

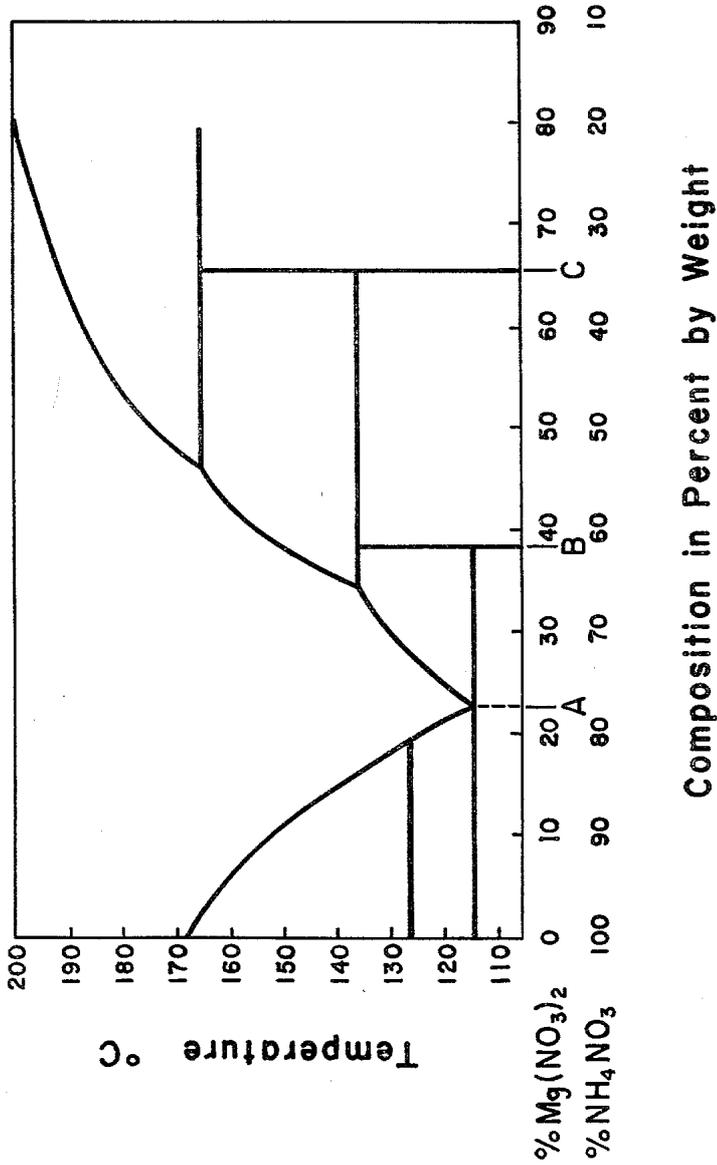
March 16, 1965

E. J. GRIFFITH

3,173,756

DOUBLE NITRATE SALTS AND METHODS FOR THEIR PREPARATION

Filed Nov. 16, 1960



INVENTOR

EDWARD J. GRIFFITH

BY

Roger R. Jones

ATTORNEY

Phase Transitions of the Ammonium Nitrate–Magnesium Nitrate System

EDWARD J. GRIFFITH

Monsanto Chemical Co., Inorganic Chemicals Division, St. Louis, Mo.

Crystal transition between Form IV and Form III ammonium nitrate was studied by hot stage microscopy, hot stage x-ray and differential thermal analyses. A method was developed to move the IV → III transition from 32° to 55° and to stabilize the transition at 55°. The phase diagram for the anhydrous system, $\text{NH}_4\text{NO}_3\text{-Mg}(\text{NO}_3)_2$, was determined and two compounds were found $\text{NH}_4\text{Mg}(\text{NO}_3)_3$ and $(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$.

TRANSITIONS of ammonium nitrate have been the subject of many scientific investigations. The salt experiences four crystal transitions in the temperature range between -20°C . and its melting temperature at 169°C . Much of the previous work has been centered about the transition between Forms IV and III, which is generally accepted as occurring near 32°C . The attention to this particular transition has resulted from the problems the transition causes during the storage of ammonium nitrate.

The 32°C . transition is in the ambient temperature range of the temperate zone and causes swelling, caking, and particle deterioration of stored ammonium nitrate when the transition occurs. The practical advantage of eliminating all transitions of ammonium nitrate under normal storage conditions is obvious. The following work describes how this was achieved as well as the interpretation of the data which led to a dimensionally stabilized ammonium nitrate.

Behn discovered that when ammonium nitrate is exhaustively dried the transition at 32°C . disappears, and it is replaced by a transition at about 50°C . Generally it is conceded the transition at 50°C . to 55°C . is a metastable transition between Forms IV and II and therefore eliminates Form III from the ammonium nitrate phase diagram (1, 2, 6, 8, 10-17).

This interpretation implies that the transition between Forms IV and III at 32°C . and the transition between Forms III and II near 82°C . have been traded for a single transition near 50°C . Also implied is that the transition temperature between Form IV and either of the higher temperature forms is a discontinuous function of the concentration of water in ammonium nitrate.

Two methods of influencing the temperature of the transition from Form IV to Form III ammonium nitrate have been studied in detail. Ammonium nitrate which has been coated with acid magenta (4) will transform from Form IV to Form III, but the kinetics of the transformation are greatly reduced. A second method depends upon lowering the temperature of the transition by the addition of a soluble salt to the ammonium nitrate. Potassium nitrate is typical and the temperature of the IV → III transition is lowered about 6°C . for each per cent of potassium nitrate which is added to the ammonium nitrate (5).

Small quantities (1% or less) of foreign salts will stabilize ammonium nitrate crystals in a temperature range in which they are not normally stable—e.g., Form II nitrate may be stabilized at room temperature by the addition of cesium nitrate to the ammonium nitrate (7). This observation suggests that very small quantities of properly chosen foreign salts should have a very large influence on the transition temperature of ammonium nitrate.

EXPERIMENTAL

The chemicals used were reagent grade except for the ammonium nitrate, which was a commercial sample manufactured by the Monsanto Chemical Co. and was better than 99.6% pure ammonium nitrate. The principal impurity in the ammonium nitrate was water.

Four techniques were employed to determine the transition temperatures of the ammonium nitrate samples. Differential thermal analyses were performed by the more or less standard techniques. A small pot furnace was used as a heat source and the rate of temperature rise was controlled with a variable transformer.

The reference sample, pure magnesium oxide, and the ammonium nitrate samples were completely sealed in glass vials to protect them from atmospheric water. The vials contained a thin thermocouple well which coincided with the axis of the vials. These wells were made in the vials by heating the bottoms of the vials to a temperature above the softening point of the glass and then forcing a sharply pointed carbon rod down the axis of the vial. The diameter of the vials was reduced at the mouth of the vial by pulling the neck of the vial to as small a diameter as possible while allowing easy entry of the samples into the vial. This allows easy sealing of the vial after the sample has been introduced without unnecessary heating of the sample.

When the vials were filled, sealed and cooled, they were placed in a steel block in which two holes had been drilled to allow a snug fit between vials and the block. The block had been machined to fit into the cavity of the furnace and was placed in the furnace. Chromel-Alumel thermocouples were fitted tightly in the wells of the vials and the furnace was closed with a stoneware cover.

The sample temperature was graphed as the x component and the difference in the sample temperature and reference temperature was graphed as the y component with a Mosely x - y recorder. This arrangement was employed for both the transition studies and the determination of the $\text{Mg}(\text{NO}_3)_2\text{-NH}_4\text{NO}_3$ phase diagram.

The sample size used during most of the work was about 10 grams and a heating rate near 2°C . per minute was found satisfactory. This rate is low enough to allow the sample to remain near equilibrium, yet high enough to yield easily detectable thermal changes at transition points.

A polarizing microscope equipped with a Thomas-Kofler hot stage was also employed to visually check the transitions. A photo-multiplier tube was used on the microscope in conjunction with an El Dorado photometer and a 10-mv. recorder to check automatically the transitions of thin films

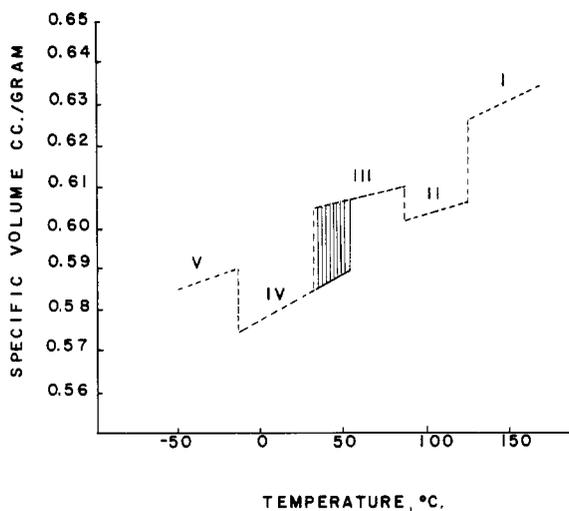


Figure 1. The specific volume of ammonium nitrate demonstrates the unlimited number of paths between Form IV and Form III when Form IV is heated

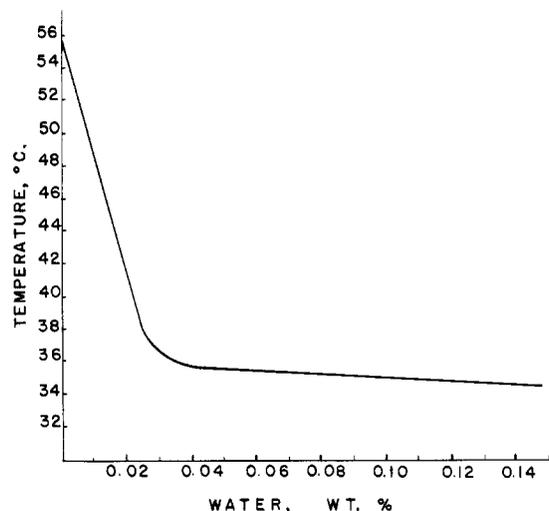


Figure 2. The influence of water on the IV \rightarrow III transition of pure ammonium nitrate

of the ammonium nitrate systems. The temperature of the hot stage was either read directly with a thermometer or was recorded by a separate recorder similar to the recorder used with a photometer. The final method used to check the transitions was based upon hot stage x-ray patterns. The x-ray equipment was a Phillips unit equipped with a hot stage obtained from the Robert L. Stone Co.

The water contents of the ammonium nitrate samples were determined by titrations with Karl Fischer reagent delivered by a Beckman automatic titrimeter. Magnesium concentrations in the ammonium nitrate samples were checked by titration with the sodium salt of ethylenediamine tetraacetic acid solutions employing a Sargent-Malmstadt Spectro-Electric titrator (9).

The samples used in the phase diagram work were prepared by weighing 100 grams of pure ammonium nitrate into a round-bottomed flask and then heating the flask until the ammonium nitrate was molten. The desired quantity of magnesium oxide was added to the ammonium nitrate in small increments, allowing sufficient time for the complete reaction of magnesium oxide before more was added. The mixtures were heated with a Glas Col heating mantle placed over a large size magnetic stirrer. Glass covered stirring bars were employed. The samples were heated until all evidence of any reaction disappeared. Several hours are sometimes required for the complete reaction between magnesium oxide and molten ammonium nitrate. An inactive form of magnesium oxide gave better results when preparing systems rich in magnesium. When the reaction was complete the melts were sparged with anhydrous ammonia for 15 minutes and then allowed to cool slowly to a crystalline solid while dry nitrogen was passed through the flask. When cool, the pH of a 10% aqueous solution was measured as well as the percentage water in the crystals. Samples in the mixed salts systems which exceeded 0.3% moisture were discarded. The samples were then bottled and stored until ready for use. In most cases the thermal measurements on the samples were made the same day the sample was prepared; but there were occasions when several days elapsed between the time the samples were prepared and the time at which the samples were studied. When there was any doubt of a sample's storage stability, the samples were kept in sealed glass vials.

DISCUSSION AND RESULTS

Form IV (orthorhombic) ammonium nitrate is the room temperature form of this salt. When Form IV ammonium

nitrate is heated a transition will occur between 32° and 55° C., depending upon the concentration of water in the ammonium nitrate. If the temperature of the transition occurs in the neighborhood of 32° C., the transition is generally accepted to be a transition from Form IV to Form III (orthorhombic); but if the transition occurs near 55° C., it is considered to be a transition from Form IV to Form II (tetragonal). Most of the data obtained in this work strongly suggests that the transition which occurs during the heating of Form IV ammonium nitrate is between Forms IV and III throughout the temperature range from 32° to 55° C. One or two samples which were studied had a phase transition at 55° C. but no transition at 82° to 90° C. This is the expected behavior for a transformation from Form IV to Form II. The 82° C. transition occurs when Form III ammonium nitrate converts to Form II. If the transition at 55° C. is the conversion of Form IV to Form II, there can be no transition at 82° C. because this is the transition of Form III to Form II, and the Form II conversion had already occurred at a lower temperature, 55° C.

Form II ammonium nitrate changes into Form I (cubic) near 125° C. and the Form I melts at 169° C. The melt is a transparent, colorless liquid similar to water in appearance.

The transition profile of ammonium nitrate is shown in Figure 1. The specific volume data were obtained from Hendricks and others (6), but the paths of the transition in the temperature range between 32° and 55° C. were modified by the author. Figure 2 shows that the transition from Form IV to Form III may occur anywhere in the temperature range between 32° and 55° C., depending upon the quantity of water in the sample. The very dry samples used in Figure 2 were obtained by heating finely ground nitrate at 90° C. for 8 hours in a forced air oven, and then transferring the ammonium nitrate for analyses while it was hot. A sample was considered to have zero water content when a 10-gram sample of the ammonium nitrate required one drop or less of Karl Fischer reagent to deactivate the automatic titrator. In each instance the ammonium nitrate was sealed in a hot glass vial and allowed to return to room temperature before the transition temperature was determined. The significant information of Figure 2 is the fact that the transition from Form IV to Form III is a continuous function of the percentage of water contained in the nitrate. This would hardly be the case if there were a change in mechanism and Form IV were converted to Form II instead of Form III at some intermediate temperature between 32° and 55° C.

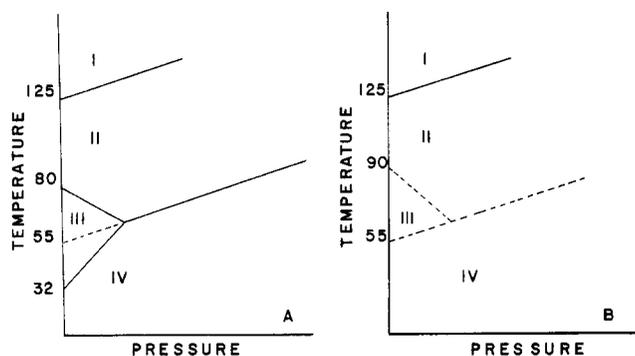


Figure 3. A. Bridgman's original data with an extrapolation added
 B. The data obtained with stabilized nitrate at atmospheric pressure suggest that for very dry ammonium nitrate the curve of Bridgman should be similar to curve B

Some salts were found to overcome the influence of dehydrating the ammonium nitrate. When as little as 0.1% sodium nitrate was added to molten ammonium nitrate and the mixture cooled to room temperature, the transition from Form IV to Form III occurred at 32° C., even for the driest ammonium nitrate the author could prepare. On the other hand, if the temperature of the IV → III transition were stabilized at 55° C. by the addition of 1.84% magnesium nitrate to the system, the addition of 0.1% sodium nitrate to the system was without detectable influence on the temperature of the transition at 55° C.

Hot stage x-ray analyses in the temperature range between 32° and 60° C. showed only Form IV and Form III crystals. This is not conclusive proof that a IV → II transition does not occur because it is very difficult to be certain that no water is absorbed in the surface crystals exposed to the x-rays, even though the sample was prepared for analysis in a dry-box and the chamber of the x-ray furnace was purged with dry nitrogen. The conclusions drawn from the above work are: the transition occurring near 55° C. is a transition between Forms IV and III; the transition at 55° C. is the equilibrium temperature for the transition from Form IV to Form III, and the 32° C. transition is the property of the binary system $H_2O-NH_4NO_3$; a transition from Form IV to Form II may occur on rare occasions but is not normal when the system is being heated, the transition from Form II to Form IV at 55° C. occurs because ammonium nitrate supercools easily and the transition between Forms II and III may be bypassed when cooling a sample.

The pressure-temperature phase diagram prepared by Bridgman (3) did much to support the theory that very dry ammonium nitrate transforms from Form IV to Form II without passing through Form III. Bridgman showed that Form III does not exist in the ammonium nitrate phase diagram at higher pressures and that a IV → II transition occurs. Because the ammonium nitrate used by Bridgman could not possibly have been anhydrous in direct contact with kerosine and because the extrapolation of the IV → II transition curves to atmospheric pressure indicates the IV → II transition should occur at 55° C.—provided the ammonium nitrate were anhydrous—some workers have accepted this phase diagram as additional proof that the IV → II transition occurs in dry ammonium nitrate at atmospheric pressure (13). It is this author's contention that had Bridgman's ammonium nitrate been exhaustively de-

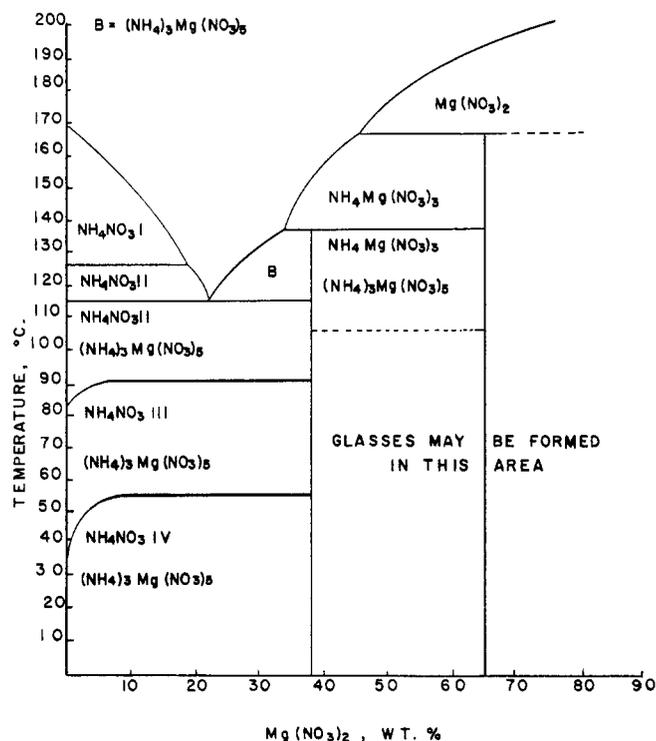


Figure 4. The phase diagram for the anhydrous system $NH_4NO_3-Mg(NO_3)_2$

hydrated, the range of stability of Form IV would have been extended from -17° C. to 55° C. and that the stable region of Form III would have been decreased to the limits from 55° C. to about 90° C. as shown in Figure 3.

Because it is much more difficult to superheat a crystal into a metastable region than to supercool it into a metastable region, heating curves were used throughout this work. Cooling was used only as a check on the heating. The importance of the use of heating curves is easily seen from the work on the phase diagram $NH_4NO_3-Mg(NO_3)_2$ in which glasses rather than crystals were often obtained when the samples were cooled from melt temperature to room temperature.

When magnesium oxide is added to ammonium nitrate and the mixture is heated above the melting temperature of the ammonium nitrate, a slow reaction occurs to produce ammonia, water, and magnesium nitrate. When as little as 0.1% magnesium oxide is added to ammonium nitrate, a noticeable change in the physical properties of the nitrate is observed and the temperature of the transition between Forms IV and III will move to a temperature near 40° C., even when the original ammonium nitrate contained enough water to experience a transition at 32° C. When the concentration of magnesium oxide is increased to 1% of the weight of the ammonium nitrate the transition is raised to 55° C. and a sample of the nitrate may be cycled in the temperature range between 20° C. and 45° C. hundreds of times without any transition occurring and without any change in the dimension of the particles occurring. Moreover, there is no caking or swelling of the sample when hundreds of cycles have been completed.

The magnesium nitrate formed from the magnesium oxide influences the ammonium nitrate in two ways. First, it dehydrates the ammonium nitrate and gives the nitrate a water-holding capacity; second, it changes the crystal habit of the nitrate. The crystals viewed under the microscope are smaller and more rounded at the ends when magnesium

nitrate is added to ammonium nitrate. There is no change in the crystal structure of the ammonium nitrate, however, because the x-ray powder pattern of ammonium nitrate is identical before and after the addition of magnesium nitrate to the system, except for the appearance of a second phase, $(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$, in the diagram.

The phase diagram for the system $\text{Mg}(\text{NO}_3)_2\text{-NH}_4\text{NO}_3$ is shown in Figure 4. Ammonium nitrate which exhibited a transition near 35° C. was chosen as a raw material for the preparation of the systems to be investigated. The rise in the temperature of the transition between Forms IV and III is a continuous function of the concentration of magnesium nitrate contained in the system until the transition temperature reaches 55° C. The temperature of the III → II transition is also influenced by the magnesium nitrate but not as strongly as in the case of the IV → III transitions.

Calcium nitrate also extends the stability of Form IV ammonium nitrate but the maximum temperature obtained for the IV → III transition was 50° C. While magnesium nitrate has considerable influence on the temperature of the III → II transition and will raise the temperature from 82° to 90° C., calcium nitrate has very little influence on the temperature of the III → II transition.

Two compounds, $\text{NH}_4\text{Mg}(\text{NO}_3)_3$ and $(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$, were formed in the concentration range of the $\text{NH}_4\text{NO}_3\text{-Mg}(\text{NO}_3)_2$ phase diagram. Both compounds have unique x-ray patterns and both melt incongruently. When as little as 5% magnesium nitrate has been formed in the ammonium nitrate by the reaction of magnesium oxide and ammonium nitrate the compound $(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$ can be detected in the x-ray patterns of the system.

Table I. Analyses of Compounds in the Phase Diagram

		Wt. %; Theory	Wt. %; Found
	$(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$		
Total nitrogen		28.84	28.58
Ammoniacal nitrogen		10.81	10.94
Magnesium oxide		10.37	10.20
	$\text{NH}_4\text{Mg}(\text{NO}_3)_3$		
Total nitrogen		24.52	24.92
Ammoniacal nitrogen		6.13	6.91
Magnesium oxide		17.64	17.59

The compositions which are very rich in magnesium nitrate are difficult to prepare, and the melting temperature is not very reliable because the system decomposes at high

temperatures. Attempts to prepare samples containing more than about 85% magnesium nitrate were abandoned because the samples must be heated to temperatures high enough to cause decomposition of the system.

Glasses rather than crystalline products can be easily prepared in the system in the region near 65% magnesium nitrate. They form more easily when the melt is not ammoniated before cooling. Once a glass has been formed it will crystallize upon reheating to 110° C. and a large quantity of heat is evolved during the crystallization.

It is impossible to state that the IV → II transition does not occur when Form IV ammonium nitrate is heated to temperatures above 55° C.; but none of the evidence supports the IV → II concept. The hot stage x-ray patterns were never completely clean and two phases, IV and III, usually co-existed; but in no instance was Form II detected below 80° C. when pure Form IV had been heated. It is therefore concluded that a II → IV transition may occur on cooling, but that IV → III transition occurs on heating ammonium nitrate, whether the transition temperature is 32° C. or 55° C.

ACKNOWLEDGMENT

The author is grateful for contributions to this work by M.D. Barnes, J.G. Stites and co-workers, and C.F. Bumgardner.

LITERATURE CITED

- (1) Behn, U., *Proc. Roy. Soc. (London)* **A80**, 444 (1908).
- (2) Bowen, N.L., *J. Phys. Chem.* **30**, 724 (1926).
- (3) Bridgman, P.W., *Proc. Am. Acad. Arts Sci.* **51**, 581 (1916).
- (4) Butchart, A., Whetstone, J., *Disc. Faraday Soc.* **1949**, p. 254.
- (5) Campbell, A.N., Campbell, A.J.R., *Can. J. Research* **24B**, 93 (1946).
- (6) Hendricks, S.B., Posnjak, E., Kracek, F.C., *J. Am. Chem. Soc.* **54**, 2766 (1932).
- (7) Hocart, R.J., Mathieu-Sicard, A., *Disc. Faraday Soc. No. 5*, 237 (1949).
- (8) *Ibid.*, 289 (1949).
- (9) Kaelble, E.F., Monsanto Chemical Company, St. Louis, Missouri, Private Communication, October 27, 1958.
- (10) Leskovich, I.A., *Zhur. Fiz. Khim.* **28**, 2255 (1954).
- (11) Makhnatkin, M.P., *Ibid.*, 552 (1954).
- (12) Morand, J., Michel, A., *Bull. Soc. Chem. France* **1953**, p. 913.
- (13) Morand, J., *Ann. Chim. (Paris)* **10**, 1018 (1955).
- (14) Tanko, K., Fukuyama, I., *J. Phys. Soc. Japan* **8**, 428 (1953).
- (15) Trimeyer, R., *Z. Krist.* **97**, 386 (1937).
- (16) Val'fkovich, S.L., Rubenchik, S.M., Kozhin, V.M., *Izvest. Akad. Nauk.S.S.R., Otdel Khim. Nauk* **1954**, p. 209.
- (17) Whetstone, J., *Acta. Cryst.* **7**, 697 (1954).

RECEIVED for review June 13, 1962. Accepted September 21, 1962.

CORRECTIONS

In the article, "Mass Transfer Studies in Perforated-Plate Extraction Towers," by M. Raja Rao [*J. Chem. Eng. Data* **7**, No. 4, 471(1962)] a figure caption was omitted. "Figure 1. Extraction of benzoic acid from toluene to water. Comparison of the present mass transfer data with that reported in the literature" should have been inserted in the first column below the first graph. The second graph is part a of Figure 2.

In the article, "Equilibrium Vapor Compositions of *p*-Dichlorobenzene-*p*-Dibromobenzene and *p*-Dichlorobenzene-*p*-Bromochlorobenzene Solid Solutions at 50° C., by Sister J.E. Callanan and N.O. Smith [*J. CHEM. ENG. DATA* **7**, No. 3, 374 (1962)] an omission occurred in Table I. Between the fourth and fifth rows of data, the following heading should appear:

The System *p*-C₆H₄Cl₂-*p*-C₆H₄BrCl

1

2

3,173,756

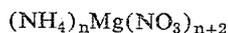
DOUBLE NITRATE SALTS AND METHODS FOR THEIR PREPARATION

Edward J. Griffith, Manchester, Mo., assignor to Monsanto Company, a corporation of Delaware
 Filed Nov. 16, 1960, Ser. No. 69,640
 12 Claims. (Cl. 23-102)

This invention relates to novel compositions of matter and methods of making the same. More specifically, the invention relates to new inorganic nitrate double salts and compositions containing the same.

Inorganic double salts are well known in inorganic chemistry, but prior to this invention no double salts of magnesium and ammonium nitrates have been reported. It has now been found, however, that under the proper conditions such double salts can be formed and once formed are stable and useful compounds.

The new compounds of this invention can be represented by the following formula:



wherein "n" represents an odd numbered integer of from 1 to 3 inclusive. New compounds of the above formula are prepared by a process which comprises introducing magnesium oxide or the equivalent into molten ammonium nitrate under such conditions that a solution of magnesium nitrate in molten ammonium nitrate results. The product can then be solidified by cooling in any suitable manner.

Double salts prepared in accordance with this invention are useful per se as fertilizers but are primarily useful as additives to impart dimensional stability to ammonium nitrate materials. In the production and storage of compact forms of ammonium nitrate, it is difficult to maintain the external and internal structure of the initial compact form because of discontinuous density changes which occur when the compact form passes in either direction through a 32° C. transition temperature. As a result of such density changes, compact forms of ammonium nitrate crack or crumble internally and may be eventually reduced to a fine powder. These undesirable phase transition effects are well known with respect to ammonium nitrate explosive and fertilizer materials. It has been found that the addition of a small percentage of one of the double salts of this invention to ammonium nitrate prior to its being formed into a compacted form results in the crystalline phase change, which is normally observed at about 32° C., not being discernible until a temperature of about 50° C. is reached. A temperature of 50° C. is above any temperature normally encountered in storage of ammonium nitrate compositions so that damage to solidified forms of ammonium nitrate as a result of temperature instability is eliminated. While magnesium nitrate alone can be employed in the stabilization of ammonium nitrate compositions, the use of a double salt in accordance with this invention is highly advantageous for the reason that ammonium nitrate compositions are much less hygroscopic when a double salt is employed for stabilization than when magnesium nitrate is employed for stabilization.

Another advantage in the use of a double salt of this invention in the preparation of temperature stabilized ammonium nitrate compositions is that the salt can readily be prepared in anhydrous form and does not result in the formation of water or other objectionable materials when added to molten ammonium nitrate. This represents the first instance of a material having this advantage as will be seen from the fact that magnesium oxide forms water when added to ammonium nitrate; magnesium nitrate is commercially available only as a hexahydrate and its addi-

tion to ammonium nitrate undesirably increases the moisture level; and magnesium carbonate produces carbon dioxide when added to ammonium nitrate and results in undesirable bubbling in the mixture. In contrast, the compounds of this invention when added as an anhydrous melt do not increase the moisture level and do not result in undesirable bubbling.

The ammonium nitrate employed in the manufacture of the new double salts of this invention can be prepared in any conventional manner except that it is preferably as low in water and free acid content as possible. The double salts of this invention are decomposed by aqueous mediums unless the medium is highly basic and any substantial quantities of free acid and water in the ammonium nitrate used in accordance with this invention may result merely in the formation of a mechanical mixture rather than in the formation of a double salt. As a general rule, the water content of a molten ammonium nitrate mixture employed in accordance with this invention should be below about 5% by weight and preferably below about 1% by weight. Low water content becomes increasingly important as the amount of free acidity in the ammonium nitrate mixture increases or, in other words, increasing free acid content is increasingly deleterious with increasing water content. As a general rule, the free acid content should not be in excess of about 1 mole of free acid for each mole of magnesium oxide to be added or the equivalent, and preferably the free acid content is such that ammonium nitrate must be decomposed with the liberation of ammonia to provide at least a portion of the nitrate anions necessary for the formation of the desired double salt.

As mentioned above, the magnesium necessary for the formation of a double salt in accordance with this invention is preferably added in the form of magnesium oxide. There are possible alternatives but the use of magnesium oxide serves to eliminate free acid which might be present in the ammonium nitrate at the time of the addition of the source of magnesium and is additionally advantageous for the reason that the shortest time interval is necessary for the formation of the desired double salt or salts. Magnesium nitrate can be employed in lieu of magnesium oxide but the use of magnesium nitrate is not advantageous for the reason that the use of this material may result in a surplus of nitrate ions and excess water being present and, as set forth above, the presence of excess nitrate ions makes the formation of double salts more difficult if not impossible. Magnesium hydroxide can be employed but the hydroxide is not readily transformed into the nitrate under the most desirable process conditions of this invention and, in addition, results in the water content of the molten ammonium nitrate to which the source of magnesium is added being raised to an undesirably high level. The use of dead burned magnesium oxide is preferable because this form hydrates less rapidly than other commercially available forms and is less apt to be hydrated by any free water present in the ammonium nitrate to which it is added.

The amount of magnesium oxide or the equivalent added to molten ammonium nitrate in accordance with the process of this invention depends upon the particular double salt that one desires to produce. If one adds less than the equivalent of about 38% by weight of magnesium nitrate, only $(NH_4)_3Mg(NO_3)_5$ will be formed; if one adds more than the equivalent of about 38% magnesium nitrate but less than about the equivalent of 65% magnesium nitrate, a mixture of $NH_4Mg(NO_3)_3$ and $(NH_4)_3Mg(NO_3)_5$ will be formed; and if one adds more than the equivalent of about 65% magnesium nitrate only $NH_4Mg(NO_3)_3$ will be formed. (Applicant has found some evidence of a double salt containing mag-

nesium nitrate in an amount more than 65% by weight but such evidence is inconclusive.

A better understanding of the character of the compositions of the present invention can be gained by reference to the drawing, which is a diagram of phase transition temperature as a function of composition expressed in terms of percent by weight of magnesium nitrate and ammonium nitrate. From this phase diagram it can be seen that when the percentage of magnesium nitrate is about 38% by weight and the percentage of ammonium nitrate is about 62% by weight, a double salt corresponding to the composition $(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$ is formed. This double salt melts incongruently at a temperature of about 137° C. and is indicated on the phase diagram at the line "B." If the percentage by weight of magnesium nitrate is below about 38% by weight, it will be seen from the phase diagram that a mixture of the double salt $(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$ and ammonium nitrate exists and forms an eutectic when the magnesium content of the mixture is equivalent to 23% by weight magnesium nitrate. This eutectic mixture melts at about 115° C. and is indicated at the point "A" on the phase diagram. When the magnesium content of a mixture is equivalent to about 65% by weight magnesium nitrate a double salt of the formula $\text{NH}_4\text{Mg}(\text{NO}_3)_3$ is formed. This double salt melts incongruously at a temperature of about 167° C. and is indicated on the phase diagram by the line "C."

The compositions of the present invention are obtained primarily as crystalline solids but can be obtained as glasses under some conditions. For example, one tends to obtain glasses when the free nitric acid or water content is excessive. Except under conditions favoring the formation of glasses, the crystalline double salts can be obtained from a molten melt by cooling the melt in any conventional manner. For example, the melt can be allowed to cool by reducing the ambient temperature to below the solidification temperature of the melt, for example, below about 110° C., or, alternatively, the molten material can be prilled by the same procedures used for prilling ammonium nitrate fertilizers. In the form of prills or the like the new double salts of this invention can conveniently be added to molten ammonium nitrate to produce a fertilizer or explosive composition stabilized against phase transition as a result of temperature fluctuations in the vicinity of 32° C.

The invention will now be illustrated by the following specific examples in which all parts are by weight unless otherwise indicated.

Example 1

In a suitable reaction vessel there is placed 36 parts of ammonium nitrate and the temperature thereof raised to about 200° C. Free ammonia is bubbled through the molten ammonium nitrate to remove excess acidity and the moisture content of the molten ammonium nitrate is reduced to 0.5%. If necessary, a tubular evaporator can be employed for this purpose. To the molten ammonium nitrate there is added a small quantity of dead burned magnesium oxide sufficient to result in turbidity. The mixture is then retained at 200° C. and agitated until it again becomes clear. Further additions of magnesium oxide are then made employing the same technique until the equivalent of a total of 65 parts of magnesium nitrate have been added. The mixture is then prilled using a conventional prilling tower and the prilled product is collected and stored in moistureproof containers. The product is a double salt of the formula $\text{NH}_4\text{Mg}(\text{NO}_3)_3$ which melts incongruously at 167° C. Chemical analysis of the prilled product was as follows:

	Theory, percent	Found, percent
Total Nitrogen.....	24.52	24.92
Ammoniacal Nitrogen.....	6.13	6.91
Magnesium Oxide.....	17.64	17.59

Existence of a double salt is clearly shown by X-ray diffraction and by the phase diagram for the system.

The procedure of this example can be practiced using only the precautions conventionally employed when handling ammonium nitrate.

The minimum length of time required for the magnesium oxide additions will vary from about 3-4 hours for small laboratory quantities up to 12-20 hours for 1000 to 1500 lbs. quantities.

Example 2

Example 1 is repeated except that 62 parts of ammonium nitrate and 38 parts of magnesium nitrate are employed. The resulting product is a double salt of the formula $(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$ which melts incongruously at about 137° C. The chemical analysis of this product is as follows:

	Theory, percent	Found, percent
Total Nitrogen.....	28.84	28.58
Ammoniacal Nitrogen.....	10.81	10.94
Magnesium Oxide.....	10.37	10.12

Again the existence of a double salt is shown by X-ray diffraction and the phase diagram.

Example 3

In a suitable reaction vessel there is placed 67 parts of ammonium nitrate and the temperature is raised to about 200° C. The moisture level of the ammonium nitrate is then reduced to about 0.5% by any suitable procedure and to the dehydrated material there is added 33 parts of magnesium nitrate. The resulting slightly acidic molten mixture is then sprayed into a prilling tower under such conditions that exceedingly small drops are formed, and preferably the spray is as fine as is possible without the loss by entrainment in the cooling medium becoming excessive. The prills are then collected and stored in moistureproof bags.

Analysis of prills prepared as above shows that the prills are composed of a glassy material which is for the most part a double salt of the formula $\text{NH}_4\text{Mg}(\text{NO}_3)_3$. The prilled material, in addition to being useful as a fertilizer, is useful as an oxidizing agent in the formulation of explosives and rocket fuels, and is highly advantageous for the last mentioned use because it contains, on an equal weight basis, latent energy in excess of that of a comparable crystalline material, such additional latent energy being approximately equal to the energy of crystallization of the crystalline material. This makes possible rocket fuels providing higher thrust per unit weight of fuel and is believed to be the first instance of a glassy ammonium nitrate material suitable for use in preparing rocket fuels. In addition, the prilled material has the advantage of having an exceptionally high bulk density, is free flowing and temperature stable under normal storage conditions.

Example 4

In a suitable reaction vessel there is placed 1000 parts of ammonium nitrate and the temperature thereof raised until the ammonium nitrate is in the molten stage. Gaseous ammonia is then introduced into the molten ammonium nitrate to remove excess acidity and the moisture content is reduced below 0.5% by weight if necessary. There is then added 5% by weight of the prilled product of Example 2 and the resulting mixture stirred until homogeneous. The mixture is then prilled to produce a product which undergoes a transition at a temperature of about 50° C. instead of the 32° C. temperature characteristic of pure ammonium nitrate.

For comparative purposes a similar product containing an equal amount of magnesium is prepared simply by adding magnesium nitrate to molten ammonium nitrate. After 15 hours at 25° C. and 62% relative humidity the

product made by the addition of magnesium nitrate had gained 1.7% by weight due to the absorption of moisture whereas the product prepared by the addition of the double salt of the formula $\text{NH}_4\text{Mg}(\text{NO}_3)_3$ had gained only 0.8% by weight. It will be seen, therefore, that the use of the double salt reduces the hygroscopicity, as compared to a product made by mixing ammonium nitrate and magnesium nitrate, by approximately 50%.

Only a very small amount of a double salt in accordance with this invention is necessary for satisfactory temperature stabilization of ammonium nitrate if the water content of the ammonium nitrate material is at a satisfactory level. Under favorable conditions a degree of stabilization can be obtained employing an amount of a double salt in accordance with this invention equivalent to only about 0.2% magnesium nitrate (i.e., 0.5%



or 0.3% $\text{NH}_4\text{Mg}(\text{NO}_3)_3$, but preferably there is employed an amount of the double salt equivalent to at least about 1% magnesium nitrate (i.e., 2.6%



or 1.5% $\text{NH}_4\text{Mg}(\text{NO}_3)_3$). There is no upper limit as to the amount of double salt that can be satisfactorily employed since the double salt in pure form is a satisfactorily stabilized composition suitable for fertilizer use, but usually there is little or no advantage in employing more than about 30% $(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$ or 18% $\text{NH}_4\text{Mg}(\text{NO}_3)_3$.

The amount of water that can be satisfactorily present in an ammonium nitrate composition stabilized with a double salt in accordance with this invention depends upon the amount of double salt employed. If the stabilized composition is substantially pure double salt, it may contain as much as 5% or more moisture and be satisfactory in all respects, but if a near minimum quantity of the double salt is to be used, the moisture content of the ammonium nitrate composition should be below about 2% and preferably below about 0.5%. If the moisture level of the stabilized product is determined to be excessive, it is an advantage of products stabilizing in accordance with this invention that the moisture level can be lowered by conventional drying techniques.

Having thus described my invention and several specific embodiments thereof, what I desire to claim and secure by Letters Patent is:

1. A composition comprising a double salt of the formula $(\text{NH}_4)_n\text{Mg}(\text{NO}_3)_{n+2}$, wherein n represents an odd numbered integer from 1 to 3 inclusive.

2. A double salt of the formula $\text{NH}_4\text{Mg}(\text{NO}_3)_3$.

3. A double salt of the formula $(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$.

4. A dimensionally stabilized ammonium nitrate composition containing at least about 0.3% of a double salt

of the formula $\text{NH}_4\text{Mg}(\text{NO}_3)_3$, said stabilized composition having a moisture content below about 5% by weight.

5. A composition according to claim 4 containing between about 1.5% and 18% of said double salt and having a moisture content below about 2% by weight.

6. A method of making double salts of the formula $(\text{NH}_4)_n\text{Mg}(\text{NO}_3)_{n+2}$, wherein n represents an odd numbered integer from 1 to 3 inclusive, which comprises adding a magnesium compound selected from the group consisting of magnesium oxide, magnesium nitrate, magnesium carbonate and magnesium hydroxide to molten ammonium nitrate having a moisture content of less than about 5% by weight and a free nitric acid content not substantially in excess of that necessary for the transformation of said magnesium compound into magnesium nitrate, stirring the molten mixture until a clear solution is obtained, and thereafter cooling said mixture to effect solidification.

7. A method according to claim 6 wherein the ratio of said magnesium compound to the ratio of ammonium nitrate is such as to produce a mixture containing the equivalent of approximately 65% by weight magnesium nitrate so that a double salt of the formula $\text{NH}_4\text{Mg}(\text{NO}_3)_3$ is produced.

8. A method according to claim 7 wherein said magnesium compound is magnesium oxide.

9. The method of claim 6 wherein the amount of said magnesium compound added is sufficient to produce a mixture containing the equivalent of 38% by weight magnesium nitrate so that a double salt of the formula $(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$ is produced.

10. A method according to claim 9 wherein said magnesium compound is magnesium oxide.

11. A prilled product comprising prills of a glassy double salt of the formula $\text{NH}_4\text{Mg}(\text{NO}_3)_3$ useful as an oxidizing agent in the formulation of explosives and rocket fuels.

12. A dimensionally stabilized ammonium nitrate composition containing at least 0.03% of a double salt of the formula $(\text{NH}_4)_3\text{Mg}(\text{NO}_3)_5$, said stabilized composition having a moisture content below about 5% by weight.

References Cited in the file of this patent

UNITED STATES PATENTS

1,840,229	Hamprecht	Jan. 5, 1932
1,868,890	Eyer	July 26, 1932
1,910,807	Mohler	May 23, 1933
2,382,298	Datin	Aug. 11, 1945
3,030,179	McFarlin et al.	Apr. 17, 1962

FOREIGN PATENTS

573,147	Great Britain	Nov. 8, 1945
---------	---------------	--------------