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METHOD FOR IMPROVING THE STORAGE STABILITY OF AMMONIUM SALTS

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This invention relates to a storage stable ammonium salt, such as an ammonium nitrate. In one aspect it relates to a method for improving the storage stability of ammonium salts, such as ammonium nitrate, by incorporating a novel stabilizing agent therewith. In one of its more specific aspects it relates to fertilizers containing ammonium salts, such as ammonium nitrate, and a novel stabilizing agent. In a further specific aspect, it relates to an improved rocket propellant.

Ammonium nitrate has enjoyed wide use of a fertilizer because of its high nitrogen content and the ready availability of the nitrogen. Like salt-peter and other nitrates, ammonium nitrate readily and easily forms explosive mixtures with other combustible substances. One of the difficulties experienced in its use, however, is its tendency to set, or cake, under conditions of shipping or storage. Another difficulty is that due to the thermal decomposition at elevated temperatures and pressures.

It is generally believed that caking occurs during storage when ammonium nitrate changes in crystal habit from plates or dendrites to needles as a result of solution and recrystallization at the surface of the ammonium nitrate particles brought about by the absorption of moisture from the surrounding atmosphere. In the solid state, ammonium nitrate occurs in five different crystal modifications with definite transition temperatures and when the salt is caused to pass from one crystal phase to another, this contributes to the caking tendency, although it is believed to a lesser extent than changes in crystal habit. This caking tendency is especially disadvantageous in the case of fertilizers since one of the requirements of any fertilizer is that it must be in condition to be distributed satisfactorily from fertilizer distributing machinery.

Many attempts have been made to overcome this caking tendency including treatments with water-proofing or moisture-repelling agents such as resins, soaps, waxes, glycerine, urea, diatomaceous earth, petrolatum, paraffin, kaolin, kieselguhr, plaster of Paris, soapstone, and the like. The use of certain inorganic salts, e.g., magnesium nitrate and calcium nitrate, have also been employed. Their application usually involves coating or dusting methods.

Ammonium nitrate is deliquescent and it takes up water from the atmosphere readily. This property complicates its use as a fertilizer and explosive. Though generally ammonium nitrate is a stable salt, careful handling is required and the complications resulting from its deliquescence may be overcome in most instances by such handling and the coating of the crystals with certain inert mineral and organic materials. While some of these materials are satisfactory in lessening the tendency for the salt to cake, their application usually involves costly processes and may result in unduly thick coating of some crystals and a discontinuous coating of other crystals. Organic materials are, in addition, objectionable because they assist the thermal decomposition of ammonium

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nitrate at elevated temperatures and pressures and in some instances have even proved hazardous.

Particular attention has been focused on the thermal decomposition of ammonium nitrate in addition to its caking tendency. Such attention in the main has been caused by several catastrophes resulting from the thermal decomposition of ammonium nitrate with explosive violence (e.g., Oppau, Germany, in 1921, and Texas City in the United States in 1947). These catastrophes indicate that ammonium nitrate is, under certain conditions of temperature and pressure, explosive per se. Ammonium nitrate decomposes readily when heated and at high temperatures and pressures it detonates. The ammonium nitrate involved in the Texas City disaster was coated with certain oxidizable material to prevent caking. This coating material it is believed added to the hazard created by the elevated temperatures and pressures resulting from a fire occurring on board the ship which was transporting the ammonium nitrate.

This invention involves the incorporation of a non-oxidizable stabilizing agent in an ammonium salt, such as solid ammonium nitrate, whereby the storage stability of the salt is improved, tending to make it less susceptible to caking and inhibiting its thermal decomposition. The stabilizing agent which I preferably employ is magnesium nitride in an amount sufficient to react with the salt to liberate ammonia which inhibits the thermal decomposition of the salt and also lessens its tendency to cake. I can also use metal amides as the stabilizing agent.

Accordingly, it is an object of this invention to provide a storage stable ammonium salt, such as ammonium nitrate, composition.

Another object is to provide a method to lessen the tendency of an ammonium salt, such as ammonium nitrate, to cake upon storage.

A further object is to provide a method to inhibit the thermal decomposition of ammonium salts, such as ammonium nitrate.

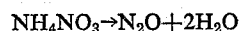
A further object is to provide an improved fertilizer.

A still further object is to provide an improved rocket propellant.

Other objects and advantages of this invention will become apparent to one skilled in the art upon reading the following disclosure and discussion.

I have now discovered that certain stabilizing agents may be incorporated in ammonium salts, such as ammonium nitrate, which will not only lessen the tendency of the salt to cake but also will inhibit the thermal decomposition of the salt. The stabilizing agents useful in the practice of this invention include certain metal nitrides. While certain metal amides are useful in the practice of this invention, generally they are extremely reactive and must be stored under inert liquid, thus making them less preferable. While any metal nitride is useful in the practice of this invention, the nitrides of certain metals of groups IA and IIA of the periodic table are preferred. These include lithium, sodium, potassium, magnesium, calcium, and barium. Aluminum nitride is also applicable in the practice of this invention. These nitrides may be prepared either by direct union of the elements or by deammonation of the amides at elevated temperatures.

On being heated, ammonium nitrate can undergo decomposition in a number of ways, depending upon the conditions of heating. Decomposition does not appear to begin until the salt melts (approximately 170° C.). When the salt is heated beyond its melting point (around 170° C.) up to about 230° C., it decomposes chiefly according to the equation:



The dissociation of ammonium nitrate also forms some

ammonia and nitric acid. When confined in a tube and heated the liberation of an excess of ammonia completely stops the decomposition, even at 50-60° C. above the normal point of decomposition. If the salt is confined and superheated from 230° C. upward, the decomposition becomes more rapid and ends by becoming explosive at the same time the salt becomes incandescent. There are at least seven ways the salt can decompose, some of these reactions proceed as concurrent or side reactions with the formation of varying amounts of higher oxides of nitrogen.

I have found that when magnesium nitride is mixed with ammonium nitrate the odor of ammonia is readily observed even at room temperature. The reaction can be observed by noting a pressure increase in the absence of any water or air. When a sufficient amount of magnesium nitride is mixed with the ammonium nitrate salt, the tendency for the salt to cake during storage is substantially lessened.

The inhibition of the thermal decomposition of ammonium nitrate by the incorporation of a sufficient amount of magnesium nitride is illustrated by the following example.

A dried sample of ammonium nitrate weighing 0.300 gram was placed in a closed reaction tube in a system provided with a pressure gage and a manifold tube for adding and removing gases. The sample size was calculated to give about 20 p.s.i. absolute on total decomposition and the pressure was registered by a Wallace-Tierman pressure gage. The remainder of the system consisted of a tube with several side arms, each with a stopcock, for evacuating the system, admitting nitrogen, and admitting other desired gases. The reaction tube was enclosed by a furnace which was preheated several degrees above the reaction temperature. The reaction tube was then evacuated to insure against the presence of substantial amounts of moisture being present. The sample was heated rapidly to within a few degrees of the desired temperature and final temperature adjustments were made as quickly as possible by adjustment with a Variac. The temperature was quickly brought up to 210° C. and the pressure reading was recorded during intervals of time. Since the decomposition of the ammonium nitrate is dependent upon the time of heating, the measurement of the increase in pressure generated by the decomposition gases as a function of time can be translated into a decomposition rate. A dried sample of ammonium nitrate weighing 0.300 gram and containing 2 percent by weight of magnesium nitride was also decomposed according to the same procedure outlined above. The results of these decompositions are set forth in Table I.

TABLE I

Thermal decomposition of ammonium nitrate and ammonium nitrate with magnesium nitride

Ammonium Nitrate		Ammonium Nitrate and 2% Magnesium Nitride	
Time (min.)	Pressure (p.s.i.)	Time (min.)	Pressure (p.s.i.)
0.....	0	0.....	0
3.....	.175	4.....	.045
5.....	.210	7.....	.060
9.....	.270	9.....	.075
13.....	.300	14.....	.110
26.....	.370	26.....	.200
42.....	.459	29.....	.220
57.....	.519	31.....	.240
70.....	.565	33.....	.255
82.....	.605	39.....	.290
97.....	.660	42.....	.300
		45.....	.310
		55.....	.320
		61.....	.335
		67.....	.350
		69.....	.350

It is apparent from the results set forth in Table I that

the decomposition of ammonium nitrate is inhibited when a small amount of magnesium nitride is incorporated therewith.

I have found that upon heating a confined sample of ammonium nitrate admixed with a small amount of magnesium nitride a slight pressure is observed even at low temperatures (i.e., below 170° C.). The slight pressure remains constant after the initial build-up. At 170° C. the reaction is slow due to the presence of the ammonia generated. This ammonia caused slower decomposition of the sample and when the ammonia was pumped off the decomposition proceeded at a fairly high rate. However, during a long period of time the pressure did not build up appreciably after once building up to a maximum pressure.

A mixture containing equal proportions of ammonium nitrate and magnesium nitride was heated to 100° C. and the temperature maintained at this point for one hour during which a continuous pressure was noted. Thus, it is apparent that even at temperatures lower than the melting point of ammonium nitrate, the magnesium nitride of the present invention will react to produce the gases which inhibit rapid decomposition.

It has been found that when samples of ammonium nitrate admixed with a small amount of magnesium nitride, in accordance with the practice of this invention, were left exposed to ambient temperatures and humidity, no caking tendency of the samples occurred, while samples of ammonium nitrate alone caked under the same conditions.

Generally the amount of magnesium nitride to be employed in the practice of this invention is in the range of 0.5 to 5 percent by weight of the ammonium salt, such as ammonium nitrate, and preferably in the range of 1.0 to 2.0 percent. Obviously in the case of a fertilizer, the amount of magnesium nitride employed should not be so excessive that the nitrogen content of fertilizer is reduced by a substantial amount. The most feasible amount to be employed will be apparent to those skilled in the art upon consideration of the application to which the ammonium nitrate is put, and other considerations. Thus, it is not intended herein that any fixed rule be set forth in that regard.

Ammonium nitrate compositions prepared by the practice of this invention finds particular application in rocket propellants. Magnesium nitride is preferably employed as the stabilizing agent in the above stated amounts and can be readily compounded with binder compositions, such as rubber-like materials, asphalt, etc. A binder such as a copolymer of methylvinylpyridine and butadiene is particularly applicable. Propellants so prepared generally will have 10 to 20 parts by weight of binder and 90 to 80 parts by weight of the stabilized ammonium nitrate.

While the practice of this invention has been found particularly advantageous in lessening the caking tendency of ammonium nitrate, it can be applied to certain other ammonium compounds, especially those suitable as fertilizers, such as ammonium sulfate, ammonium carbonate, ammonium phosphate, and the like, which likewise exhibit a tendency to cake upon storage. The fertilizer produced by the practice of this invention may be mixed with other materials known in the art.

While the invention has been described particularly in connection with ammonium nitrate and magnesium nitride, and other preferred embodiments of this invention, it is to be understood that this description is illustrative only and is not intended to limit the invention. Various modifications will be apparent to one skilled in the art upon study of this disclosure and it is believed such modifications are within the spirit and the scope of this invention.

Having described my invention, I claim:

1. A method for improving the storage stability of an ammonium salt, which comprises incorporating in said salt a small but stabilizing amount of a metal nitride.

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2. A method for improving the storage stability of an ammonium salt selected from the group consisting of ammonium nitrate, ammonium sulfate, ammonium carbonate and ammonium phosphate, which comprises incorporating in said salt a small but stabilizing amount of a metal nitride.

3. The method according to claim 2 wherein the amount of said metal nitride is in the range of 0.5 to 5.0 percent by weight of the ammonium salt.

4. The method according to claim 2 wherein the amount of said metal nitride is in the range of 1.0 to 2.0 percent by weight of the ammonium salt.

5. The method of claim 2 wherein said metal nitride is magnesium nitride.

6. The method of claim 2 wherein said metal nitride is calcium nitride.

7. The method of claim 2 wherein said metal nitride is aluminum nitride.

8. A method for improving the storage stability of ammonium nitrate, which comprises mixing said salt with magnesium nitride in an amount in the range of 0.5 to 5.0 percent by weight of the ammonium salt.

9. A new composition of matter comprising a solid ammonium salt and a minor but storage stabilizing amount of a metal nitride.

10. A new composition of matter comprising an ammonium salt fertilizer selected from the group consisting of ammonium nitrate, ammonium sulfate, ammonium carbonate and ammonium phosphate, and a minor but storage stabilizing amount of a metal nitride.

11. A new composition of matter according to claim 10 in which said salt is ammonium nitrate.

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12. A fertilizer according to claim 10 in which said metal nitride is present in an amount in the range of 0.5 to 5.0 percent by weight of the ammonium salt.

13. A fertilizer according to claim 10 in which said metal nitride is present in an amount in the range of 1.0 to 2.0 percent by weight of the ammonium salt.

14. A fertilizer according to claim 10 wherein said metal nitride is magnesium nitride.

15. A fertilizer according to claim 10 wherein said metal nitride is calcium nitride.

16. A fertilizer according to claim 10 wherein said metal nitride is aluminum nitride.

17. A new composition of matter comprising solid ammonium nitrate in admixture with magnesium nitride in an amount in the range of 0.5 to 5.0 percent by weight of the ammonium salt.

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