Study on the Crystal Habit Modification of Ammonium Nitrate

III. Application to AN-FO

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6. Application to AN-FO

6-1. Introduction.

An interesting applicaion of the habit modified ammonium nitrate to inustrial explosives is ammonium nitrate fuel oil explosive (AN-FO).

Recently AN-FO have been developed and widely used in the U. S. A. because of the advantages in safe handlings and economy.

Unfortunately however, these explosives can not be free from disadvantage of lower sensitivity than that of conventional explosives, since no any self explosive component is present in the former. Hence the AN-FO heretofore known is hard to be detonated by means of a blasting cap or a common detonating fuse, and it further requires relatively greater diameter to obtain steady state detonation. For this reason the AN-FO finds rather limited use in our country where scales of blasting operations are generally small.

During the course of an investigation of the habit modification of ammonium nitrate, it has been discovered that the modified crystal, being mixed with fuel oil displayed enough explosive properties for use in smaller scale blasting operations.[1)2)] In the present paper concerning with the modified crystal AN-FO, process of preparation properties of the AN-FO, and of the modified crystal are described.

6-2. Process of preparation of the AN-FO

The process of preparation of the AN-FO here in question is called "wet process" as it includes crystallization from mother liquor, and the product contains considerable amount of water. They are remarkable points of the process. Other points to be mensioned are; neither crushing nor drying of ammonium nitrate are required, overall the process is carried out in safety, and the production costs are low.

The process is shown in figure 1. A saturated aqueous solution of ammonium nitrate at about 32°C is prepared in a tank, which is equipped with an agitator and with a jacket for cooling, and a small amount of crystal habit modifying substance is added. The solution is cooled down to 10 or 20°C in one or two hours. Then the habit modified

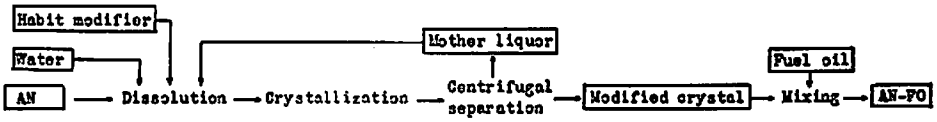

Fig. 1. Process of the preparation of the modified crystal AN-FO, which is calld "wet procss".

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ammonium nitrate is crystallized out. The mixture of mother liquor and crystal is discharged to a centrifuge which is set under the tank, and they are separated. The separated mother liquor is pummped up the tank and is used for ammonium nitrate dissolution of next ronud; thus the liquor is availed repeatedly. As a starting material of the process, industrial grade ammonium nitrate is available. From the economical point of view, however, hot concentrated aqueous solution of ammonium nitrate, whose water content is up to 5 per cent, is preferable. Such a solution is found in processes of ammonium nitrate plant of several types e.g. Stengel process, graining process and prilling process. The centrifugally dehydrated modified crystal which still holds 4 to 5 per cent water shows enough sensitivity to detonation when it is mixed with fuel. So it may be offered to on-site mixing or "do-it-yourself" operation. The mixing with fuel is carried out quite easily as the modified crystal is oil absorptive in its nature. Simple hand mixing or any type mixers are possibly used.

6-3. Explosion properties, and factors affecting them.

6-3-1. Measurment of the explosive sensitivity.

As it has been mentioned the aim of the present study is to produce AN-FO whose explosive sensitivity is so high that it obtains steady state detonation even in a small diameter cartridge. For this purpose, several factors affecting the explosive sensitivity was studied. The explosive sensitivity was expressed by a critical diameter which was defined as a cartridge diameter of 50 per cent detonation. In general, three variables determine the explosive sensitivity; they are strength of initiation, confinement of cartridge, and cartridge diameter. In the present study, the charge was wrapped with a thin paper, and was initiated by a No. 6 detonator. Cartridges of various diameters were prepared and the percentage of detonation was measured.

6-3-2. Temperature of crystallization.

Crystallization of the modified ammonium nitrate was achieved by lowering of the solubility with cooling. A large quantity of the crystal might be obtained by a cooling started at high temperature with a big temperature reduction, but this resulted in degradation of the sensitivity. Figure 2 shows range of crystllization temperature and explosive sensitivity of the AN-FO. As it is shown the crystals from 30 to 20°C have the highest sensitivity. On the other hand the crystals from higher temperatures and from lower ones have the lower sensitivity. The reason is that in a lower temperature range, solubility of the modifying substance is too small, while at higher temperature than 32°C, crystallized ammoninm nitrate is III phase

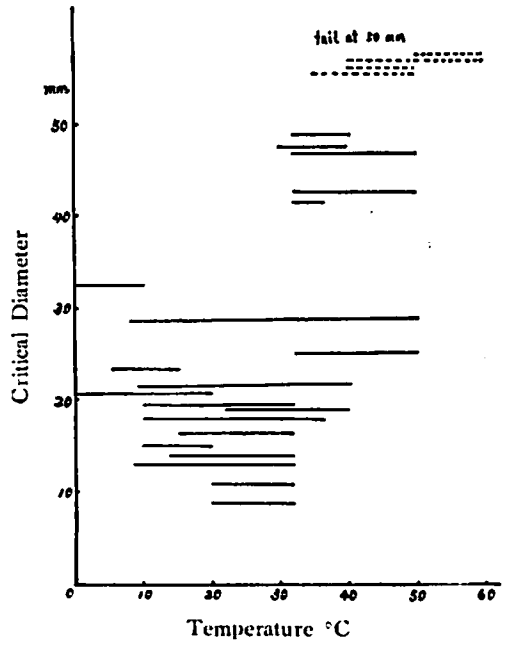
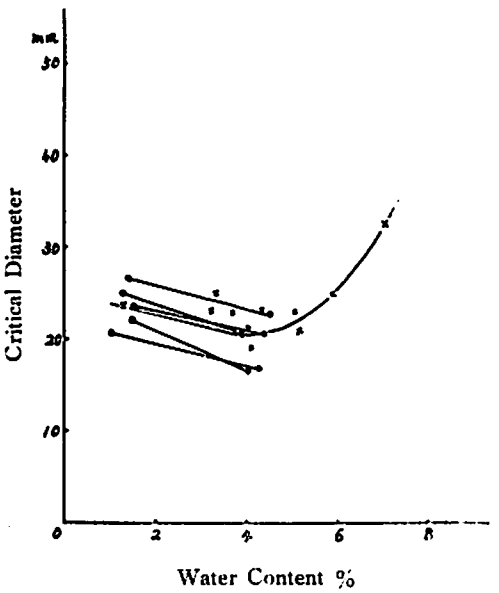


Fig. 2 Range of crystallization temperature versus explosive sensitivity of the AN-FO. Sensitivity is indicated in critical diamaeter.

which is subjected to a different type of modification.

6-3-3. Water content.

In the earlier stage of the work, it was considered that water content in the crystal might decrease explosive sensitivity of the AN-FO. Hence water content of the crystal was reduced to less than 1 per cent. The drying of the modified crystal was a troublesome process; it must be worked in temperature range of IV phase, below 32°C, otherwise the condition of the modification would be changed, and the sensitivity would be decreased. Later it was found that the modified crystal with 4 to 5 per cent water, which was only treated by a centrifuge, had a higher sensitivity than dried ones. This was quite a promising discovery for the industrialization of the modified crystal AN-FO. The external form of the modified crystal is favorable for centrifugal dehydration. It is easy and efficient. Figure 3 shows relations between water content and explosive sensitvity. Tied points show the results obtained from the crystals of the same batch.



Fig, 3, Relations between water content and explosive sensitivity.

6-3-4. Selection of fuel.

The modified crystal was mixed with 5 per cent of various fuels, and the explosive sensitivity of the mixtured was measured. The results are shown in table 1. Some

Table. 1. Explosive sensitivity of mixtures of the modified crystal and 5% various fuels.

Fuels	viscosity, c. p.	Boiling pt.,°C	Critical dia. of mixture of the modified AN, mm
No. 1 light oil	3.0		9
Heavy oil A		340(95%)	9
Liquid paraffine	190		17
Kerosene		280(95%)	9
Toluene	0.6	110	13
Xylene	0.6	140	11
Solvent naphtha			15
Crude tar			15
Creosote oil			11
m-Cresol	21	202	fail at 50
Phenol	11.6	182	fail at 50
Nitro benzene	2.0	211	15
Anilin	4.4	184	fail at 50
Ethyl alcohol	1.2	78	21
Turpentine oil			fail at 50
Olive oil	800		15
Rapeseed oil	1000		17
Linseed oil	500		17
Caster oil	6500		19
Paulownia oil			25
Carbon black			fail at 50

properties, volatility, inflammability, viscosity, chemical stability, smell and cost were investigated together with explosive sensitivity, and No. 1 light oil were adopted. This is a close

Teble. 2. Properties of No. 2 fuel oil (ASTM) and No, 1 light oil (Japanese Industrial Standard).

	No. 1 light oil	No. 2 fuel oil
Flash point (min.)	50°C (122°F)	100°F or legal
Pour point(max)	-10°C (14°F)	20°F
Distillation temp.(90%)	350°C(662°F)	675°F
Kinematic viscosity	at 30°C(86°F) 2.5 cst	at 100°F. 4.3 cst

equivalent to No. 2 fuel oil, which is widely used for ANFO in the U.S.A.. Table 2 shows properties of No. 2 fuel oil and No. 1 light oil in comparison.

6-3-5. Fuel oil content.

Fuel oil content decides the sensitivity and power of the AN-FO. From figure 4 it is seen that the modified crystal itself does not

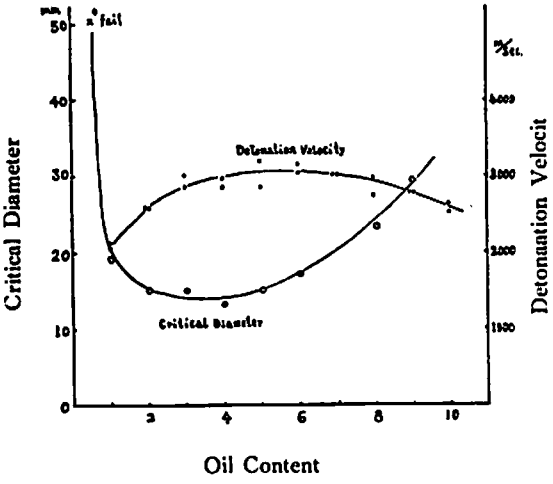


Fig. 4. Fuel oil content versus explosive sensitivity and detonation velocity of the AN-FO. Detonation velocity was measured in 35 mm dia. paper cartridges.

explode. This fact is quite important for "do-it-yourself" operations from a view point of safe handling. With 5.5 percent oil, the mixture is oxygen-balanced.

6-3-6. Explosion properties.

Explosion properties are summerized in table 3.

Tabel. 3, Explosion properties,

Drop hammer test (5 kg hammer)	24 cm
Velocity of detonation in 35mm dia. steel tube	4700m/s
Hess brizance	12.1mm
Ballistic pendulum	69.0mm
Gap test (multiples of dia.)	
on a sand bed	1.5-2.0
in water of 0.3m deep	5.0-6.0

6-2-7. Storage test.

The modified crystal AN-FO showed little degradation of sensitivity on storage of long periodes. Experimental results are shown in figure 5. We can understand this fact if we assume that the modified crystal is always renewed with variation of external conditions, since the crystal holds enough water to keep the modifying substance in an active state. In addition the crystal is completely free from caking, which is a common defect of ammonium nitrate explosives.

6-4. Properties of the modified crystal relating to explosive sensitivity.

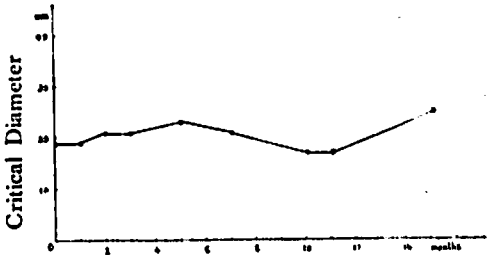


Fig. 5. Variation of explosive sensitivity on storage.

6-4-1. Particle diameter distribution.

A remarkable point of the modified crystal AN-FO in that the crystal is not subjected to drying and crushing. So the particle size is determined during the course of crystallization, dehydration and other operations. Particle size is intimately related to explosive properties, and is an important factor to be considered while its definition is a very confusing problem, because the crystal is fibrous or dendritic as it is seen on microphotographs[3]. In addition the crystal is so fragil that the size is reduced on handling. An estimate of the particle size distribution odtained dy sieve test with Tylor mesh is shown in figure 6.

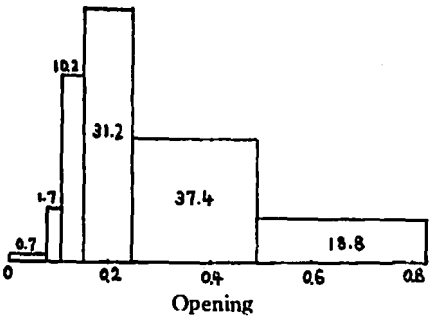


Fig. 6. Particle size distribution.

6-4-2. Specific surface.

Specific surface of ammonium nitrate is closely related to explosive sensitivity of AN-FO. In the present study measurment of the specific surface was carried out by air permeability methol, which had been based by Kozeny and Carman. Descriptions of the apparatus used and the specific surfaces of ammonium nitrate of various origins were given by K. Hino and M. Yokogawa.[4] The samples in the present paper were modified and ordinary ammonium nitrate crystals which were previously classified with Tylor mesh. The result is shown in figure 7. The modified crystals have far greater specific surfaces than ordinary ones as we expected from their apperance. This fact explains in part high sensitivity of the modified crystal AN-FO.

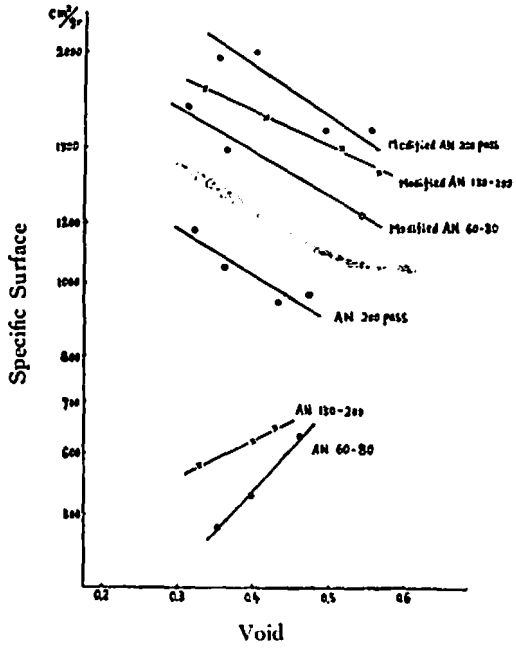


Fig. 7. Specific surfaces of the modified crystals. They are plotted against void of the crystals packed in a sample cylinder of the measuring apparatus.

6-4-3. Wetting properties.

Surfaces of modified crystal on which molecules of the modifying substance is adsorbed with their polar group, while turning the nonpolar group outward, are expected to be rather lipophilic. In other words the surfacec are given affinity to oily substances by the adsorption, and the fuel oil easily spreds over the surfaces. Thus the contact between oxydizer and fuel is close in the case of the modified AN-FO. This is another reason why the AN-FO has high sensitivity.

Wetting properties are expressed by contact angles. When the contact angle between a solid and a liquid is small, it is defined that the liquid wets the solid well. Contact angle between a powder and a liquid is measured by a capillary method. In the method the sample powder is filled in a glass tube and the lower end of the tube is immersed in the liquid, then the latter rises through the capillary. According to Washburn the velocity of rising is shown by the next equation.

$$dh/dt = r\gamma\cos\theta/4\eta h \quad \cdots\cdots(1)$$

where h: height of the liquid at time t
r: diameter of the capillary
γ: surface tension of the liquid
θ: contact angle
η: viscosity of the liquid.

Integrating the equation (1), we get,

$$h^2 = r\gamma t\cos\theta/2\eta \quad \cdots\cdots(2)$$

In the present experiment, samples of ammonium nitrate crystals preliminarily sieved for the range between 60 and 80 mesh were filled in glass tubes of 1 cm diameter. The liquids were saturated aqueous solution of ammonium nitrate and No. 1 light oil, properties of which are shown in table 4.

Table 4. Properties of the liquids which were used for measuring the wetting property.

property	Viscosity c. p.	Surface tension, dyne/cm
AN sat. aqueous soln.	1.4	55
do., added 0.05% habit modifier	1.4	29
No. 1 light oil.	3.0	29

Equation (2) is written as

$$h_w^2 = r\gamma_w t \cos\theta_w / 2\eta_w \quad \cdots\cdots(3)$$

$$h_o^2 = r\gamma_o t \cos\theta_o / 2\eta_o \quad \cdots\cdots(4)$$

in which suffixes w and o mean that they relate to aqueous solution and oil respectively. From the epuations (3), (4), we get

$$h_o^2/h_w^2 = \gamma_o\eta_w \cos\theta_o/\gamma_w\eta_o \cos\theta_w$$

$$k\cos\theta_o\eta\cos\theta_w \quad \cdots\cdots(5)$$

From experimental reusults, the value k cos $\theta_o$cos θ_w was calculated. The results are shown in table 5. The value of the modified ammonium nitrate is greater than that of ordinary one. This apparently indicates that the modified crystal is wetted more easily by oil than in the case of ordinary one.

Table 5.

t,	Ordinary crystal			Modified crystal		
min.	h_w	h_o	$k\cos\theta_o/\cos\theta_w$	h_w	h_o	$k\cos\theta_o/\cos\theta_w$
10	12.2	8.8	0.52	3.3	5.8	3.55
20	15.8	11.0	0.48	4.3	8.1	3.55
30	17.9	12.4	0.48	5.1	9.6	3.54
40	19.6	13.0	0.44	5.8	10.9	3.55
50	21.2	13.4	0.40	6.5	11.8	3,29
60	22.2	13.9	0.39	7.0	12.8	3,35
70	23.0	14.2	0.38	7.4	13.8	3.54
80	24.3	14.4	0.35	7.8	14.2	3.33
90	24.6	15.2	0.38	8.1	14.8	3.35
100	25.1	15.4	0.38	8.4	15.4	3.35

Summary

A process for the preparation of the modified crystal AN-FO was studied. This included crystallization of the modified crystal from a saturated aqueous solution containing a habit modifying substance, and mixing of fuel oil with "wet" crystal. Explosion properties of the AN-FO was studied experimentaly. The modified crystal itself did not explode with a No. 6 cap, however, the crystal mixed with No. 1 light oil had enough explosive sensitivity.

The modified crystal was found to have greater specific surfaces and affinity to oily substance. These properties have been considered to be reasons why the modified crystal AN-FO had high explosive sensitivity.

Acknowledgement

The research was conducted under the direction of Dr. Kumao Hino. I thank for his suggestions and criticisms rendered during the course of the work.

References

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硝安の結晶癖変化に関する研究

(第三報) 硝安—燃料油系爆薬への応用

土屋能男

晶癖変化硝安の興味ある応用は硝安—燃料油系爆薬である。その製造法は湿式法であつて，特徴は 1. 晶癖変化性物質を含有する母液よりIV相の硝安結晶を析出させ，2. その乾燥粉砕を行うことなく，水分 4—5%の状態で燃料油と混合する。この爆薬は爆発性成分を含まないにも拘らず著しく高い起爆感度を有する。一方，変形結晶そのものは6号雷管で起爆されない。この性質は所謂 "do-it-yourself" 爆薬として好適である。更に又これは長期間貯蔵しても感度の低下が殆んどなく，且完全に非固結性である。

高い起爆薬感度の原因は変形結晶に求められる。これは通常の結晶に比し遙かに大きな比表面積を有することが空気透過法により測定された。又その結晶表面には晶癖変化性物質がその分子内に有する疎水基を外方に向けて吸着していると考えられ，通常の結晶より親油性であることが予想されるが，粉末柱毛管上昇法による水及油に対する濡れの測定によりこれが確かめられた。