

## UNITED STATES PATENT OFFICE

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PROCESS OF PRODUCING AMMONIUM  
NITRATE-CONTAINING COMPOSITION

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The present invention relates to improve-  
ments in the production of ammonium nitrate  
compositions, and is especially applicable where  
it is required that the composition should be in  
a form in which the crystals are tightly com- 5  
pacted together, for instance when it is to be  
formed into compressed masses or into granules  
produced by comminution to a limited extent of  
larger compressed forms.

At temperatures ranging from about  $-18^{\circ}$  C. 10  
to the transition point occurring at  $32.3^{\circ}$  C. the  
stable crystal form of ammonium nitrate is a  
rhombic bipyramidal form of specific gravity  
1.716, designated by the Roman numeral IV; be-  
tween the transition point occurring at  $32.3^{\circ}$  C. 15  
and the other transition point occurring at  $84^{\circ}$   
C. the stable crystal form is rhombic and of  
specific gravity 1.654, designated by the Roman  
numeral III, and between the last mentioned  
transition point and the one occurring at  $125^{\circ}$  C. 20  
the stable crystal form is tetragonal designated  
by the Roman numeral II.

In the production and storage of compact  
forms of ammonium nitrate compositions, for  
example explosive or power gas generating  
charges, whether produced by casting or by com- 25  
pression, it has always been a matter of diffi-  
culty to ensure the maintenance of the external  
form and internal structure of the compacted  
charge owing to the discontinuous density  
changes that occur as a result of subjecting the  
compact charge to temperature changes passing  
in either direction through the transition point  
occurring at  $32.3^{\circ}$  C. Owing to the large dif-  
ference in specific gravity between the forms III 30  
and IV, as a result of such temperature changes  
the compact ammonium nitrate compositions  
may crack or crumble internally or may shrink  
or expand so as to part from or damage some  
other object which it is required to maintain 35  
fixedly in contact with the charge. Such oc-  
currences may lead to serious consequences in  
connection with the use of the charge: for in-  
stance crumbling or cracking increases the burn-  
ing surface of a power gas generating charge 40  
and hence the rate at which pressure is devel-  
oped by it. The transition of ammonium nitrate  
occurring at  $32.3^{\circ}$  C. is facilitated by the presence  
of moisture.

It is known that in solid solutions of potas- 40  
sium nitrate in ammonium nitrate obtained  
either by co-crystallisation from aqueous solu-  
tions made by dissolving the two salts in water,  
or by solidification of fused mixtures of the two  
salts, the transition point occurring at  $32.3^{\circ}$  C. 45

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is lowered and the transition point occurring at  
 $84^{\circ}$  C. is raised. It has been stated that solid  
solutions containing more than 8% potassium  
nitrate prepared by either of the aforesaid meth-  
ods never become completely converted from  
form III to form IV however far below  $32.3^{\circ}$  C.  
the temperature is reduced.

Campbell and Campbell (Canadian Journal of  
Research, volume 24B July 1946, pages 93 to 108),  
who have recently studied this phenomenon,  
state that solid solutions obtained by either of  
these two methods can be kept indefinitely at  
room temperature with ammonium nitrate in  
form III without undergoing transformation into  
form IV and that the solid solutions show no  
discontinuous volume change between approxi-  
mately  $1^{\circ}$  C. and  $100^{\circ}$  C. In order to induce the  
transformation of form III into IV they state  
that it is necessary to cool the solid solution to  
a temperature below  $1^{\circ}$  C., but indicate that once  
it has taken place the retransformation of form  
IV into form III in a solid solution containing 5%  
potassium nitrate is brought about by heating  
it to approximately  $22^{\circ}$  C. These observers sug-  
gest that even when the proportion of potassium  
nitrate in the solid solution is as high as 10%  
the transformation of form III into form IV may  
occur eventually if the solid solution is kept long  
enough at a sufficiently low temperature, for in-  
stance  $-10^{\circ}$  C., particularly if it is moist. These  
observers further state that in order to lower the  
transition point below  $32.3^{\circ}$  C. it is quite insuffi-  
cient merely to mix the potassium nitrate with  
the ammonium nitrate, and that the mass must  
be melted up or crystallised from a mixed aque-  
ous solution of the two salts.

It has also been proposed in British Patent No.  
573,147 inter alia to produce ammonium nitrate  
explosive or propellant compositions showing  
relatively small density changes when exposed to  
temperature cycles, by a process comprising fus-  
ing together, in the presence of added water, a  
mixture containing the ammonium nitrate and  
a minor proportion of potassium nitrate, or  
evaporating to dryness an aqueous solution of  
the said mixture, and subjecting the resulting  
product in either case to such thorough drying  
conditions that the water content is less than  
0.1%.

The production of ammonium nitrate com-  
positions suitable for use, for instance as ex-  
plosive, propellant and power gas pressure pro-  
ducing charges, smoke compositions, insecticidal  
and fungicidal vaporizing charges and the like  
by casting fusion mixtures is of somewhat limited

applicability, for instance on account of the possibility it affords for ingredients of the wholly or partly molten composition to separate from one another, e. g., by segregation of solid ingredients or of immiscible liquid phases and has the disadvantage of a certain decomposition hazard encountered at the high temperatures. The preparation of solid solutions of potassium nitrate in ammonium nitrate by co-crystallisation from a solution of the two salts is a troublesome operation since it is difficult to obtain crystalline products of uniform composition and since the solid solution is more difficult to dry off than either of its components.

These disadvantages are avoided by the method employed in the present invention, which is applicable to the manufacture of compositions suitable for use e. g. as explosive propellant, gas pressure, smoke, insecticidal or insect repelling or fungicidal charges, or as fertilizers, which may include other appropriate inorganic and/or organic constituents e. g. trinitrotoluene and other explosive bodies, alkali metal chromates, ammonium bichromate, phosphates, chlorides, sulphates, oxalates, vapourisable insecticides, fungicides and insect repellents, waxes and so forth.

As a result of our X-ray investigations we have made the remarkable and unexpected discovery that after a simple mixture of powdered potassium nitrate with solid particles of ammonium nitrate has been maintained at a temperature higher than 32.3° C. which may be up to about 100° C., in the absence of any appreciable percentage of moisture the potassium nitrate is effective in stabilising the ammonium nitrate crystal as modification III at temperatures from 32° C. down to at least 0° C. Thus by maintaining the mixture for a sufficient length of time at a temperature above 32.3° C. the discontinuous density changes ordinarily experienced on passing ammonium nitrate compositions through a temperature cycle passing through 32.3° C. are avoided, so that for instance compressed charges of the compositions will neither crumble nor crack.

According to the present invention the process for the production of compositions comprising ammonium nitrate and potassium nitrate comprises mixing together ammonium nitrate and powdered potassium nitrate and maintaining the mixture thus formed within a temperature range of about 32° C. and about 100° C. for a time long enough to ensure that the ammonium nitrate is stabilised substantially as modification III.

The ammonium nitrate used for mixing with the potassium nitrate may be either in the form of powder or small granules.

At least 8% potassium nitrate reckoned on the sum of the ammonium nitrate and potassium nitrate is found to be required to attain stabilisation of the ammonium nitrate in form III, where stability is required at temperatures of the order of -10° C., but quantities say from 1% upwards may be sufficient for practicable purposes where such low temperatures are not reached e. g. to prevent the breaking up of granular fertilisers or compressed pellets, under appropriate circumstances. In some cases it is possible to obtain the stabilisation of the ammonium nitrate in form III even if other additional solid components are present during the heat treatment with potassium nitrate e. g. inorganic salts, such as chromates, phosphates; ammonium oxalate, guanidine nitrate or nitroguanidine. In other

cases it may be necessary to carry out the potassium nitrate treatment before the other solid components are introduced, e. g. waxes. The progress of the stabilization action of the potassium nitrate may be followed by observation of the changes on cycling in compressed pellets made from samples taken, from time to time, from the material being exposed to temperatures in the range between 32° C. and about 100° C. Since this temperature cycling of the compressed mass itself involves exposure of the mixture to a temperature above 32° C. thus tending to complete the action if the time of exposure of the mixture has been insufficient, it is safer to apply a test that does not involve repeated cycling, for instance to determine the temperature-time heating or cooling curve of a sample so as to determine the presence or absence of a transition point, or to plot a volume-temperature curve by observing the density changes by means of a dilatometer so as again to see whether or not a transition point is present. Best of all however is to subject samples taken from time to time to X-ray examination. The X-ray diffraction pattern of ammonium nitrate powder in the form IV differs markedly from that of ammonium nitrate powder in form III, and the presence of for example about 10 per cent of potassium nitrate has been found by us to have no noticeable effect on the respective patterns. The diffraction pattern ultimately attained by the method of our invention is almost indistinguishable from that obtained from a cooled and powdered fusion mixture containing the same proportion of ammonium nitrate and potassium nitrate. By comparison of photographs it is therefore easy to find the minimum time of exposure of the mixture to the temperature, between about 32° C. and about 100° C., beyond which further time of exposure produces no appreciable further change in the X-ray pattern.

At temperatures of 40-50° C. complete stabilisation may be expected to take place in about 10-30 hours depending on the degree of subdivision of the ammonium nitrate and the potassium nitrate and the intimacy of the primary admixture, even if the mixture is agitated only before its exposure to the temperature above about 32° C. The moisture content may also have some effect on the time required, but the reaction proceeds readily even when recently dried ammonium nitrate and potassium nitrate are used, and even in the presence of drying agents such as dehydrated ammonium oxalate.

According to a modification of the invention, in place of potassium nitrate there may be used other water soluble potassium salts that react metathetically with an excess of ammonium nitrate to form potassium nitrate; for example, potassium sulphate, potassium chloride, potassium dihydrogen ortho phosphate, potassium oxalate, and potassium chromate. In this case the presence of at least a small amount of moisture during the mixing is advantageous.

When potassium nitrate is used it is desirably in finely powdered condition. The ammonium nitrate may be in ordinary crystal powder condition, but the invention is also applicable for the treatment of ammonium nitrate granules produced by a spray process.

The compositions produced according to the process of the present invention have been found to be particularly suitable in the production of compressed charges comprising ammonium nitrate and potassium nitrate.

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The invention is illustrated by the following examples in which the parts are parts by weight except where otherwise indicated.

*Example I*

The ammonium nitrate was in the form of crystal clusters passing a 60 mesh British Standard Specification screen and contained 0.1-0.2% moisture. 450 parts of this ammonium nitrate were ground together with 50 parts pulverised potassium nitrate having a grist fine enough to pass a 170 mesh B. S. S. screen, until the whole of the product passed through a 100 mesh B. S. S. screen, the mixing being conducted at room temperature. An X-ray powder photograph of the mixture at this stage was the same as that of a sample of ammonium nitrate in form IV, and even after storage at 18° C. of a sample of the mixture for two weeks the X-ray photograph was still substantially the same. The rest of the freshly ground material was heated to 45° C. and stored at that temperature for 18 hours, and then allowed to cool and, was kept for a week at room temperature. On examination the X-ray powder photograph was substantially identical with that obtained from a solid solution of potassium nitrate and ammonium nitrate of the same percentage composition prepared by fusion and cooling, and was also substantially identical with that of a sample of ammonium nitrate III. Further heating at 45° C. for 6 hours produced no detectable difference in the X-ray photograph. Pellets of the composition 1½" in diameter compressed under a pressure of 2 tons per sq. in. showed a diametric expansion of only 1.56% after 16 temperature cycles between 0 and 50° C. and did not crumble or crack. Compressed pellets made from a pulverised congealed fusion mixture of the same percentage composition showed about the same diametric expansion when similarly cycled. The pulverulent mixture may be mixed with e. g. potassium chromate and ammonium bichromate and gamma hexachlorocyclohexane and compressed into pellet form, to give an insecticidal vapour generating pellet which will not crumble with temperature variations on storage, or it may be mixed with trinitrotoluene and pelleted to give an Amatol explosive that will resist volume changes tending to shatter it on alternating hot and cold storage.

*Example II*

The ammonium nitrate used was spray crystallised material passing a 16 mesh and retained on a 25 mesh B. S. S. screen, and had an initial natural bulk density of 0.917 grams per c. c. Four temperature cycles between 0° C. and 50° C. sufficed to reduce the natural bulk density of a sample of this material to 0.778 grams per c. c. and to cause serious cracking and disintegration of the granules. The remainder of the granular material was mixed with 10% of its weight of potassium nitrate of grist fine enough to pass through a 200 mesh B. S. S. screen, after the granules had been moistened with 2% of their weight of a saturated solution of ammonium nitrate in water, these operations being conducted at room temperature. The moistening of the ammonium nitrate granules enabled the potassium nitrate particles to adhere to them instead of segregating away from them. A small portion of the mixture was stored at 20° C. for 24 hours, and a heating curve was plotted for it. This indicated a sudden break at approximately 32° C. showing that the ammonium nitrate was still

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present below that temperature in form IV and was undergoing transition into form III at approximately 32° C. The remainder of the mixture was heated to 50° C. and stored at that temperature for 24 hours, and was thereafter cooled to room temperature, and a heating curve plotted for it. This heating curve showed substantially no evidence of a break between 0° C. and 50° C., thus indicating that the transition from the form IV into form III had been substantially completed; and an X-ray powder photograph carried out on a ground sample of the material was practically identical with that of a sample of ammonium nitrate III. On temperature cycling the granules 7 times between 0° C. and 50° C. their bulk density was only reduced from 0.860 to 0.855, and the granules showed no signs of disintegration. The granules are especially suitable for employment in the manufacture of low velocity detonating explosive compositions by admixture with vegetable carbohydrate materials, liquid explosive nitric esters and other customary ingredients of such compositions. They may also be employed as a granular fertiliser.

*Example III*

450 parts crystalline ammonium nitrate as used in Example I were ground together with 50 parts potassium oxalate with a grist fine enough to pass a 170 mesh B. S. S. screen until the whole passed through a 100 mesh screen, these operations being conducted at room temperature. The ground mixture was then heated to 50° C. and maintained at the temperature for 24 hours, and a sample was taken. The remainder of the mixture was maintained for another 6 hours at the same temperature and was then cooled, and a further sample was taken. Each of the samples was compressed at 2½ tons per sq. in. pressure into a cylindrical mould of 1½" diameter. Each pellet was then subjected to 16 temperature cycles between 0-50° C. and it was found that their initial diameters had increased by only 1.3% in each case. X-ray powder photographs of the hot stored mixtures after standing at ordinary temperature for some days showed that the ammonium nitrate had been stabilised in the III form.

The pulverulent composition may be used as a constituent of compressed gas pressure producing charges containing say potassium chromate or ammonium bichromate as sensitiser of thermal decomposition as an added ingredient.

*Example IV*

865 parts crystalline ammonium nitrate as used in Example I were ground together with 60 parts of potassium nitrate of a grist fine enough to pass a 170 mesh B. S. S. screen and 75 parts anhydrous ammonium oxalate of the same grist as the potassium nitrate, until the mixture all passed a 100 mesh screen. These operations were conducted at room temperature. The ground mixture was then heated to 45° C. and maintained at that temperature for 18 hours. After cooling and standing for 4 to 5 days at 15-17° C. the X-ray diffraction pattern was found to be practically identical with that of a congealed fused mixture of ammonium nitrate and potassium nitrate in the proportions 90:10.

The product may be used for all purposes similar to that indicated for the product of Example III, which it resembles in enabling a compressed pellet of the gas pressure producing

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charge to be produced which will resist the usual disruptive effect of temperature cycling.

We claim:

1. A process for the production of a composition comprising ammonium nitrate and potassium nitrate which comprises mixing together ammonium nitrate and powdered potassium nitrate and maintaining the mixture thus formed within a temperature range of about 32° C. and about 100° C. for a time long enough to ensure that the ammonium nitrate is stabilized substantially as modification III which is that modification having a rhombic crystal form, a specific gravity of 1.654 and stable between the transition points normally occurring at 32.3° and 84° C.
2. A process as claimed in claim 1 wherein the ammonium nitrate used for mixing with the potassium nitrate is in the form of powder.
3. A process as claimed in claim 1 wherein the ammonium nitrate used for mixing with the potassium nitrate is in the form of small granules.
4. A process as claimed in claim 1 wherein at least 8 per cent potassium nitrate is present reckoned on the sum of the ammonium nitrate and potassium nitrate where stability of the ammonium nitrate in modification III is required at temperatures of the order of -10° C.
5. A process as claimed in claim 1 wherein the mixture of ammonium nitrate and potassium nitrate maintained within a temperature range of about 32° C. and about 100° C. for the time aforementioned includes at least one additional solid component.

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6. A process as claimed in claim 5 wherein the additional solid component is an inorganic salt.

7. A process as claimed in claim 6 wherein the inorganic salt is selected from the group consisting of chromates and phosphates.

8. A modification of the process as claimed in claim 1 wherein a water-soluble potassium salt other than potassium nitrate is used which reacts metathetically with an excess of ammonium nitrate to form potassium nitrate.

9. A process as claimed in claim 8 wherein the water-soluble potassium salt is selected from the group consisting of potassium sulphate, potassium chloride, potassium dihydrogen orthophosphate, potassium oxalate, and potassium chromate.

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