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Preparation of ADNBF with low-acidity by reactive crystallization

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Abstract−Acidity of ADNBF (7-amino-4,6-dinitrobenzofuroxan) crystallized from acetic acid taken as a reaction medium was found to be 0.14-0.2%, which is not acceptable in view of the long term stability of final products. Inclusion of acetic acid during azidation reaction of the TeNA (2,3,4,6-tetranitroaniline) to ATNA (3-azido-2,4,6-trinitroaniline) and formation of ADNBF crystals from ATNA in acetic acid was found to be the main reason for the high acidity of as-synthesized ADNBF crystals. In the present experiments, to reduce the acidity of ADNBF, ATNA, which is an intermediate compound, was separated from acetic acid, and ADNBF crystals were obtained by thermolysis of ATNA from various solvents. The acidity of ADNBF crystals from ethanol was found to be 0.05-0.06%, and their shape and size distribution were cubic or tetragonal and 5-30 μm, respectively, which may be suitable for applying the explosive for- mulations.

Key words: 7-Amino-4,6-dinitrobenzofuroxan, Acidity, Long-term Stability

INTRODUCTION

In the development of munitions, crystal quality of energetic materials such as purity, electroconductivity and microstructure including defects, surface roughness, etc., should be characterized for achieving the desired performance of the final formulation. Also, control of the crystal shape, size and size distribution is a vital parameter which determines the compactibility and processability during formulations [1-3]. In addition, the long-term stability of final products, *i.e.*, in-service safety and final designed performance of munitions, should be assured [4]. One of important factors which affect long-term stability of munitions is residual acid content of energetic materials. Therefore, acidity level of energetic materials should be precisely controlled below the specified value of military standards.

For more than 20 years, research on insensitive munitions has been extensively made [5,6]. One of those efforts is the development of desensitized energetic materials by reducing internal defects of the sensitive energetic materials such as RDX (cyclotrimethylenetrinitramine) and HMX (cycletetramethylenetetranitramine) [7]. Another way is the design and synthesis of new, intrinsically insensitive energetic compounds with high energy.

For example, NTO (5-nitro-1,2,4,-triazol-3-one) and TATB (triaminotrinitrobebzene) have been successfully developed as insensitive explosives [6]. Strong intra- and intermolecular hydrogen bonding and/or their symmetrical structure have been known to be responsible for their unusual physico-chemical behaviors. Currently, they have been in service as a component in PBX (polymer bonded explosive) systems and melt-castable explosives. When designing energetic compounds, insertion of the asymmetric heterocyclic nuclei with amino and heterocyclic N-oxide provides the improvement of the oxygen balance, density, stability as well as insensitivity.

ADNBF (7-amino-4,6-dinitrobenzofuroxan, $C_6H_3N_5O_6$, monoclinic, $P2_1$, a=11.957 Å, b=9.863 Å, c=7.180 Å, β= 98.131°, Z=4) has been regarded as an insensitive explosive, whose impact sensitivity is similar to that of TNT [8-13]. Norris [8,10] reported the synthetic routes of the ADNBF by the reaction of 5- (or 7-) chloro-4,6-dinitrobenzofuroxan in CH_2Cl_2 under gaseous ammonia atmosphere. He prepared TeNA (2,3,4,6-tetranitroaniline) from inexpensive ortho-aniline with direct nitration. Then, TeNA was converted into ADNBF under the azidation reaction with NaN_3/CH_3COOH as shown in Fig. 1. In this synthetic route, without the isolation of the unstable azido compound, ATNA (3-azido-2,4,6-trinitroaniline), the thermolysis in acetic acid leads to ADNBF. Weber [13] invented an improved process for the exothermic conversion of the suspended TeNA to ATNA in acetic acid through the addition of the aqueous NaN_3 solution instead of the solid NaN_3. Hence, ADNBF crystals are precipitated into acetic acid by the solvolysis of ATNA. One Advantage of those processes is that one-pot reactive crystallization of TeNA with sodium azide in acetic acid leads to high yield of high-purity ADNBF without isolation of intermediate compound, ATNA. In this method, ADNBF crystals with cubic shape and particle size ranging from 10 to 30 μm can be obtained.

However, the acidity of as-synthesized ADNBF crystals via routes given by Norris and Weber was found to be very high, which was not applicable to explosive formulation. It is believed that acetic acid included during precipitation of ADNBF crystals was responsible for the high acidity of the final products. In the present work, various solvents were investigated as thermolytic medium of ATNA instead of acetic acid during the synthesis of ADNBF as shown in Fig. 1. Here, we report the results of the two-step reactive crystallization undertaken to obtain ADNBF crystals with a desirable acidity and crystal morphology for military applications.

EXPERIMENTS

1. Materials

TeNA was supplied by Hanwha Co. (Korea). Reagent grade of

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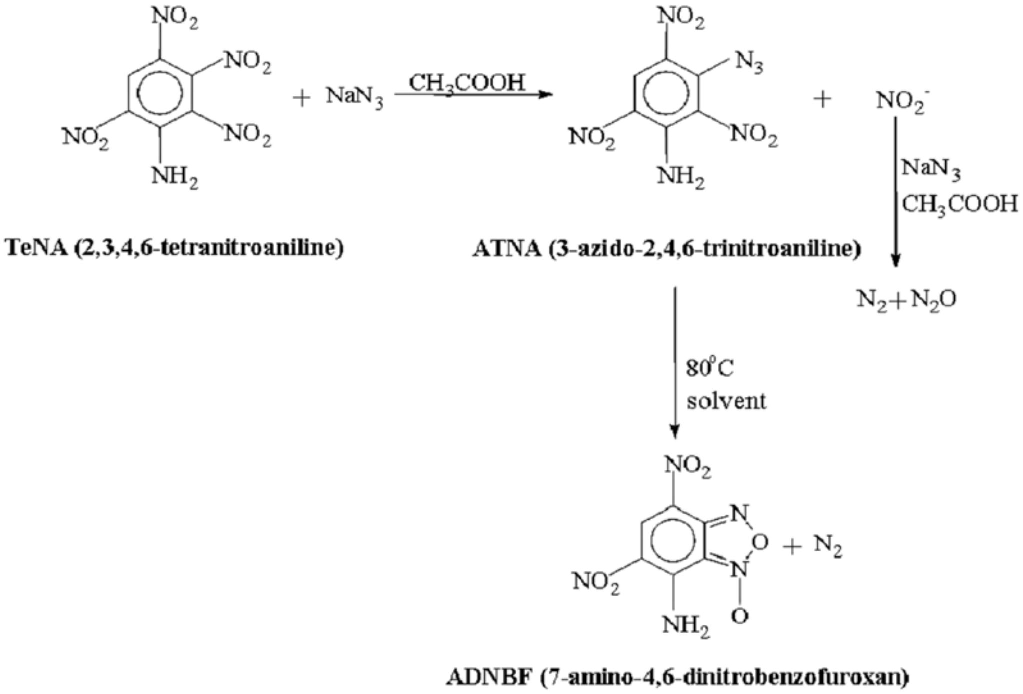


Fig. 1. Synthetic route of ADNBF [7].

all chemicals was purchased from Aldrich (USA) and used without further purification otherwise specification. Double distilled water was used in the present experiments.

2. Preparation of ADNBF Crystals from TeNA

A typical experimental run for ADNBF from acetic acid was carried out by the following procedure: 200 cm^3 of acetic acid and 40.3 g (0.147 M) of TeNA are placed into a 500 cm^3 double-walled reactor equipped with an axial turbine type impeller at the given temperature. Fig. 2 shows typical reaction temperature profiles with various coolant temperatures of the reactor which are controlled by a thermostat (RM20S, Lauda, Germany) with an accuracy of ±0.01 °C. In this figure can be seen a sudden temperature change within 10 minutes. At this period, gas evolution is vigorously commenced and the temperature of the reaction mixture increases abruptly up to 110 °C, depending on the coolant temperature. Gas evolution indicates the rapid exothermic reaction due to the formation of the benzofuroxan ring by the radical attack of the unstable nitrene with the adjacent nitro group. Also, another reason is the reaction of azide ions with the displaced nitrite ions to form N_2 [8,10,13,14].

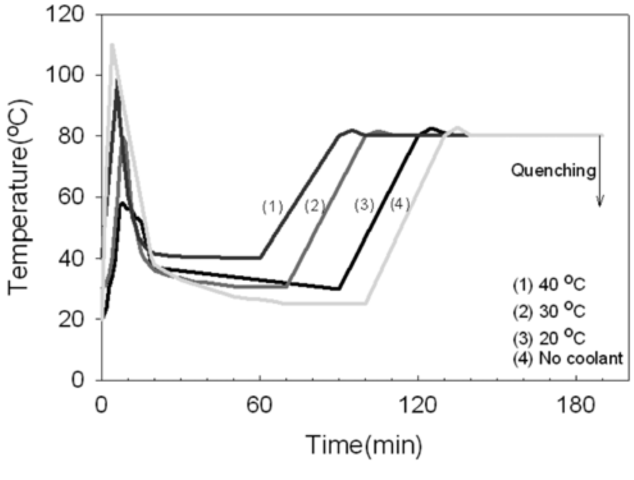


Fig. 2. Temperature profiles during the reaction of TeNA with NaN_3 from acetic acid.

The final reaction point can be realized by the color change and the temperature drop to initial temperature of the reaction mixture, as can be seen from Fig. 2. Then the reaction mixture is heated up to 80 °C and kept for 2 h to complete the ring formation reaction of benzofuroxan. Finally, the reaction mixture is cooled to room temperature and light orange-colored ADNBF crystals are filtered and washed with distilled water and dried.

When the other solvent was used instead of acetic acid, ATNA precipitated from acetic acid was filtered from the reaction mixture and washed several times with distilled water until pH of the filtrated solution reached 7.0. For synthesis of ADNBF, 2 g of ATNA was slowly dispersed to 20 cm^3 of the reaction solvent maintained at 25 °C in a jacketed reactor with an axial turbine type impeller.

3. Characterization

The crystal structure and morphology of the ADNBF crystals and reaction intermediates produced from the present work were investigated by PXRD (powder X-ray diffractometry, Miniflex, Rigaku, Japan) and SEM (scanning electron microscopy: S-4300, Hitachi, Japan) at an acceleration voltage of 25 kV. FT-IR (Fourier transform infrared spectroscopy) spectra were measured over the frequency range of 400-4,000 cm^{-1} at a minimum resolution of 4 cm^{-1} and recorded on a Nicolet 380 (Thermo Fischer Scientific Inc., USA). Azidation products of TeNA from NaN_3/CH_3COOH were analyzed by NMR (nuclear magnetic resonance spectroscopy, UNITY-500, VARIAN, USA) and TLC (thin layer chromatography: CM-10, Spectronic, USA; UV Lamp: ENF-260C). Thermal analysis was also performed by DSC (differential scanning calorimetry: STA-31500, Standton Redcroft, England) calibrated previously with indium. Samples (30 mg) were put into aluminum DSC pans and sealed. The temperature was programmed to start from 25 to 250 °C with a ramping rate 1 °C/min.

4. Acidity of ADNBF Crystals

The procedure of acidity measurement of ADNBF crystals was modified from the MIL-DTL-4544C, which is a part of an acidity determination for HMX [15]. 5 g of the dried ADNBF crystals, accurately weighed in a clean 100 cm^3 beaker, was suspended in 20 cm^3 of DMF (dimethylforamide) delivered from a graduated cylinder. The beaker was immersed in a hot water bath with occasional swirling until the ADNBF crystals were completely dissolved, giving an orange solution. Then, 50 cm^3 of the triple distilled water was added. The mixture was cooled to room temperature and titrated with 0.01 N sodium hydroxide solution using phenolphthalein or methyl red as an indicator. A blank titration was also carried out, and the titration results of the blank solution corrected for acidity of the reagents used. The acidity of the as-synthesized ADNBF crystals was calculated by the following equation.

$$\%\ \text{acidity (as } CH_3COOH) = \frac{6.0(V-v)N}{W} \qquad (1)$$

where V is volume (cm^3) of sodium hydroxide solution titrated in sample, v is volume (cm^3) of sodium hydroxide solution titrated in blank solution, N is normality of sodium hydroxide solution used and W is weight of specimen on a dry basis, in grams.

RESULTS AND DISCUSSION

As shown in Fig. 3, TeNA, ATNA and ADNBF crystals were confirmed by FT-IR spectrum in the range of 400-4,000 cm^{-1}. Our interest was focused on the range of 900-2,100 cm^{-1}, because the spectral differentiation among the compounds is made obviously on their carbon-nitrogen bonds. The strong broad absorption occurred in the range 2,090-2,150 cm^{-1} for ATNA. It is due to the N_3 asymmetric stretching. The second peak of the N_3 symmetric stretching band is centered at 1,250-1,320 cm^{-1} [16,17].

Characteristics of the benzofuroxan ring of ADNBF are C=N band at 1,610-1,660 cm^{-1}, for the N→O band at 1,260-1,280 cm^{-1}. The primary amine (-NH_2) of the benzofuroxan ring displays two well-defined peaks which are due to asymmetric (higher frequency) and symmetric stretching vibration at 3,400-3,500 cm^{-1}. The primary amine-of benzofuroxan ring exhibits C-N stretching absorption at 1,000-1,250 cm^{-1} and -NH_2 scissoring band at 1,550-1,650 cm^{-1}. The strong absorption at 840-880 cm^{-1} is assigned to =C-H out-of-bending, which is typical for penta-substituted aromatic compounds. =C-H stretching and C=C stretching vibrations occur at 3,010-3,040 cm^{-1} and at 1,670 cm^{-1}. The nitro groups of all compounds were confirmed by the stretching vibrations at 1,510-1,550 cm^{-1} (asymmetric) and 1,320-1,350 cm^{-1} (symmetric) [17].

XRD patterns given in Fig. 4 also clearly differentiate TeNA, ATNA and ADNBF crystals. Figs. 5(a) and 5(b) represent SEM images of the TeNA from Hanwha Co. and ATNA synthesized from the present work, respectively. Shape of TeNA is cubic but ATNA needle-like. Figs. 5(c) and 5(d) show the different morphology of ADNBF crystals synthesized from acetic acid by adding NaN_3 and NaN_3/H_2O, respectively. When NaN_3 as an azidation reactant was added, cube-like ADNBF crystals with size of 10 to 30 mm were obtained. Addition of aqueous NaN_3, however, leads to formation of plate-like ADNBF crystals. Cube-like ADNBF crystals synthesized from Norris's method seem to be applicable to the explosive formulations.

However, the acidity of the ADNBF crystals prepared in the present work was measured to be 0.14-0.2%, which is much higher than that of general military criterion on the residual acidity [15]. Two addition methods of NaN_3 or NaN_3/H_2O did not give any significant difference in acidity of final ADNBF crystals. The high acidity level of the precipitated crystals was responsible for the inclusion of acetic acid entrapped from azidation reagent. To reduce acidity of ADNBF crystals, it is definitely necessary to modify the syn-

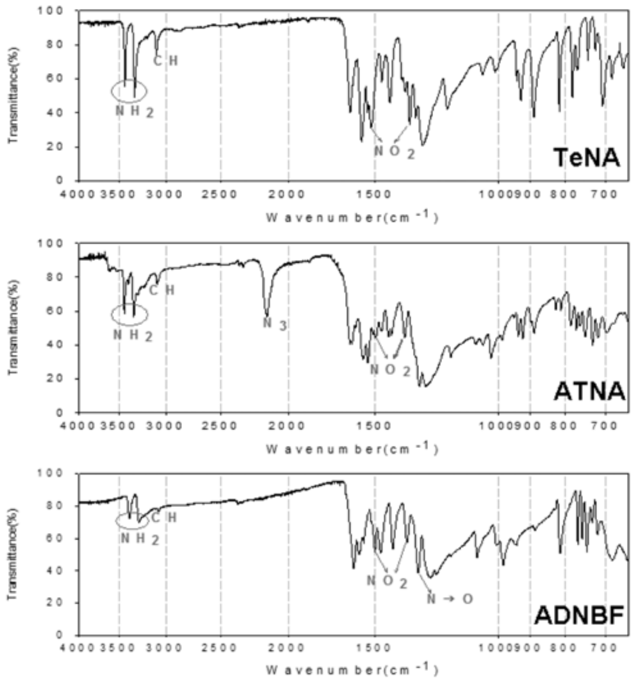


Fig. 3. FT-IR spectra of TeNA, ATNA and ADNBF.

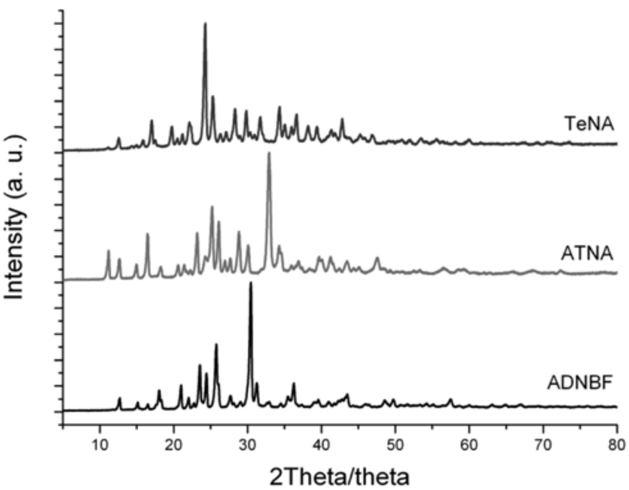
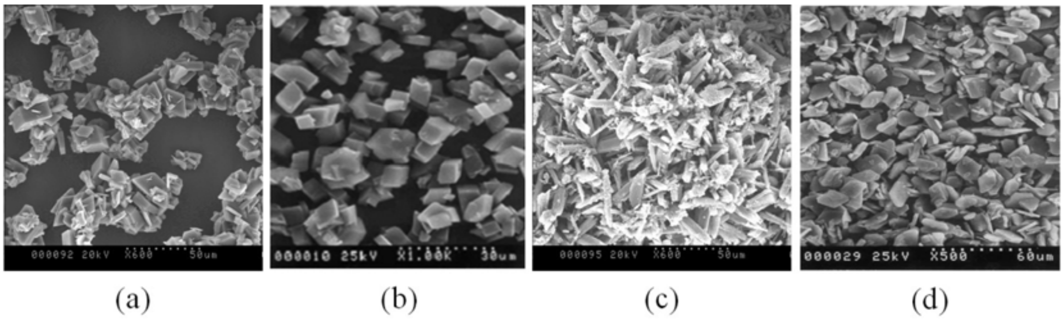


Fig. 4. XRD patterns of TeNA, ATNA and ADNBF.



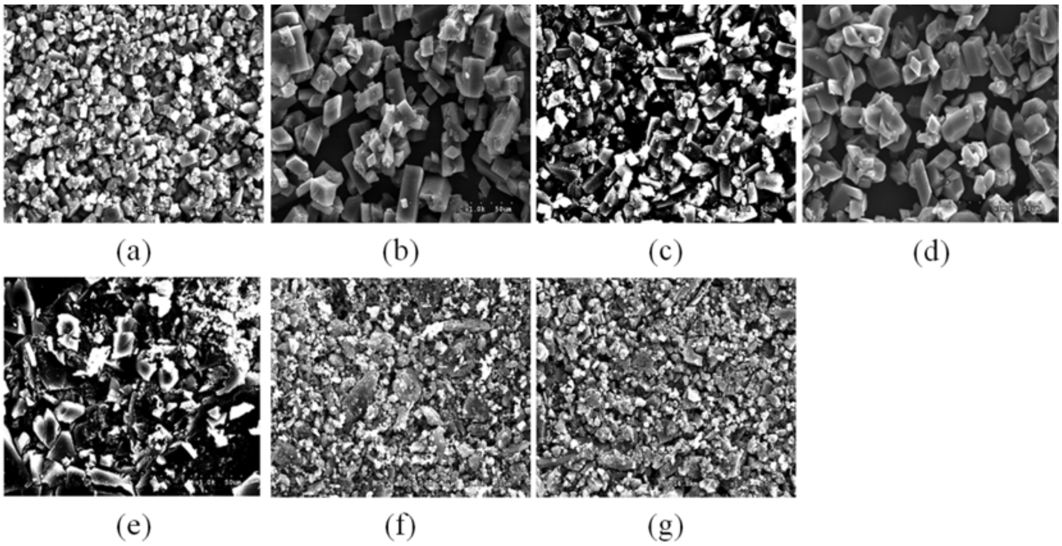
(a) (b) (c) (d)

Fig. 5. SEM images of (a) TeNA, (b) ATNA, (c) ADNBF with NaN_3 powder and (d) ADNBF with NaN_3 aqueous solution.

thetic path of ADNBF proposed by Norris [10].

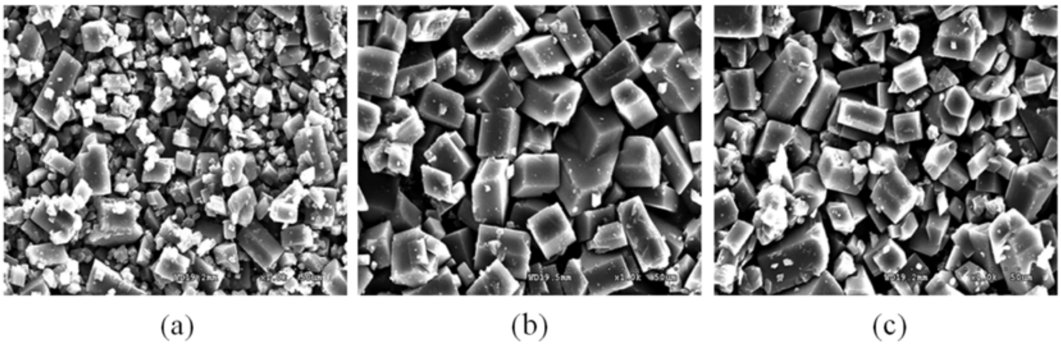
The alteration of the azidation reaction medium may be a possible way to reduce the residual acidity of the ADNBF crystals. Sodium azide and anhydrous acetic acid (or aqueous acetic acid) would commence a disproportion reaction generating stoichiometric mixtures of hydrogen azide and sodium acetate. Since hydrogen azide is a very weak acid as a potential electrophilic reagent, acidic environments are of great importance to facilitate the introduction of the azide groups for the synthesis of the organic azides [18-20]. In the present work, two-step synthesis of ADNBF, which consisted of the azidation reaction of TeNA in NaN_3/CH_3COOH as reaction medium and further thermolytic decomposition of azidation products in various solvents, was carried out.

Fig. 6 shows the SEM images of ADNBF crystals obtained from methanol, ethanol, butanol, toluene, acetonitrile, n-hexane and pure water. The morphology of the ADNBF crystals from methanol, etha-



(a) (b) (c) (d)
(e) (f) (g)

Fig. 6. SEM images of ADNBF obtained by the reactive crystallization of ATNA from (a) methanol, (b) ethanol, (c) butanol, (d) toluene, (e) acetonitrile, (f) n-hexane and (g) pure water.



(a) (b) (c)

Fig. 7. SEM images of ADNBF obtained by the reactive crystallization of ATNA from ethanol with reaction temperature of (a) 57 °C, (b) 67 °C and (c) 76 °C.

Table 1. Measured acidity of ADNBF crystals obtained from various solvents

Solvent	Acidity (%)
Acetic acid	0.14-0.20
Water	0.08-0.09
Toluene	0.07-0.08
Ethanol	0.05-0.06

nol and butanol (Figs. 6(a), 6(b) and 6(c)) is shown to be cubic with size of 3-10 μm, tetragonal with size of 10-30 μm, and irregular shape with size of 10-20 μm, respectively. ADNBF crystals from toluene (Fig. 6(d)) are shown to be rhombic with size of 10-20 μm. On the other hand, ADNBF crystals from acetonitrile, n-hexane and water (Figs. 6(e), 6(f) and 6(g)) are shown to be irregular and their size distribution is very broad. In the case of water, because of density difference, ATNA crystals floated up on the water surface and thus there was a difficulty in mixing. Fig. 7 represents the SEM images of ADNBF crystals from ethanol at the various reaction temperatures. All crystals show that the morphology of the ADNBF crystals is cubic or tetragonal with aspect ratio less than 2. In this figure, crystal size is shown to be 5-20 μm at 57 °C, 15-20 μm at 67 °C and 10-20 μm at 76 °C, respectively.

Table 1 lists the measured values of acidity of ADNBF obtained from various solvents. As a whole, by replacing acetic acid as a reaction medium, it was found that the acidity levels of ADNBF were dramatically reduced from 0.14-0.2% to 0.05-0.06% from ethanol and 0.07-0.08% from toluene. However, we could not reduce the acidity level of ADNBF further, because ADNBF was found to be formed during formation of ATNA by the reaction of TeNA with NaN$_3$ from acetic acid even if the temperature of the reactor kept as low as 10 °C. It might be explained by some hot spots which may be generated during the reaction of TeNA with NaN$_3$. As shown in Fig. 2, as soon as TeNA reacts with NaN$_3$, the temperature of a reaction mixture increases abruptly within a few minutes and some nuclei of ADNBF crystals seem to be generated. Table 2 represents the results of analysis of the products by azidation reaction between TeNA and NaN$_3$/CH$_3$COOH, where the molar ratio of NaN$_3$ to TeNA was taken to be about 2 : 1 to remove completely the residual nitrite ions. Results of DSC, TLC and NMR indicate the simultaneous formation of ADNBF and ATNA. In the reaction temperature range of 25 to 60 °C, the fraction of ATNA in the product of azidation reaction was found to be from 0.73 to 0.82.

In summary, to reduce the acidity of ADNBF crystals, ethanol and toluene were found to be good candidates as reaction media instead of acetic acid. Ethanol is much better than toluene for downstream processes such as washing crystals and cleaning the reactor with water, because ethanol is hydrophilic. Therefore, based on acidity level, crystal shape, crystal size and experimental feasibility, ethanol would be a good alternative as the reaction medium for the formation of ADNBF with thermolysis of ATNA.

CONCLUSIONS

The present work clearly shows that the acidity level of ADNBF can be reduced by replacing a reaction medium instead of acetic acid in the final step of reactive crystallization of ADNBF. Among various solvents tested for the crystallization of ADNBF from ATNA, ethanol was found to be the most suitable for controlling the acidity and morphology of crystals. The acidity of ADNBF crystals obtained from ethanol was about 0.05-0.06% and the shape was cubic or tetragonal with aspect ratio less than 2. Their sizes ranged from 5 to 30 μm, and thus ADNBF crystallized from ethanol may be applicable to explosive formulations.

ACKNOWLEDGMENTS

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NOMENCLATURE

ADNBF : 7-amino-4,6-dinitrobenzofuroxan
ATNA : 3-azido-2,4,6-trinitroaniline
HMX : cycletetramethylenetetranitramine
N : normality of sodium hydroxide solution
NTO : 5-nitro-1,2,4,-triazol-3-one
PBX : polymer bonded explosive
RDX : cyclotrimethylenetrinitramine
TATB: triaminotrinitrobebzene
TeNA: 2,3,4,6-tetranitroaniline
v : volume of sodium hydroxide solution titrated in blank solution [cm^3]
V : volume of sodium hydroxide solution titrated in sample [cm^3]
W : weight of specimen [g]

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Table 2. Results of DSC, NMR and TLC analysis of precipitates obtained by reaction of TeNA with NaN$_3$ from acetic acid

Initial/maximum temperature (°C) of reaction mixture during reaction of TeNA with NaN$_3$	Results		
	DSC	NMR	TLC
10/25	110.95 °C (ATNA) 277.13 °C (ADNBF)	ADNBF : ATNA=1 : 3.84	R_f=0.18 (ADNBF) R_f=0.5 (ATNA)
10/40	118.25 °C (ATNA) 278.37 °C (ADNBF)	ADNBF : ATNA=1 : 4.44	R_f=0.18 (ADNBF) R_f=0.5 (ATNA)
10/60	138.04 °C (ATNA) 276.11 °C (ADNBF)	ADNBF : ATNA=1 : 2.70	R_f=0.18 (ADNBF) R_f=0.5 (ATNA)

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