Study on The Crystal Habit Modification of Ammonium Nitrate.

I. Crystallographical Properties.

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(Received Dec. 20, 1960).

1. Introduction.

The objects of our study are to inquire into the crystal habit modification of ammonium nitrate caused by adsorption of surface active substances on the growing surfaces of the crystal, also to explain some other properties of the crystal and to turn the results to improve properties of industrial explosives.

Ordinary crystal form of ammonium nitrate is (110) prisms at normal temperature. In some cases crystals grown from aqueous mother liquor containing certain surface active substances show different habits, i.e. fibrous, needlelike, lathy or platy. The phenomenon, crystal habit modification, has attracted many researchers' attention. The works of de Lisle about 1783 and of Leblanc 1802 are classical examples mentioned in the textbooks. Later P. Gaubert, W. C. France,[1] H. E. Buckley[2)3)] and J. Whetstone have made valuable contributions to the subject. General aspects and many instances of habit modification are extensively worked in the writing of H. E. Buckley.[3] So far as we know, the habit modification of ammonium nitrate is first treated by A. Butchart and J. Whetstone,[4] though in the paper the habit modifying substances are described only about sulfonated dyes. J. Whetstone has investigated mostly the habit modification of ammonium nitrate with sulfonated dyes, and presented a new theory for adsorption of dyestuffs[5], but his distinguished work was the application of the modified crystal to protect ammonium nitrate from caking.[6)~10)]

In the present investigaion we have made efforts to find habit modifying substances among many organic substances, and such substances are dealt inclusively under the name of the surface active substances including dyes, dye-intermediates and surface active agents. Although considerable attention has been paid to habit modification with sulfonated dyes, comparatively little is known of habit modification with such substances. Still more we suggest to apply the modified crystals to ammonium nitrate fuel oil type explosives (AN–FO), for the explosive AN–FO becomes exceedingly sensitive owing to the modified ammonium nitrate. In this paper, the first one of the series, crystallographical properties of habit modified ammonium nitrate are described.

2. Crystal Structure Analysis by X-ray Diffraction.

2–1. Determination of the Crystal System.

There are many kinds of surface active substances which are adsorbed on the growing crystal surfaces of ammonium nitrate and modify its crystal habit. The substances are summerized and discussed later. In this section, several kinds of typically habit modified ammonium nitrate crystals are selected and their crystal structure is studied by x-ray diffraction. The x-ray diffraction of pure ammonium nitrate crystal was examined

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foremost by C. D. West[11]. The latest x-ray diffractometric data on ammonium nitrate IV, the stableform at room temperature, are shown in the A.S.T.M. card[12]. In our experiments pure ammonium nitrate and habit modified crystals are examined by powder diffractometry.

Samples for the test were prepared by grinding in an agate mortar and passing through a Tyler 325-mesh screen. Diffraction angles of all kinds of ammonium nitrate tested coincided substantially, though the intensity of diffraction differed on a count of preferred orientation. The modified crystals were apt to take the orientation. One of the examples is illustrated in Fig. 1. It is shown that the change in appearance of the crystal has no relation to inner structure of the crystal. The crystal system of pure and habit modified ammonium nitrate are the same. That is to say the change is modification of the crystal habit.

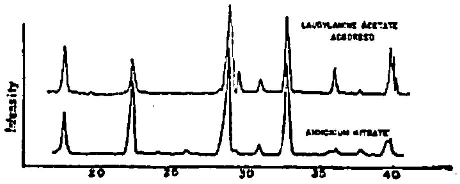

Fig. 1. X-ray diffraction patterns of pure and habit modified ammonium nitrate crystals.

2-2. Accurate Determination of the Lattice Size.

2-2-1. Introduction.

It was determined in the last section that the crystal system of pure ammonium nitrate and that of habit modified ones were the same. In this section we test more precisely whether the lattice sizes are changed or not. In some cases of habit modification in which foreign substances go into the space lattice, expansion or contraction of the space lattice may be observed. If foreign substances are merely adsorbed onto the surface or interstice, on the contrary, no change of the lattice size will be observed. Therefore accurate determination of the lattice size is an appropriate way to determine the action of the surface active substances.

2-2-2. Experimental.

The lattice constants of pure ammonium nitrate and that of habit modified crystals were determined by x-ray diffraction method. Although the accurate determination is usually carried cut by powder photograph method, we made use of specrometric powder technique due to the next reasons: 1. We just needed to determine the difference of the lattice constants between pure and habit modified ammonium nitrate, not the absolute value of them. 2. The increase in accuracy using photographic method is not so large in comparison with effort and time needed, for there is no proper line in higher Bragg angle.

With the incre ase in Bragg angle θ, the measured value of interplaner spacing raises precision. It is readily explained by differentiating the Bragg equation with respect to θ:

$$2d \sin \theta = n\lambda,$$

$$2\Delta d/\Delta\theta \sin \theta + 2d \cos \theta = 0,$$

$$\Delta d/d = -\cot \theta \cdot \Delta\theta \quad \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

On the other hand with increasing angle the intensity of diffraction line is decreased, and diffraction measurement meets with a difficulty in practice. These points were taken into account and diffraction from, (002) (020), (102) planes were adopted. According to the Bragg equation higher angle diffraction can be attained by longer wavelength radiation concerning with the same spacing, therefore C_rK_α radiation, which is the longest x-ray commonly used, was adopted.

The samples of habit modified ammonium nitrate were crystallized from the mother liquor containing a surface active substance.

After being dried up the samples were prepared for x-ray analysis by grinding in an agate mortar and passing through a Tyler 325-mesh screen. The surface active substances selected for the test were laurylamine acetate, sodium dinaphthyl methane disulfonate, 1, 6-Cleve's acid→G acid, and Acid Magenta (C. I. 42685). The instrumental conditions were as follows.

Geiger-counter x-ray spectrometer "Geigerflex",

C_rK_α radiation : $\lambda=2.2909$Å,

Filament current : 8mA, Voltage : 30kV,

Slits : 2.5°–2.5°–0.4, Time const. : 4,

The experimental results are shown in Fig. 2.

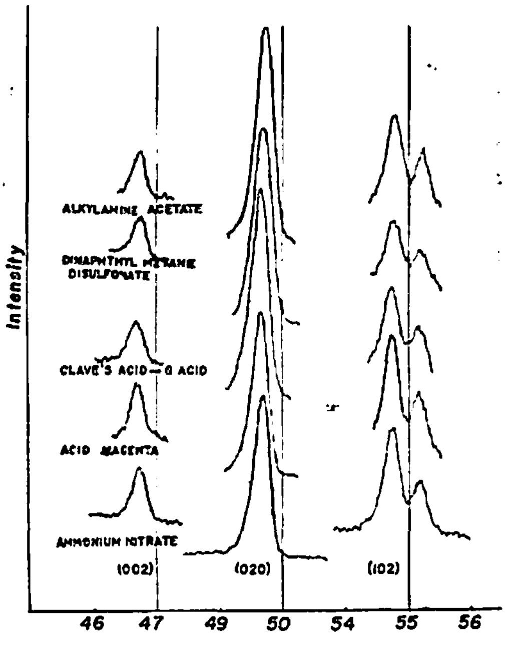

Fig. 2 X-ray diffraction angles of pure and habit modified ammonium nitrate crystals.

2–2–3. Discussion.

As it is shown in Fig. 2, the deviation of observed angles of modified ammonium nitrate from that of pure ammonium nitrate $\Delta(2\theta)$ is less than 3′. On the measurement the maximum error is probably caused by eccentricity of specimen, it means that the surface of specimen is displaced from the center of goniometer. from the simple geometrical consideration the error is expressed by the equation :

$$\Delta\theta=2u\cos\theta/R,$$

where $\Delta\theta$: error in Bragg angle,

u : displacement of the specimen,

R : dia. of the goniometer, 185cm.

From the experimental conditions we substitute $\theta=46°42'/2$, and $\Delta\theta=3'/2$, then we get $u=0.04$mm. Actually we cannot eliminate this magnitude of displacement, that is, in this measurement observed deviations $\Delta(2\theta)$ $<3'$ are not significant but experimental error.

In an orthorhombic lattice, interplaner spacing d is given by the equation :

$$1/d^2=(h/a_0)^2+(k/b_0)^2+(l/c_0)^2.$$

for (002) plane

$$d=c_0/2,$$

accordingly

$$\Delta d/d=\Delta c_0/c_0 \quad \cdots\cdots\cdots\cdots\cdots\cdots(2)$$

From the equation (1) and (2)

$$\Delta c_0/c_0=-\cot\theta\cdot\Delta\theta.$$

from the experimental conditions,

$$\theta=46°44'/2,\ \Delta\theta=3'/2=4.4\times10^{-4}\text{rad.},$$

and $c_0=5.745$Å,

it follows that

$$\Delta c_0/5.745\text{Å}=-\cot(46°44'/2)\times4.4\times10^{-4},$$

or $\Delta c_0 \doteqdot 0.006$Å.

For other axes similar results are obtained in the same way.

2–2–4. Conclusion.

No significant change was found in the lattice constants of the habit modified ammonium nitrate within the experimental error 0.006Å. It would appear therefore that the adsorption of the surface active substances did not affect interplaner spacing, and be able to assume that the surface active substance was adsorbed on the surfaces or interstices of the crystal.

2–3. Determination of the Axes of the Modified Crystal by Rotation Crystal Photography.

It was pointed out by C. D. West[1)] that recrystallization from water at room temperature gave (110) prisms. In our experiments most modified crystals held the habit extending parallel to the *c* axis.

A single crystal of modified habit, being considered typical one of that species of adsorbing substance was picked out of the mother liquor, dried up carefully and prepared for the test. Modified crystals were fibrous, needlelike, lathy or platy prolonged to a direction. The crystal was first oscillated around the direction and diffraction photograph was taken by copper K_α radiation using cylindrical camera. An example of such an oscillating crystal photograph is shown in Photo. 1. This is taken from a platy crystal, which is crystallized out of mother liquor containing sodium dinaphthylmethane disulfonate as an adsorbing substance, oscillating around the axis parallel to the longest direction.

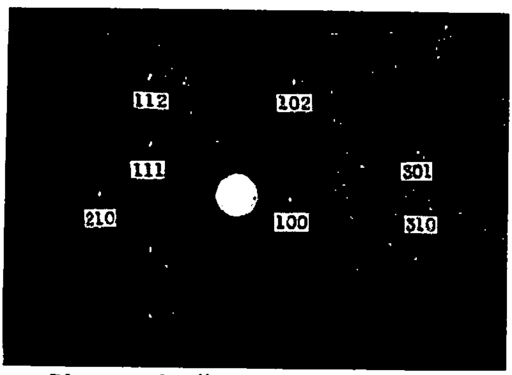

Photo 1 Oscillating Crystal photograph of a Habit Modified Ammonium Nitrate

From the distance between two layer lines in the photograph the period of the lattice construction parallel to the axis is calculated to be 0.75Å. Then the axis is supposed to be the *c* axis and positions of the diffracted points are calculated. The results are essentially in conformity with the positions of the spots in the photograph. In this way the axis is determined to be the *c* axis. In case of platy crystal another oscillating photograph is taken around the other axis perpendicular to the *c* axis and in the plane, and then the axis is determined to be the a axis. The developed face of the platy crystal must be (010) accordingly.

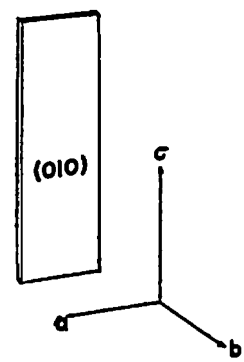

Fig. 3 Direction of the axes of platy crystal, sodium dinaphthylmethane disulfonate adsorbing cryatal

3. Optical Properties of the Habit Modified Ammonium Nitrate.

The habit modifications are classified into two groups, one is platy or lathy and the other is needlelike or fibrous. For the former group, about a hundred of surface active substances which give platy crystals have been discovered, and without exception all of them are (010) habit modifiers. Fortunately this face is quite easily detected by optical method and this fact facilitates the investigation.

3–1. Optical Properties of Ammonium Nitrate IV.

Optical properties of ammonium nitrate IV are asfollows.

biaxial negative,
optical axial plane (100),
acute bisectrix *b*,
optical axial angle $2V=35°$,
refractive indices, electric vector parallel to *b*, $\alpha=1.413$,

to a, $\beta=1.611$,
to c, $\gamma=1.637$,

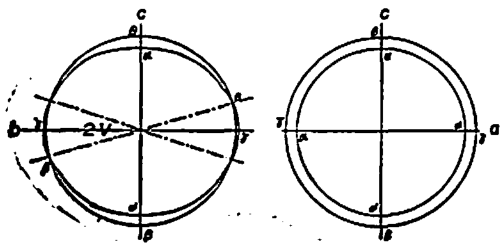

Fig. 4 Optical indices

Ammonium nitrate IV has NO_3 triangles arranged parallel to (010) plane. When electric vector of a ray is in the plane, polarization of NO_3 is far greater than the case when the electic vector is perpendicular to the plane. Therefore two refractive indices in the NO_3 triangle plane are greater than the perpendicular one. This is illustrated in Fig. 5.

3–2. Determination of the Axes by Conoscope.

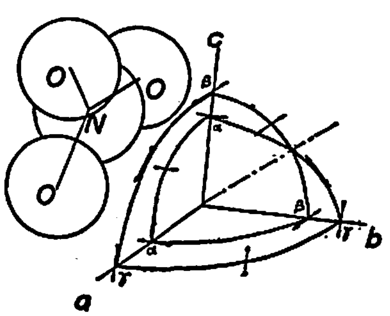

Fig. 5 Orientation of the NO_3 ion triangle and refractive indices.

Watching the platy modified crystal having (010) habit, placed on a microscope slide flatwise, through conoscope using an objective of numerical aperture of 0.65, we see two melatopes in the interference figure. In other words, when we see the melatopes, the face in question is determined to be (010). As we can recognise from Fig. 4 the direction passing two melatopes is the c axis and the other one which is perpendicular to the c axis and in the plane is the a axis.

All kinds of platy modified crystals having crystalized on a microscope slide showed clear interference figures and melatopes when the concentration of surface active substances was more than a critical concentration, then it was certified that the crystals had (010) habit.

Summary

Habit modified ammonium nitrate crystals were studied crystallographically, which were crystallized out of the mother liquor containing certain surface active substances being adsorbed on the growing surfaces of the crystal. X-ray analysis showed that the change in appearance of tho crystal had no relation to the inner structure, that is, the change was modification of the crystal habit. The adsorption of the surface active substances had no effect on the lattice size of ammonium nitrate crystals. Oscillating crystal photography and conoscopic observations showed that all the platy modified crystals had (010) habit.

Acknowledgement

We wish to express our thanks to Dr. K. Hino, Chief, Explosives Research Section of the Nippon Kayaku Co. Ltd. for suggestions rendered during the course of this work, and to Mr. M. Sasaki, Faculty of Engineering, University of Tokyo and to Mr. E. Asada, Tokyo Kogyoshikensho for giving instructions and help in x-ray analysis.

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硝酸アンモンの結晶癖変化に関する研究
(第一報) 結晶学的研究

土屋能男・山本祐徳

界面活性物質の吸着により硝酸アンモン結晶の外形が変化する現象—晶癖変化—及びその工業爆薬への応用について研究を行つた。本報では先ず変化結晶の結晶学的性質について報告する。

界面活性物質を含む母液から晶出させた各種の変化結晶の結晶構造は純粋な硝安結晶と同一であることがX線回折により確かめられた。又稍々精密な格子定数の測定により各種変化結晶は実験誤差 0.006Å 以上の格子定数の変化は認められなかつた。これは吸着が結晶表面にのみ行なわれることを示す。次に変化結晶の結晶方位を振動結晶写真法及び光学的方法により決定した。変化結晶は二群に大別され一つは針状或は繊維状であり他は板状であるが，後者は例外なく (010) 面が発達している。(010)は光学的に容易に検出し得る。

ニュース

試料の爆発を逆に利用する簡単で早い有機微量元素分析装置

日本曹達の小田仲彬研究部長は，今迄最もタブーとされていた，試料の爆発を逆に利用する簡単で速度の早い有機微量元素分析装置を完成，すでに同社工場の分析工程に用いている。

従来の有機微量分析法は特殊技術を要したが，小田部長は，全く別の観点から特殊技術を必要としない分析法を確立することに着目，まず炭水素分析について研究し爆発を利用する分析装置の発明に成功したものである。

同社によると，この装置では試料の特性，例えば爆発性や揮発性の如何を問わず，あらゆる試料の燃焼形式を一元化し，焼却に特殊技術を要する操作を全く必要としないうえ，試料の焼却は著しく迅速化されるという。つまり試料は常時加熱されている試料焼却部へ投入すると，数秒を出ずに爆発的に燃焼し，投入してから10秒後には既に主な焼却は完了する。

この方法による分析所要時間は，試料焼却5分以内，吸収管のはかり量15分，計20分以内であり，分析の精度と正確度はあらゆる試料に対して従来法と同等であるという。(技術ジャーナル 36—2—17)

爆発寸前に消炎剤を使用して災害防止——

日本油脂と松尾鉱業は共同研究で，炭鉱坑内や硫黄鉱坑内において起り易いところの発破時の衝撃や燃焼による二次的ガス爆発や粉じん爆発を防止するすぐれた方法を完成した。これらの災害を防止する方法として水タンピング法，水充てん法，爆薬に安全被筒を用いる方法が行われて来たが，手数，経費，爆薬の爆発効果の減退等の面から見て難点がある。これに対して此の方法は，主薬包の爆発寸前に水か，消炎効果のある塩類の水溶液，又は溶液状の不燃性ガス発生体，もしくは前記塩類不燃性ガス発生体の1種または2種以上の含水ゲルを，爆発力により分散し穿孔内に充満させて発破時の災害を防止するものである。この含水ゲルはポリエチレン，ビニール系樹脂その他合成樹脂膜や可燃性包装材料につつむか，ゴムスポンジ，多ほう性合成樹脂，海綿，コルクなどの吸水性材料に吸収させる。消炎効果のある塩類としては食塩，塩化カリ，ほう砂，ほう酸ソーダ，しゆう酸アンモニウムなど，また不燃性ガス発生体としては重炭酸ソーダ，炭酸ソーダ，炭酸カリなどがあげられている。(技術ジャーナル，80号，36—4—7，抄録)