Central European Journal of Energetic Materials, **2005**, *2*(4), 55-62.
ISSN 1733-7178

Self-sensitizable Characteristics of Modified Ammonium Nitrate

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Abstract: Ammonium nitrate has been modified by evaporative recrystallization from its mixture solution with hexadecyl trimethyl ammonium bromide and sodium dodecyl sulfate. The physical property of the modified compound has been investigated by SEM, DSC, specific surface area and particle size measurements. The results show that in comparation with common ammonium nitrate, the modified ammonium nitrate has an irregular crystal shape, greater specific surface area, better particle size distribution, lower heat of crystal pattern transition and higher transition temperature. These indicate the modified ammonium nitrate has a mesoporous structure with good self-sensitizable, anti-hygroscopic and anticaking performances as an oxidizer of industrial explosive.

Keywords: ammonium nitrate, modification, explosive properties

Introduction

Ammonium nitrate (AN) is extensively used as non smog oxidizer of industrial explosives and propellants because of low cost, wide resources of AN, and little smog produced by burning AN. However, lower sensitivity, serious caking and hygroscopicity of AN influence available properties of propellants and industrial explosives which are made from AN [1].

In order to overcome above shortages, many research staffs have tried their best to obtain some valid methods in which utilizing surface-active technology is effective in practice[2], namely, AN can be recrystallized from saturated solution of AN under some certain process by action of surfactants. The recrystallized AN is light, porous, so physical properties of the modified AN is different from that of common AN [3].

Experimental

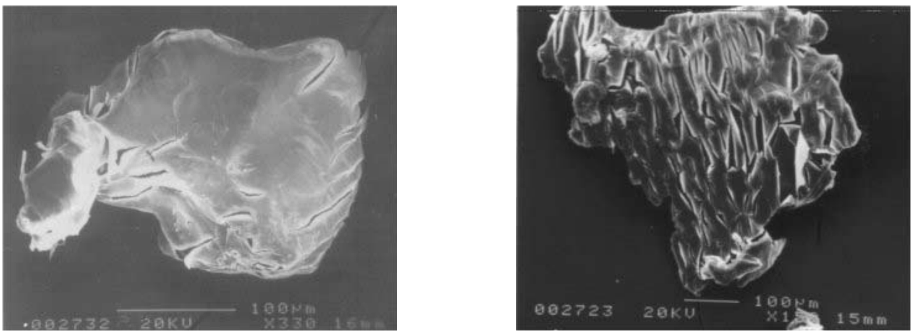
Preparation of modified AN

The surfactants of 0.5% mass concentration are added to the 88~92% AN solution with temperature 125~130 °C.The system is dried under vacuum of -0.085 ~ -0.095 MPa for 15 minutes. The modified AN, which has light porous structure, is obtained (water concentration < 0.03%).

Results and Discussion

Shape analysis

The shapes of AN are observed through SEM. Compared with common AN, surface of the modified AN is quite irregular, its body has many holes and cracks, crystal shape disproportionates and contains a large number of micro-gas pockets. The photos of SEM are shown in Figure 1.



(a) common AN (b)modified AN

Figure 1. SEM photos of AN.

Size ratio of crystal faces which absorb surfactants results in crystal shapes disproportionation. The irregular shape characteristics of the modified AN treated by surfactants is obviously seen from Figure 1.

According to “heat point”theory [4],under action of explosion shock wave from outside, micro-gas pockets in the modified AN particles are compressed in adiabatic condition, then form “heat points” of high temperature and high pressure. These “heat points” increase sensitivity of the modified AN.

The distributions of pore radius and pore volume

Determination of the relation between pore radius and pore volume of the modified ammonium nitrate and the distribution of pore radius with NOVA1000 specific surface instrument. The specific surface data are represented in Table 1.

Table 1. Pore radius and pore volume of the modified ammonium nitrate

Pore radius [nm]	Pore volume [μL g^{-1}]	Pore volume/total volume [%]
20~10	0.87	15.41
10~5	1.78	31.52
5~4	6.10	10.80
4~3	0.94	16.65
3~2	1.09	19.30
2~1	0.37	6.55

Note: In the modified ammonium nitrate the pore having radius greater than 20 nm was not observed.

The total volume of pore, whose pore radius R_P is more than 1.0 nm, is 5.68 mL g^{-1}.

According to the standard of IUPAC pore radius grade: the pore whose $R_P \geq 50$ nm is wide pore, the pore whose $R_P = 2\text{-}50$ nm is mesopore, the pore whose $R_P = 0.7\sim2$ nm is supper laciness, the pore whose $R_P \leq 0.7$ nm is extreme laciness [5]. It is shown from Table 1 that the 95% micropore of the modified ammonium nitrate is mesopore. The exact version should be mesopore, but it is used to being called micropore.

On the basis of self-sensitizable effect of the modified ammonium nitrate, laciness (super and extreme laciness) is invalid. In order to produce the modified ammonium nitrate explosive, the modified ammonium nitrate must be mixed with wood powders and fuel oil, so even though the micropore of R_P less than 2.0 nm is formed, it can be blocked with the fine wood powders, especially with the fuel oil and can not exist. Wide pore also should be avoided. Obviously, too many wide pores will influence the porosity. If the porosity is too low, it will affect the heat point numbers directly and wont be favorable for the self-sensitizable effect. Therefore, mesopore is the better pore radius range. It wont be blocked by fine wood powders and oil, Moreover, it can make the fine wood powders and oil well-distributed on the pore surface, and then the oxidizing agent with big specific surface and large mesopore numbers are mixed with combustible substances in the state of zero-oxygen balance to form industrial explosive. The explosive with the enough pores and heat points has the best initiation sensitivity and the most complete state of detonation.

The distributed results of pore volume and pore radius of the modified ammonium nitrate and common ammonium nitrate are shown in Figure 2.

It is clear to know from Figure 2 that the pore volume of the modified Ammonium nitrate is larger than that of common ammonium nitrate. Moreover, it is shown from Table 1 that more than 95% valid pore radius of modified ammonium nitrate is in mesopore pore range, which is extremely beneficial to initiative effectiveness of the modified ammonium nitrate.

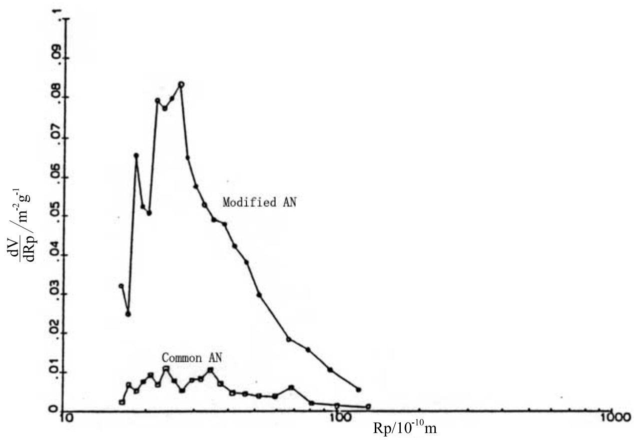


Figure 2. The plot of comparison between the modified AN and common AN for size distribution of micro-pore.

Distribution of particle size

Distributions of particle size for two kinds of AN are tested separately. The results are shown in Figure 3.

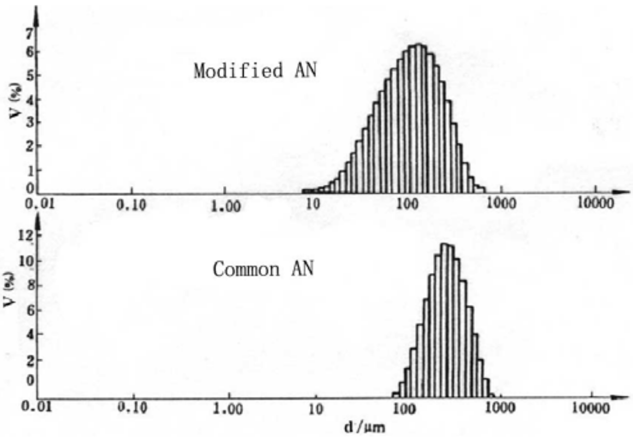


Figure 3. Particle size distribution curves of AN.

It is shown from Figure 3 that particle size of the modified AN mainly distributes in range from 10 to 1000 μm. Average particle size of the modified AN treated with surfactants (87.6 μm) is lower than that of common AN. Compared with common AN, the modified AN has wider particle size distribution, more micro-powders and better grade arrangement. If the modified AN is mixed with combustible agents, well-distributed degree of mixed system can beneficially increase explosion velocity. Explosion properties of mixed explosive according to mixing reaction mechanism of industrial explosive will be increased.

Specific surface area measurement

Specific surface area of the modified AN (3328.54 cm^2 g^{-1}) is 4.4 times bigger than that of common AN (756.48 cm^2 g^{-1}).So it benefits to increase velocity of explosion reaction and complete extent of explosion reaction.

Crystal pattern transition of modified AN studied by DSC

Under 1 atm, AN has five thermodynamically stable crystal structures. Each structure exists at temperature range [6], if temperature changes, it is convertible between different crystal patterns. The transition is one of main caking reasons. Crystal pattern transition is accompanied by heat change. So its extent can be determined according to heat change of AN in temperature by DSC analysis. The results are shown in Table 2.

Table 2. Data in DSC picture of AN

Peak Number	Common AN Position of peak [°C]			Transition Heat [J g^{-1}]	Modified AN Position of peak [°C]			Transition Heat [J g^{-1}]
	Start	End	High		Start	End	High	
1	46.5	62.8	54.4	21.2	50.9	64.8	56.5	23.7
2	89.4	101.4	95.5	9.9	126.6	135.8	129.8	55.1
3	125.2	133.8	129.6	55.7	166.9	178.1	172.8	76.3
4	163.4	175.2	171.3	76.4				

The experimental results indicate that crystal pattern transition number of the modified AN declines, crystal pattern transition position moves back compared with common AN. It is because of combination between polar groups of surfactants and ion of AN through electrostatic action. It harasses action between ammonium ions and nitrate radical ions in AN molecules to some extent, so intrinsic crystal pattern transitions of AN don't easily happen with temperature change. Some transitions are held back, and lead that number of transition declines and transition position moves back.

Research on hygroscopicity of modified AN

Dried modified AN and common AN with particle size ranging from 0.045 mm~0.200 mm are weighed, and separately placed into condition under which relative humidity is 70% and 90% respectively. Over a period of time, their hygroscopic increments are also weighed, their hygroscopic rates are calculated and the results are also shown in Table 3.

Table 3. Hygroscopic rates of common AN and modified AN

Samples	Average Mass [g]	Relative Humidity [%]	Average time [h] 2	4	6	8	20	30
Common AN	2.4671	70	0.61	1.19	1.960	2.48	6.37	8.93
	2.5012	90	2.30	4.23	6.11	8.35	14.13	17.10
Modified AN	2.4173	70	0.24	0.45	0.72	0.93	2.22	2.94
	2.3995	90	0.47	1.60	2.47	3.35	4.80	5.27

Table 3 indicates that hygroscopic rates of the modified AN are greatly lower than that of common AN. It is reasoned that the modified AN is treated with selected surfactants, polar groups of surfactants combine with ion in AN surface, and unpolar groups of surfactants form a close hydrophobic film, the thin film prevents validly from contacting between AN molecules and water molecules outside. So hygroscopicity of the modified AN is low.

Anti-caking property measurement of the modified AN

Anti-caking property of the modified AN and common AN respectively pressed and formed in the same model under 1.47MPa pressure are tested, their break forces are regarded as indices of anti-caking property. If there is a big break force, AN is easily to cake. Otherwise, AN is not easily to cake. The results are shown in Table 4.

Table 4. Data of resistance to compression of caking AN(N)

Average	1	2	3	4	5	Average
Common AN	479.2	480.2	477.5	475.9	477.4	478.0
Modified AN	86.9	87.7	83.4	81.2	84.1	84.7

The experimental results indicate that anti-caking property of the modified AN is significantly superior to that of common AN. From photos of SEM (Figure 1), it can be seen that common AN crystal is more tight, crystal particles closely knit through "salt bridge", intrinsic crystal pattern transition and hygroscopicity keep it firm, so common AN easily cakes, the modified AN particles connect each other by means of ting branch shape structure. This structure is loose. Moreover, hygroscopicity and crystal pattern transition of the modified AN are improved by action of surfactants, therefore, the modified AN has better anti-caking property.

Explosion properties

Common AN and modified AN used as oxidizer are mixed with wood powders and fuel oil used as reduction agent in mill machine to prepare industrial explosive according to mass ratio 92 : 4 : 4. The explosion properties are listed in Table 5.

Table 5. Explosion properties

Oxidizer in formula	Charge density [g cm^{-3}]	Explosion velocity [m s^{-1}]	Gas distance [cm]	Brisance [mm]	Storage [month]
Common AN	0.90~0.95	2600 ±50	2	9 ±1	6
Modified AN	0.90~0.95	3200 ±50	4	13 ±1	10

From Table 5, it can be seen that explosion properties of industrial explosive produced by modified AN is better than that of industrial explosive produced by common AN.

Summary

Compared with the common AN, modified AN has more irregular crystal shape, larger numbers of micro gas-pockets, wider particle size distribution and better particle size grade arrangement, smaller particle size of average value, bigger specific surface area, more excellent anti-hygroscopicity and anti-caking property. The industrial explosive produced by the modified AN has more excellent explosion and physical properties.

Acknowledgements

The authors would like to thank the Nanjing University of Science and Technology for the financial and technical support.

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