ISSN 1070-4272, Russian Journal of Applied Chemistry, 2017, Vol. 90, No. 9, pp. 1392−1396. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © I.A. Vyazenova, V.A. Taranushich, V.M. Chernyshev, V.A. Bogdanova, 2017, published in Zhurnal Prikladnoi Khimii, 2017, Vol. 90, No. 9, pp. 1134−1138.

Phase Stabilization of Ammonium Nitrate by Double Addition of Potassium Nitrate and Melamine

I. A. Vyazenova*, V. A. Taranushich, V. M. Chernyshev, and V. A. Bogdanova

Platov South-Russian State Polytechnic University (NPI) Novocherkassk,
ul. Prosveshcheniya 32, Rostov-on-Don oblast, 346428 Russia
**e-mail: tnv_irina@inbox.ru*

Received January 26, 2017

Abstract—Methods for providing stabilization of ammonium nitrate and expanding the application field of this oxidizing agent in gas-generating compositions used for various purposes were sought for. The results of a study of the physicochemical properties of ammonium nitrate with a melamine–potassium nitrate double additive introduced by mechanical mixing and crystallization from an aqueous (nonaqueous) solution at the boiling point are presented. The phase diagrams of the ammonium nitrate–melamine and ammonium nitrate–melamine–potassium nitrate systems, based on the results of a differential-thermal analysis, demonstrated that a phase-stable ammonium nitrate can be formed by using the method of crystallization from an aqueous (nonaqueous) solution at the boiling point. The resulting samples were examined by IR spectroscopy and X-ray diffraction analysis, and a conclusion was made that a new thermodynamically stable phase can be formed in the system with individual additives, and the introduction of a double additive leads to a combined effect: a thermodynamically stable crystal structure is formed, with the simultaneous slowing down of the nucleation and growth of a new phase in the course of a phase transformation.

DOI: 10.1134/S1070427217090038

Ammonium nitrate (AN) is a promising oxidizing agent for highly energetic gas-generating fuels that can be used in various fire-extinguishing systems based on gas generators, systems for intensification of oil extraction, those aimed to produce selective gases, autonomous systems for refloating of sunken objects, automobile safety bags, etc. [1–6].

The four polymorphic modifications in the temperature range from –50 to +100°C, and, accordingly, three phase transformations (V ↔ IV at –17°C, IV ↔ III at 32°C, and III ↔ II at 84°C) restrict the application of this readily available and inexpensive oxidizing agent in gas-generating formulations because the shape, volume, and density of crystals change in the course of a phase transformation (at 32°C, there occurs transition from one rhombic modification to another, which is accompanied by a 3% increase in the crystal volume; at a temperature of 84°C, crystals of the rhombic bipyramidal form become rhombic monoclinic, with the crystal volume decreasing). Therefore, articles based on AN will disintegrate in storage. One more characteristic feature of AN is its ability to crystallize into the so-called intermediate or metastable form II' at a temperature of 54–55°C, with unit cell parameters different from those for II phase [II', tetragonal unit cell (Å): $a = 5.68$, $c = 4.92$; II, tetragonal unit cell (Å): $a = 5.75$, $c = 5.00$] [7, 8].

It has been found that introduction of a potassium nitrate (PN) additive can stabilize AN in phase III in a prescribed temperature interval due to the formation of an energetically stable formulation that is a mixture of solid solutions and double salts, formed in the course of joint crystallization of the components from a solution or melt [9]. The effect of stabilization of the AN phase state upon addition of certain organic substances due to the intermolecular interactions has been observed [10–12]. An analysis of the existing methods for phase stabilization of AN made it possible to distinguish three effective ways: thermodynamic, kinetic, and combined. A thermodynamically stable AN–additive formulation can be obtained via introduction of isomorphic atoms, e.g., potassium ion (potassium nitrate) into the AN unit cell; the kinetic way consists in controlling the appearance and growth rates of nuclei in a phase transformation of AN; and the combined way includes development of a thermodynamically stable structure and the simultaneous control over processes in which a new AN phase nucleates and grows.

Effective gas-generating formulations containing PN and melamine are known [13–15]. Therefore, these two components can be used as phase-stabilizing additives for AN.

The goal of our study was to analyze the effect of the double additive containing an inorganic compound PN and organic substance melamine (2,4,6-triamino-1,3,5-triazine) on the physicochemical properties of AN.

It was expected that introduction of a double additive via isothermal crystallization from an aqueous or nonaqueous solution at the boiling point would eliminate the phase transitions of AN and simultaneously provide high performance of the fuel based on this oxidizing agent.

EXPERIMENTAL

We used AN of chemically pure grade, PN of analytically pure grade, and melamine of pure grade. Samples of the system were obtained in two ways, by mechanical mixing and by isothermal crystallization from an aqueous or nonaqueous solution (ethylene or butylene glycol) at the boiling point [16]. After the drying and separation of the <500 μm fraction, AN samples with additives were examined by physicochemical analytical methods: differential-thermal, IR spectroscopic, and X-ray diffraction XRD) analyses [17–19]. The results obtained were used to construct phase diagrams and make conclusions.

The AN–melamine phase diagram (mechanical mixing) shows in the whole range of concentration under study an additivity of the physicochemical characteristics of the starting components: the phase transformations of AN and melamine are preserved. An analysis of the phase diagram of the system produced via crystallization from an aqueous or nonaqueous solution at the boiling point (Fig. 1) demonstrated that the IV–III phase transition of AN is preserved up to 50% content of melamine (curve *1*).

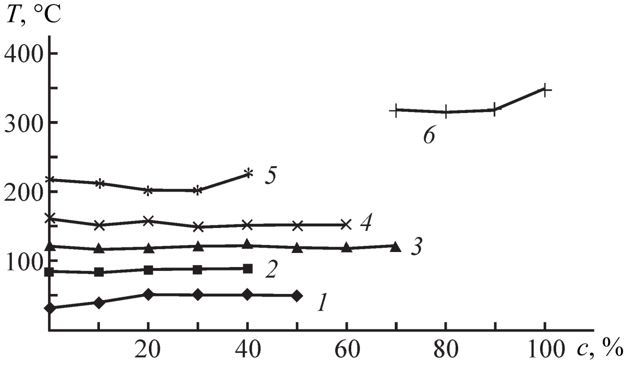

Fig. 1. Phase diagram of the AN–melamine system (isothermal crystallization from an aqueous solution at the boiling point). (*T*) Temperature and (*c*) melamine content. (*1*) IV–III AN phase transition, (*2*) III–II AN phase transition, (*3*) II–I AN phase transition, (*4*) AN melting, (*5*) AN decomposition, (*6*) melamine decomposition.

Raising the amount of the additive further results in that crystals are formed in the intermediate state II', with transition to phase I of AN (absence of curves *1* and *2*). Raising the content of melamine to more than 70% leads to a phase stabilization (absence of curves *1–3* corresponding to phase transitions in AN), which may be due to the slower rates of nucleation and growth of a new phase in the course of the phase transformation of AN, i.e., this occurs due to the kinetic factor of the phase stabilization of AN. An eutectic with mp 150°C is observed for samples containing up to 60% AN (curve *4*).

An analysis of the system with a double PN–melamine additive (crystallization from an aqueous or nonaqueous solution at the boiling point) demonstrated that introduction of 5% PN leads to a phase stabilization of AN at melamine content exceeding 20% due to the combined influence exerted on AN crystals by the thermodynamic and kinetic factors. Raising the amount of PN additive to 10, 20, and 30% results in that the AN phase transition IV–III completely disappears, i.e., the thermodynamic stabilization factor starts to predominate due to the formation of a stable AN–PN structure. The AN phase transition II–I is preserved up to melamine content of 80%, and the eutectic at 150°C, up to AN content of 10%.

Analysis of the IR spectra of samples in the AN–melamine system with varied composition shows that, on changing the method by which solid phases are obtained to that via crystallization at the boiling point (irrespective of the solvent used: water, ethylene- or butylene glycol), the crystals precipitated into the solid phase

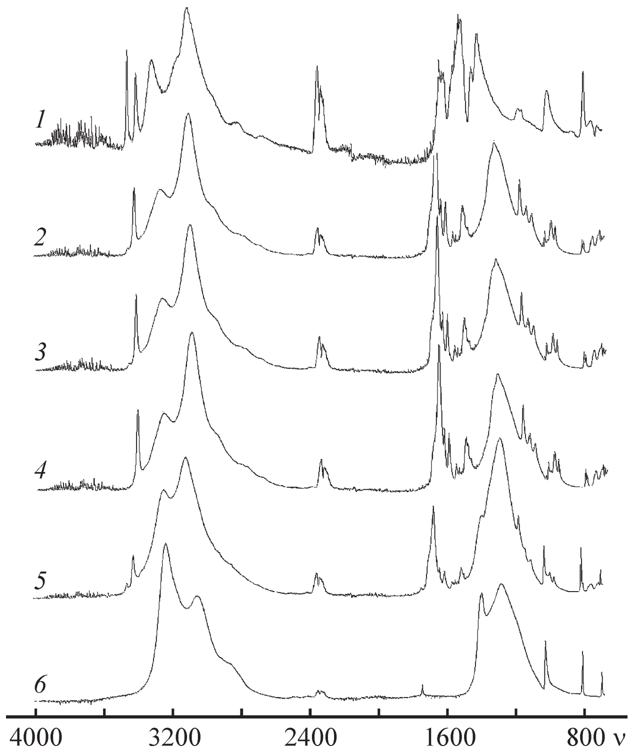

Fig. 2. IR spectra of the AN–melamine system (isothermal crystallization from an aqueous solution at the boiling point). (ν) Wave number. Content (%): (*1*) 100 melamine, (*2*) 40 melamine–60 AN, (*3*) 30 melamine–70 AN, (*4*) 20 melamine–80 AN, (*5*) 10 melamine–90 AN, (*6*) 100 AN.

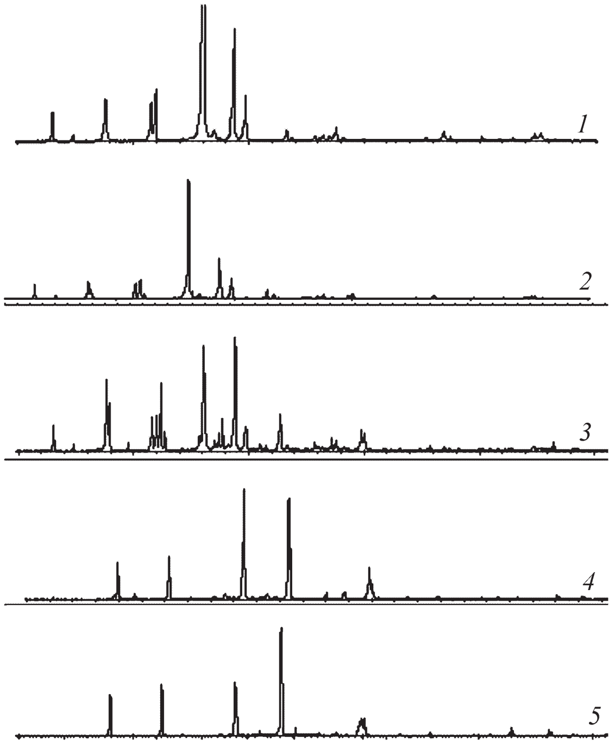

Fig. 3. XRD patterns of samples in the AN–melamine system (isothermal crystallization from an aqueous solution at the boiling point). Content (%): (*1*) 100 melamine, (*2*) 80 melamine–20 AN, (*3*) 50 melamine–50 AN, (*4*) 10 melamine–90 AN, (*5*) AN phase IV ($\lambda_{\mathrm{Cu}K_\alpha}$, 2θ = 10–50).

contain functional groups of melamine [3115 cm^{-1},N–H (secondary amines) and 1647 cm^{-1}, C=N bond (cyclic vibrations)]. Also, ammonium ions [3300 cm^{-1} (stretching vibrations) and 1411 cm^{-1} (bending vibrations)] and NO_3^- ions (1297 cm^{-1}) appear in the spectra (Fig. 2, curves *1*–*6*) [18].

As the AN content increases, changes are observed in the intensity of vibrations of the functional groups, with the melamine band still dominating. This is indicative of an active interaction of modifier molecules with AN ions, with the possible formation of a thermodynamically stable melamine-based phase. Introduction of the PN additive into the solid phases in amounts of 5 to 30% has no effect on the IR spectra of the samples.

An XRD analysis of samples in the AN–melamine system demonstrated that the joint crystallization of AN with 10% melamine yields crystals with the common crystal lattice that is close to AN phase IV (Fig. 3, curve *4*) and raising the content of melamine to 50% (curve *3*) gives a structure different from those of the starting compounds, melamine and AN (curves *1* and *5*, respectively) [19]. Further increase in the content of melamine results in that a phase is formed with crystal structure close to that of melamine (curve *2*). This appearance of the XRD pattern confirms that there is an active interaction in the AN–melamine system to give a new phase in the course of the joint crystallization and indirectly confirms the combined effect on the phase stability of the structures being formed.

Introduction of the second additive (10% PN) into the AN–melamine system has no effect of the structure of the solid phases being formed (Fig. 4). This means that the main part is played in phase-stable crystals by melamine, which can be incorporated in the form of clusters between the crystalline blocks of AN, with thermodynamically stable formulations formed at a simultaneous kinetic influence on the growth of nuclei of a new AN phase [11].

The results obtained in the study confirmed the efficiency of the combined method for affecting the phase transformations in AN via formation in the course of crystallization of a thermodynamically stable structure with additive components and a simultaneous influence exerted on the kinetics of the process in which nuclei of a new phase are formed and grow in these phase transformations.

The method we developed can yield a phase-stable NA-based oxidizing agent that improves the ecological properties of combustion products (due to the absence of a condensed phase and toxic components) and makes lower the production cost of solid fuels because of the use of the inexpensive AN. It becomes possible to control the phase-stable AN-based formulation via joint crystallization with an organic substance (melamine) or with a potassium nitrate–melamine double additive. In the AN-based oxidizing agent, the PN additive serves as oxidizing agent and, simultaneously, acts as initiator of the thermal decomposition of AN. Melamine will execute in these compositions several functions; it is a gas-forming component (fuel) that releases when decomposing the nontoxic and fire-proof nitrogen and also can serve as a binder and provide technological and mechanical properties of the whole gas-generating formulation. One more advantage of the given method for obtaining an AN-based oxidizing agent is the possibility of varying the relative amounts of the additive components, PN and melamine. This will make it possible to control the combustion temperature of the formulation and expand the applicability area of the gas-generating composition [20–23].

CONCLUSIONS

(1) It was found that samples of the ammonium nitrate–melamine system, produced by crystallization from an aqueous or nonaqueous solution (ethylene and butylene glycol) at the boiling point and containing 50% melamine and more, exhibit phase stability due to the formation of a new crystal structure. This was confirmed by physicochemical analytical methods, differential-thermal, IR spectroscopic, and X-ray diffraction analyses.

(2) It was shown that introduction of the second potassium nitrate additive into the ammonium nitrate–melamine system (crystallization from an aqueous or nonaqueous solution at the boiling point) results in that phase-stable samples are formed at a lower melamine content: with 5% potassium nitrate, stabilization occurs at 20% lower content of melamine, and with 10% and more potassium nitrate, at 0% melamine. This effect is due to the combined influence exerted by additives on the phase stabilization of ammonium nitrate due to the formation in the crystallization process of a thermodynamically stable structure with the additive components and to the simultaneous effect on the kinetics of the process in which a new phase nucleates and grows in phase transformations of ammonium nitrate.

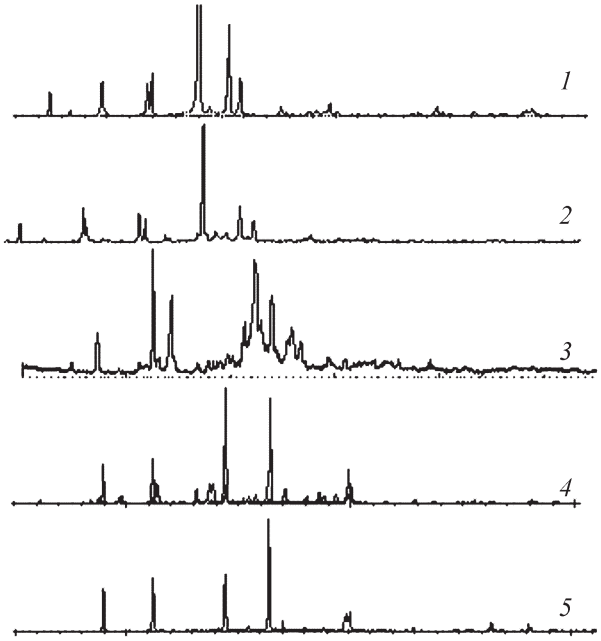

Fig. 4. XRD patterns of samples in the AN–melamine-10% PN system (co-crystallization from an aqueous solution at the boiling point). Content (%): (*1*) 100 melamine, (*2*) 90 melamine–10 AN, (*3*) 70 melamine–30 AN, (*4*) 50 melamine–50 AN, (*5*) AN phase IV (λ_{CuK}, 2θ = 10–50).

(3) The results obtained in a study of the system constituted by ammonium nitrate and double potassium nitrate–melamine additive confirmed that a phase-stable ammonium nitrate can be obtained as a result of the combined effect: formation of a thermodynamically stable structure with potassium nitrate and melamine (solid solutions, double salts, eutectic) and the simultaneous kinetic hindrance of the process of nucleation and growth of a new phase in the course of the phase transformation of ammonium nitrate due to the incorporation of the organic additive in the form of clusters between crystalline blocks of ammonium nitrate.

ACKNOWLEDGMENTS

Te study was carried out on the equipment of the Collective Use Center “Nanotechnologies” [Platov South-Russian State Polytechnic University (NPI)].

REFERENCES

1. Ul’yanova, E.V., Denisyuk, A.P., Zo Tve, E., and Rusin, D.L., *Usp. Khim. Khim. Tekhnol*., 2011, vol. 25, no. 12 (128), pp. 30–34.
2. Wada Yusuke and Arai Mitsuru, *Sci. Technol. Energ. Mater.,* 2010, vol. 71, nos. 1, 2, pp. 39–43.
3. RF Patent 2 298 540 (publ. 2007).
4. RF Patent 2 326 923 (publ. 2008).
5. RF Patent 2 481 319 (publ. 2013).
6. RF Patent 2 539 959 (publ. 2015).
7. Chernyshev, A.K., Levin, B.V., Tugolukov, A.V., et al., *Ammiachnaya selitra: svoistva, proizvodstvo, primenenie* (Ammonium Nitrate: Properties, Production, Application), Levin, B.V. andTugolukov, A.V., Eds., Moscow: ZAO Infokhim, 2009.
8. Anuj A. Vargeese, Satyawati S. Joshi, and Krishnamurthy, V.N., *J. Hazard. Mater*., 2009, no. 161, pp. 373–379.
9. Klykin G.F. and Taranuchich, V.A., *Russ. J. Appl. Chem*., 2007, vol. 80, no. 12, pp. 1958–1961).
10. Golovina, N.I., Nechiporenko, G.N., Nemtsev, G.G., et al., *Russ. J. Appl. Chem*., 2007, vol. 80, no. 1, pp. 25–31.
11. Golovina, N.I., Nechiporenko, G.N., Nemtsev, G.G., et al., *Russ. J. Appl. Chem*., 2008, vol. 81, no. 10, pp. 1613–1619.
12. RF Patent 2 363 691 (publ. 2007).
13. RF Patent 2 259 987 (publ. 2005).
14. RF Patent 2 388 737 (publ. 2010).
15. RF Patent 2 456 260 (publ. 2012).
16. Melikhov, I.V. and Merkulova, M.S., *Sokristallizatsiya* (Cocrystallization), Moscow: Khimiya, 1975.
17. Gorshkov, V.S., Timashev, V.V., and Savel’ev, V.G., *Metody fiziko–khimicheskogo analiza vyazhushchikh veshchestv* (Methods for Physicochemical Analysis of Binders), Moscow: Vysshaya shkola, 1981.
18. Kazuo Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Intersci. Publ., 1986.
19. JCPDS PDF–2 database [Electronic resource], Powder Diffraction Database PDF-2 Release 2012; http:www.icdd.com
20. US Patent 7 081 175 (publ. 2006).
21. US Patent 6 811 626 (publ. 2004).
22. US Patent 6 887 326 (publ. 2005).
23. RF Patent 2 423 339 (publ. 2011).