goes far towards elimination of the difficulties involved in the use of ammonium nitrate, there still have existed difficulties which up to the present time have been insurmountable. One of these obstacles results from the well-known fact that ammonium nitrate undergoes crystal modification on storage when changes in temperature occur. These changes in crystal structure cause a reduction of the strength of the particles and are accompanied by measurable changes in volume and enthalpy. The following table shows the properties of different crystalline forms of ammonium nitrate and the temperatures at which the transformations take place.

Table I

Phase reaction	Type of modification	Temp. °C.	Vol. change, cu. in./lb.	Heat of inversion, B. t. u./lb.
Melt				
I	Liquid-cubic	169.6		32.8
I II	Cubic-tetragonal	125.2	-0.36	21.4
II III	Tetragonal-orthorhombic (a)	84.2	+0.22	9.4
III IV	Orthorhombic-orthorhombic (b)	32.1	-0.61	9.0
IV V	Orthorhombic-pseudohexagonal	-9.4	+0.47	2.9
II IV	Tetragonal-orthorhombic	50.5	-0.36	

^a Also known as orthorhombic.

^b Also known as orthorhombic pseudotetragonal.

The most important temperature-induced transformation, from the standpoint of our invention, is the one at 32.1° C., since this tempera-

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ture is often encountered with summer storage conditions. The speed at which these changes take place is relatively fast, it being reported (Ross et al., "Preparation of Ammonium Nitrate for Use as a Fertilizer," U. S. Department of Agriculture, Technical Bulletin No. 912) that when the orthorhombic form is maintained at 28° C. it will undergo complete transformation into the pseudotetragonal form in 90 minutes.

Weakening of the ammonium nitrate particles, if not complete physical disintegration, is caused by this critical change in temperature. The weakened condition increases caking during storage and generally makes an inferior fertilizer material. One of the principal reasons why ammonium nitrate has not been used in rocket propellents is that the volume changes which accompany the transition from one phase to another, occurring within the ordinary temperature ranges, result in the pellets containing ammonium nitrate being reduced to powder while in storage.

We have now discovered that this tendency of ammonium nitrate particles to disintegrate is considerably reduced, and in most instances completely overcome, and the disadvantage inherent in solid ammonium nitrate referred to above therefore avoided, by adding, to ammonium nitrate, certain secondary components. We have found that the addition of these substances to ammonium nitrate increases the strength of the crystals without otherwise appreciably affecting the ammonium nitrate. In accordance with the present invention, there are used as secondary components ammonium sulfate and ammonium phosphate.

In regard to the method of incorporating these inorganic additives with the ammonium nitrate, we have found that the desired amounts of the secondary components and ammonium nitrate may be mixed thoroughly in the molten state, followed by cooling to give solid ammonium nitrate with the desired properties. Alternatively the secondary components may be introduced along with the reactants in the process used to prepare the ammonium nitrate. While either of these methods may be used to advantage, we prefer to use the latter, and in particular where the process used to prepare the ammonium nitrate is that disclosed in co-pending U. S. patent application, Serial No. 745,729, in which substantially anhydrous molten ammonium nitrate is continuously produced in a one-step process from ammonia and nitric acid at temperatures above the melting point of ammonium nitrate. When using

that process, the materials for eliminating temperature induced disintegration are fed to the reactor as a mixture with the nitric acid or the ammonia. In some instances it is desirable to add to the nitric acid a material different from that desired in the final ammonium nitrate product, but one which upon reacting with ammonia will give the desired compound. For example, if the desired secondary component is ammonium sulfate, excellent results are obtained when sulfuric acid is mixed with the nitric acid in the desired proportion before contact with the ammonia. The desired results are also obtained when phosphoric acid is added to the nitric acid before contact with the ammonia. The exact composition of the compound formed, when phosphoric acid is used in our process, has not been definitely established, but for simplification the product will be referred to as ammonium phosphate.

The secondary components must be added within certain limits in accordance with my invention. While the exact amount of material to be added will, of course, depend upon several variables such as kind of compound added, use to be made of the product, and conditions under

Minor component in anhydrous product	Degree of disintegration (percent fines)
0 (100% NH_4NO_3).....	69.5-100
1.0% P_2O_5	5.15
1.05% $(\text{NH}_4)_2\text{SO}_4$	5.0
2.08% $(\text{NH}_4)_2\text{SO}_4$	1
2.0% $(\text{NH}_4)_2\text{SO}_4$	None

While the stability of ammonium nitrate is increased by the addition of any member of the group consisting of ammonium sulfate and ammonium phosphate, the addition of certain members gives the added advantage of also reducing the rate of moisture absorption by the ammonium nitrate. The following table shows the results obtained from several absorption tests on pure ammonium nitrate and after the addition of secondary components. The samples were prepared exactly as described above for the stability tests and each sample subjected to various humidities, as shown, at a constant temperature of 25° C. for ten days.

Table III

Minor component, percent	Orig. moisture, percent	Percent increase in wt. on exposure to various humidities					
		31%	43%	51%	61.5%	71.2%	81.1%
0 (100% NH_4NO_3).....	0.277	-0.12	0.04	0.03	0.05	3.40	18.80
1.05% $(\text{NH}_4)_2\text{SO}_4$	0.225	-0.04	0.06	-0.005	0.35	1.9	7.37
0.477% P_2O_5 +2.08% $(\text{NH}_4)_2\text{SO}_4$	0.290	-0.03	-0.046	-0.036	0.06	1.0	6.40

which the product will be stored, best results are obtained when the various materials are added in concentrations of between about 0.25 and 5.0% of the total product. Larger amounts may be added, but the final composition will then exhibit properties of the secondary component as well as those of ammonium nitrate. In addition, an ammonium nitrate product containing a combination of the two secondary components exhibits the improved properties referred to. Owing to the manner in which our compositions are made these compositions are free from alkali metal salts;

In the following tests, which were run to determine the extent of disintegration of various ammonium nitrate materials, the ammonium nitrate was made by the process disclosed in U. S. Serial No. 745,729, which has been issued as Patent No. 2,568,901. The secondary component was introduced along with the nitric acid feed and the product was made as small pellets or particles according to the method disclosed in U. S. Serial No. 75,852. Tests were made by placing 10 grams of each sample in a stoppered glass vial and alternately heating and cooling the vials. The vials containing the ammonium nitrate material were placed in an oven at 55° C. for three hours and then removed and held at room temperature (about 22° C.) for three hours. The heating and cooling cycle was repeated five times for each sample. At the end of this operation, the pellets were examined, and all that were about 3/4 or more of their original size were removed from the fines that were produced during the temperature changes. Table II, below, shows the percentage of the original samples that were classed as fines.

While the above describes the preferred embodiments of our invention, it will be understood that modifications may be made therein and departures therefrom within the scope of the specification and claims.

This case is a continuation-in-part of our application, U. S. Serial No. 75,852, filed February 11, 1949, now abandoned.

What we claim is:

1. A process for preventing the physical disintegration by temperature fluctuations of ammonium nitrate produced by the reaction of ammonia and nitric acid, which comprises adding and thoroughly mixing with said acid before said reaction sufficient quantities of sulfuric acid to give an ammonium nitrate product containing from about 0.25 to 5.0% of ammonium sulfate.

2. A process for preventing the physical disintegration of ammonium nitrate by temperature fluctuations which comprises incorporating and thoroughly mixing with molten ammonium nitrate from about 0.25 to about 5.0 percent of ammonium sulfate.

3. A process for preventing the physical disintegration of ammonium nitrate by temperature fluctuations which comprises incorporating and thoroughly mixing with molten ammonium nitrate from about 0.25 to about 5 per cent of an ammonium salt, selected from the group consisting of ammonium sulfate and ammonium phosphate, and forming the resulting melt into pellets.

4. A process of preventing the physical disintegration by temperature fluctuations of ammonium nitrate produced by the reaction of ammonia and nitric acid, which comprises adding and thoroughly mixing with said acid before

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said reaction a small amount of an acid, selected from a group consisting of sulfuric and phosphoric acids, sufficient to produce an ammonium nitrate product consisting essentially of ammonium nitrate in which there is incorporated from about 0.25 to 5.0% by weight of an ammonium salt, corresponding to the added acid.

5. A solidified melt in pellet form having the properties of a substantially pure ammonium nitrate and consisting essentially of ammonium nitrate and from about 0.25 to 5.0 per cent by weight of an added admixed ammonium salt, selected from a class consisting of ammonium sulfate and ammonium phosphate, the quantity of added ammonium salt present being sufficient to reduce the tendency to physical disintegration of the pellets by temperature fluctuations; said composition being free from alkali metal salts.

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