

系と同質の過程の上に、更に混合系特有な過程が重ねられたものである。その特有な過程は $kD^{n_{es}}$ なる項によつて示される。この項を具体的に説明し得るモデルは、固体燃焼面における粒子の表面積あるいは体積に関係したものではない。

終りに、本実験について終始御指導を仰いだ東京大学疋田教授、並びに本校野村教授に厚く感謝する。

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Studies of Combustion of Composite Propellants IV Effects of Particle-size of Ammonium Perchlorate and of Oxidant-fuel Ratio on Burning Rate

Takeshi Ito

It was stated in a previous paper that an effect of particle-size of ammonium perchlorate on burning rate might be manifested when the perchlorate with a uniform particle-size was used. In this study the following examinations were performed: (1) Quartile deviation (Q_n) and Kramer's modulus (K) were calculated from cumulative curves of size-distribution. (2) Correlation between mean volume-surface diameter (D_{es}) and mass burning rate (\dot{m}) was examined. (3) Correlation between weight percent of the perchlorate and the rate was examined.

The results of examination (1) were summarized in Table 1. Adequate samples of the perchlorate powder (A, B, C, D, E and G) were selected among those of Table 1. The results of examinations (2) and (3) were shown in Fig. 3 and Fig. 5 respectively. The mass burning rate increased as the particle-size decreased (Fig. 3). The effect of the oxidant-fuel ratio on the burning rate may be independent on the partic-

le-size. (The curves of D, E and G in Fig. 5 were approximately parallel in a range from 65% to 80% of the perchlorate.) The curves in Fig. 3 were well represented by the following equation (Fig. 4).

$$\dot{m} = \dot{m}_0 - kD^{n_{es}}$$

Here \dot{m}_0 , k and n are constants for the ratio. These constants obtained are shown in Table 2.

As is shown in Table 2 the value of n varies with the ratio. Values similar to those of Table 2 could not be obtained from total surface area or total volume of the particles and of the binder at a burning surface. The fact is that the factors affecting reaction area at the burning surface may not be largely responsible for the burning characteristics of composite propellant. For the moment it can only be said that a manner of mixing of oxidizer and fuel gas-streams to form a flame reaction zone will play an important role in the burning process and will offer a possible explanation for the term of $kD^{n_{es}}$. (Defense Academy)

Study on the Crystal Habit Modification of Ammonium Nitrate.

II. Habit Modifiers, General Discussions and Alkylamines.

Yoshio N. Tsuchiya

Crystal habit of ammonium nitrate is modified by the adsorption of certain foreign substances. An interesting application of the modified crystals to industrial explosives is ammonium nitrate-fuel oil explosives. The modified crystal shows high explosive sensitivity when mixed with fuel oil, besides having low caking tendency.

In the previous paper¹⁾, the habit modified ammonium nitrate crystals were examined crystallographically. In the present, habit modifiers especially alkylamines are treated and the mechanism of the habit modification is discussed.

4. Habit Modifiers, General.

Habit modification of ammonium nitrate was treated in the work of R. Hocart et al²⁾, which dealt with the oriented overgrowths on mica, and in the works of J. Whetstone et al³⁾, in which sulfonated dyes were only the habit modifier discussed. In our work habit modifiers are found out from many organic substances. They are dyestuffs, dye-intermediates, surface active agents and other organic reagents.

4-1. Crystallization Test.

The habit modifiers were found out as follows. A saturated aqua solution of amm-

onium nitrate at 32°C was taken in a small test tube and a small amount of a habit modifier sample was added. This test tube was immersed in a bath and cooled through the night to about 10° or 15°C. During the process ammonium nitrate was crystallized gradually. We payed attention to keep seed crystals in the solution to prevent much supersaturation which would cause fluctuated results. The resulted crystals were compared with pure ammonium nitrate crystals having obtained from blank tests and habit modifying effect of the sample was determined.

About two thousand of samples were tested in this way and about two hundred were found to have some effect. Crystallographical orientation of these crystals were determined by microscopic obserbations. Photographs of the modified ammonium nitrate crystals, are shown in fig. 1.

Types of habit modification are roughly classified into two groups. One includes fibrous and dendritic crystals elongated along the C axis, the other, (010) platy or tabular ones. As we related in the previous report, all the platy or tabular ones were (010) habit. Typical ones of these habit modifiers are shown in the following tables.

Table 1. Crystal habit modifying substances, first group.

Class	Name	Formula	Effect	Critical conc*.
Cationic surfactant	Laurylamine acetate	$C_{12}H_{25}NH_2 \cdot CH_3COOH$	fibrous	0.001
Anionic surfactant	Sodium lauryl-sulfate	$C_{12}H_{25}OSO_2Na$	dendritic	0.005
do.	Sodium dodecyl-benzene sulfonate	$C_{12}H_{25} \begin{array}{c} \diagup \\ \diagdown \end{array} SO_2Na$	dendritic	0.01

*The minimum effective concentration, more than which habit modification is observed in a certain condition, indicated in weight per cent of mother liquor.

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* Research Section, Asa Factory, Nippon Kayaku Co. Ltd., Yamaguchi Prefecture.

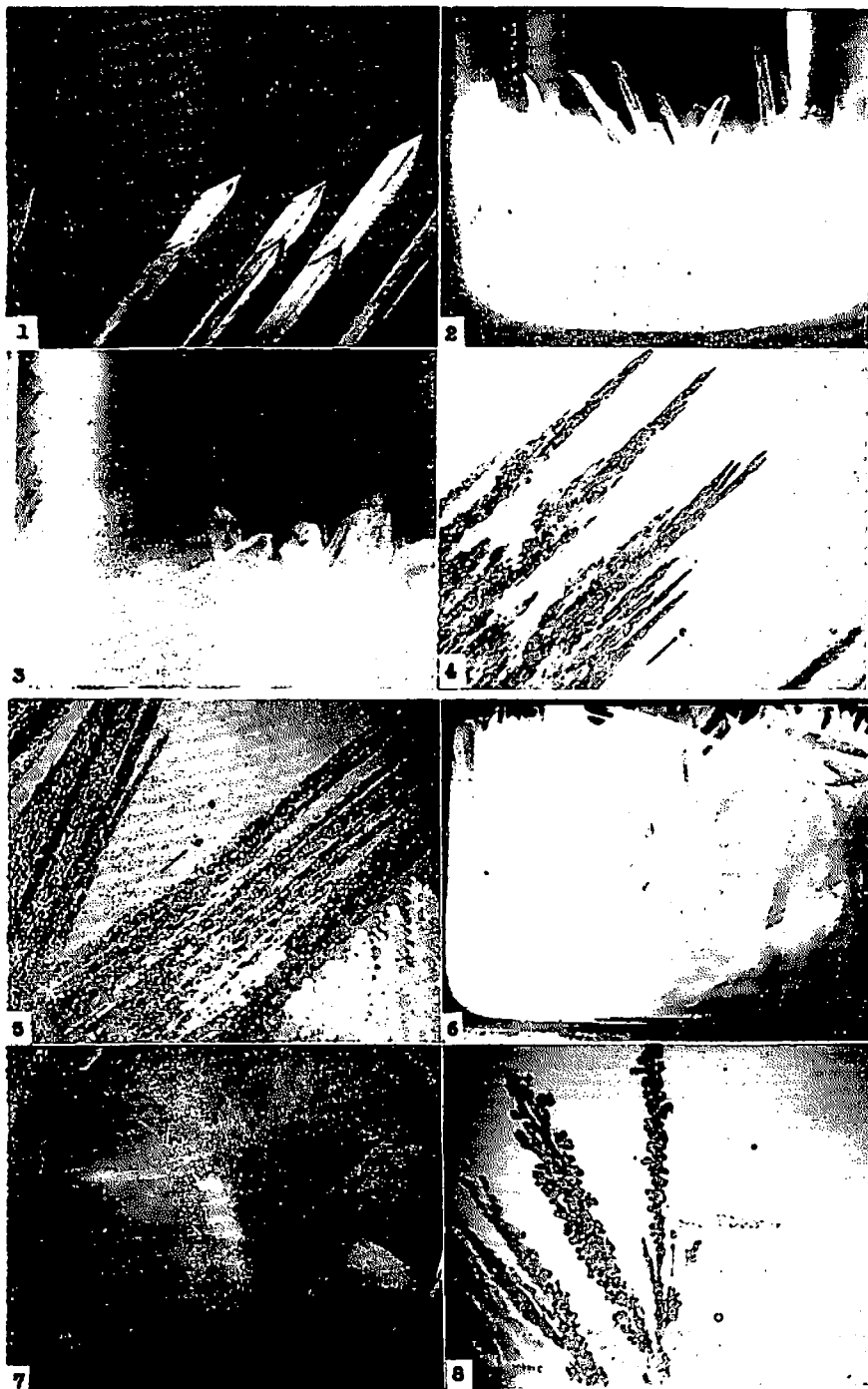
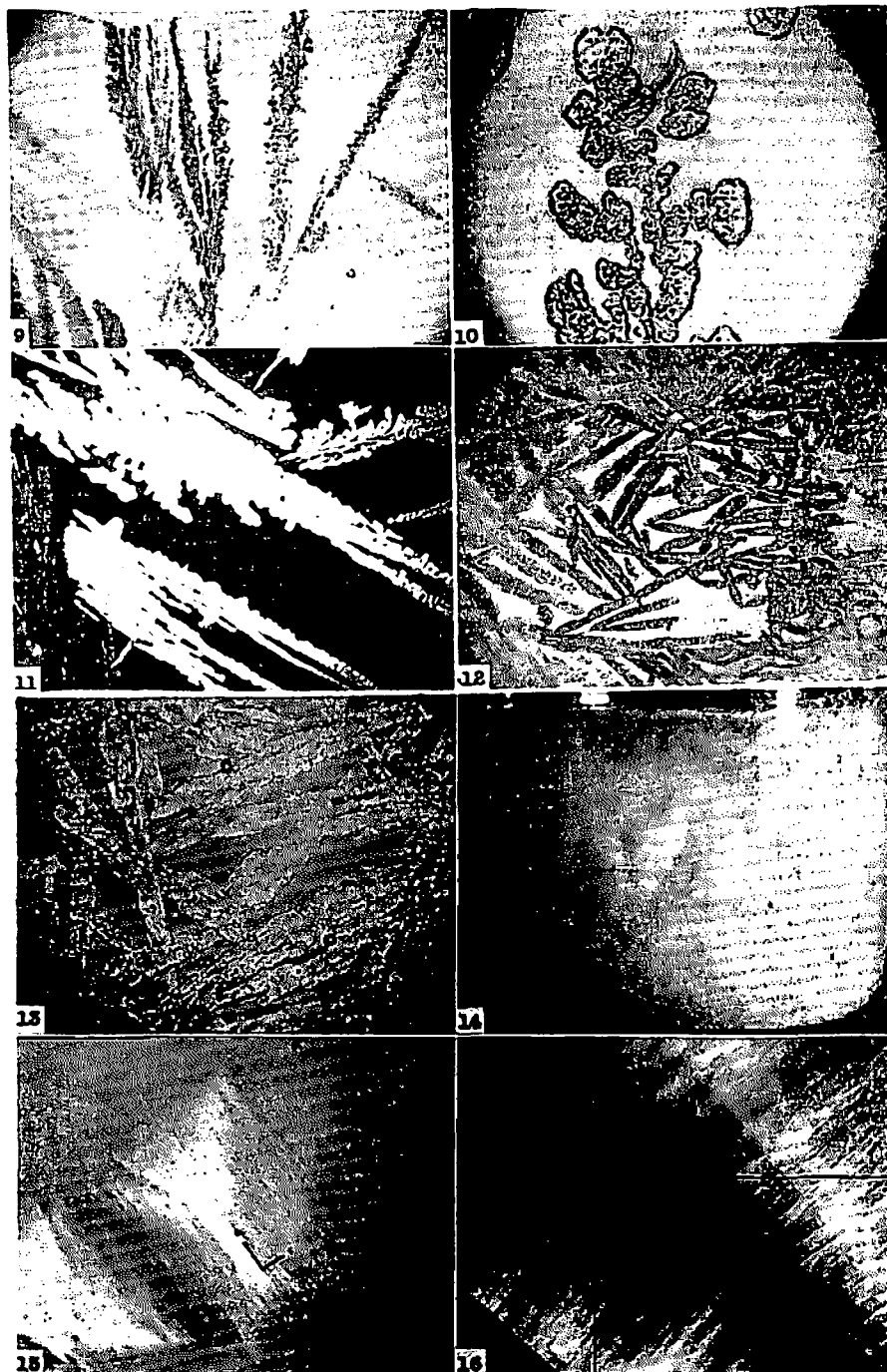
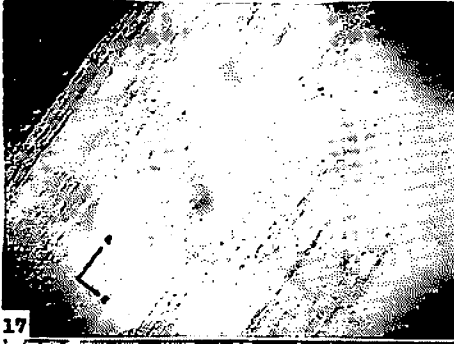


Fig. 1 Photographs of modified ammonium nitrate crystals.

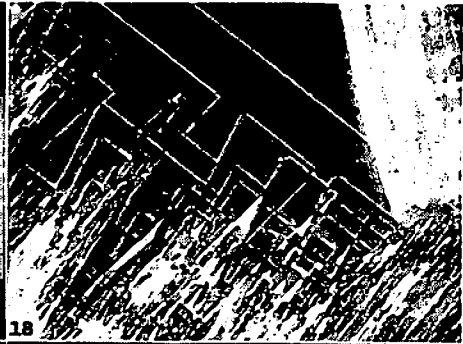
1. Standard (010) prisms, crystallized from water on a microscope slide, rate of crystal growth along the c axis is 0.03 mm/sec, objective $\times 10$.
2. Do., growth in a beaker, growth rate 3cm/10hr.
3. Do., growth rate 1cm/10hr.
4. Laurylamine acetate adsorbed, growth rate 0.07mm sec, objective $\times 10$.
5. Do., objective $\times 40$.
6. Do., in a beaker.
7. Do.
8. Sodium lauryl sulfate adsorbed, dendrite, objective $\times 10$.



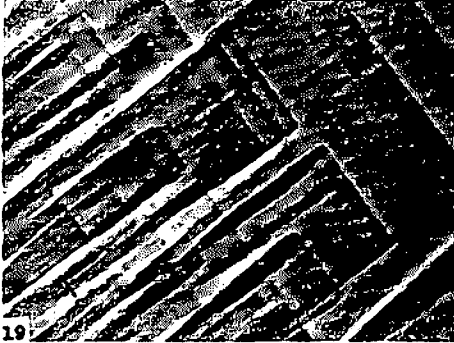
9. Do.
 10. Do., objective $\times 40$.
 11. Do., crossed nicol, each part of the dendrite has the same orientation.
 12. Sodium dodecylbenzene sulfonate adsorbed.
 13. Do., objective $\times 40$.
 14. Do., in a beaker.
 15. Sodium dinaphthyl methane disulfonate adsorbed (010) plate, so thin that it cannot be seen clearly.
 16. Do., conc. of the modifier in mother liq. is about 1%, crossed nicol.



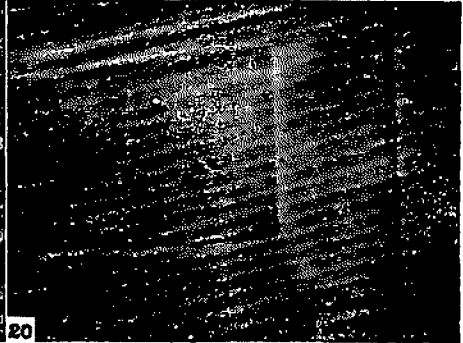
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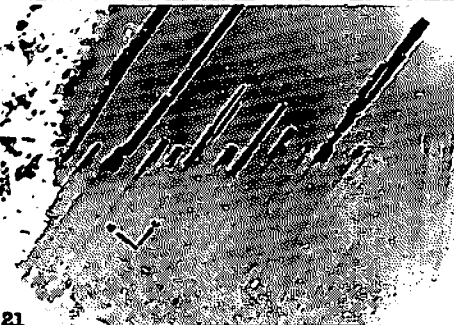
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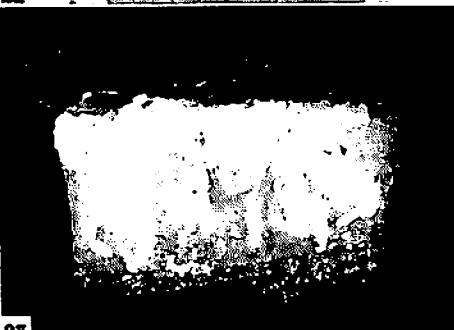
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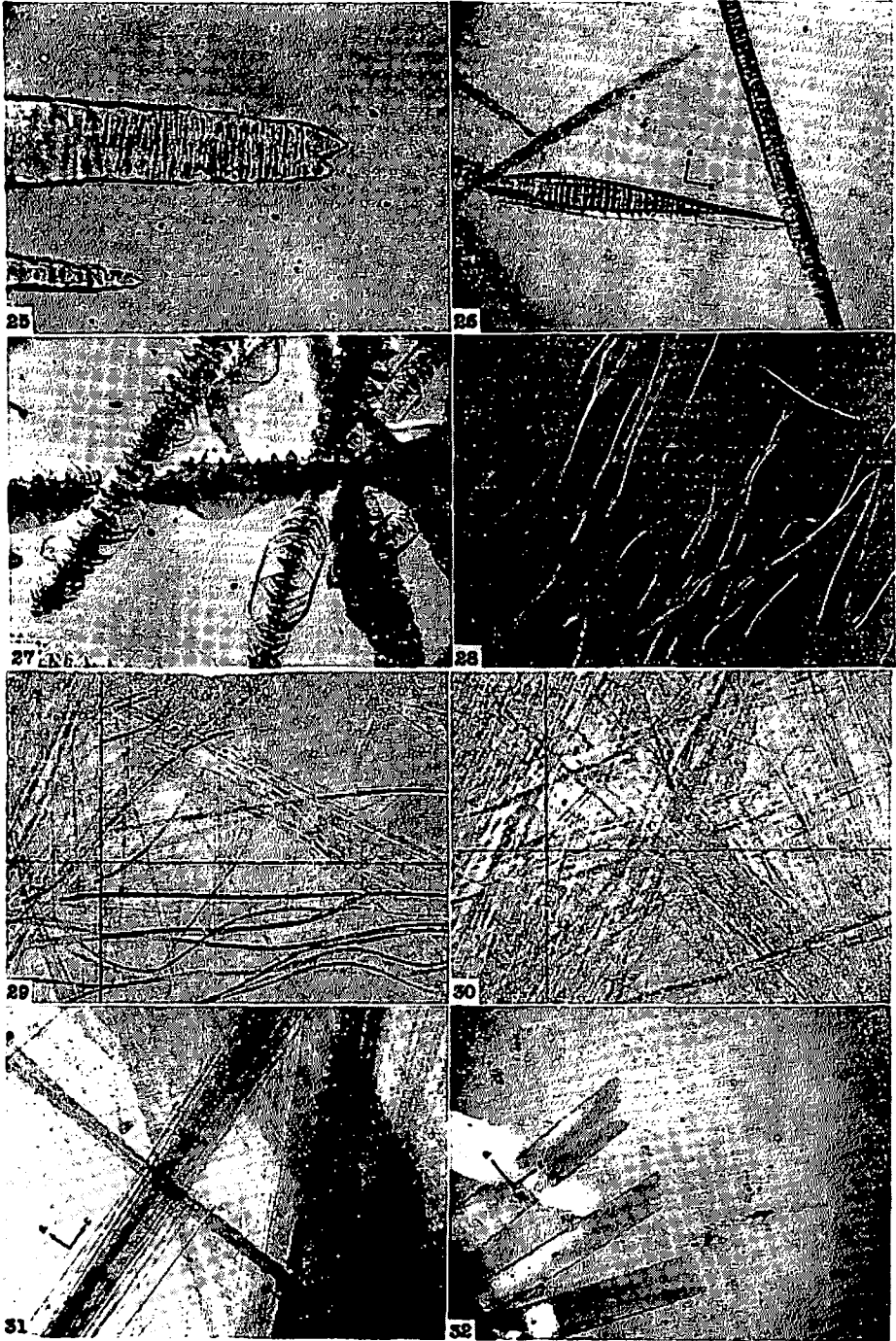
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- 17. Do., conc. of the modifier in mother liq. is about 5%.
- 18. Do., phase contrast microscope dark-high, layer formation is clear.
- 19. Do.

- 20. Do. objective $\times 40$.
- 21. A habit change, (010) to (110).
- 22. Do., in a beaker.
- 23. Do.
- 24. Acid Magenta adsorbed (010) plate.



25. Do.

26. Do., (010) and (110).

27. Do.

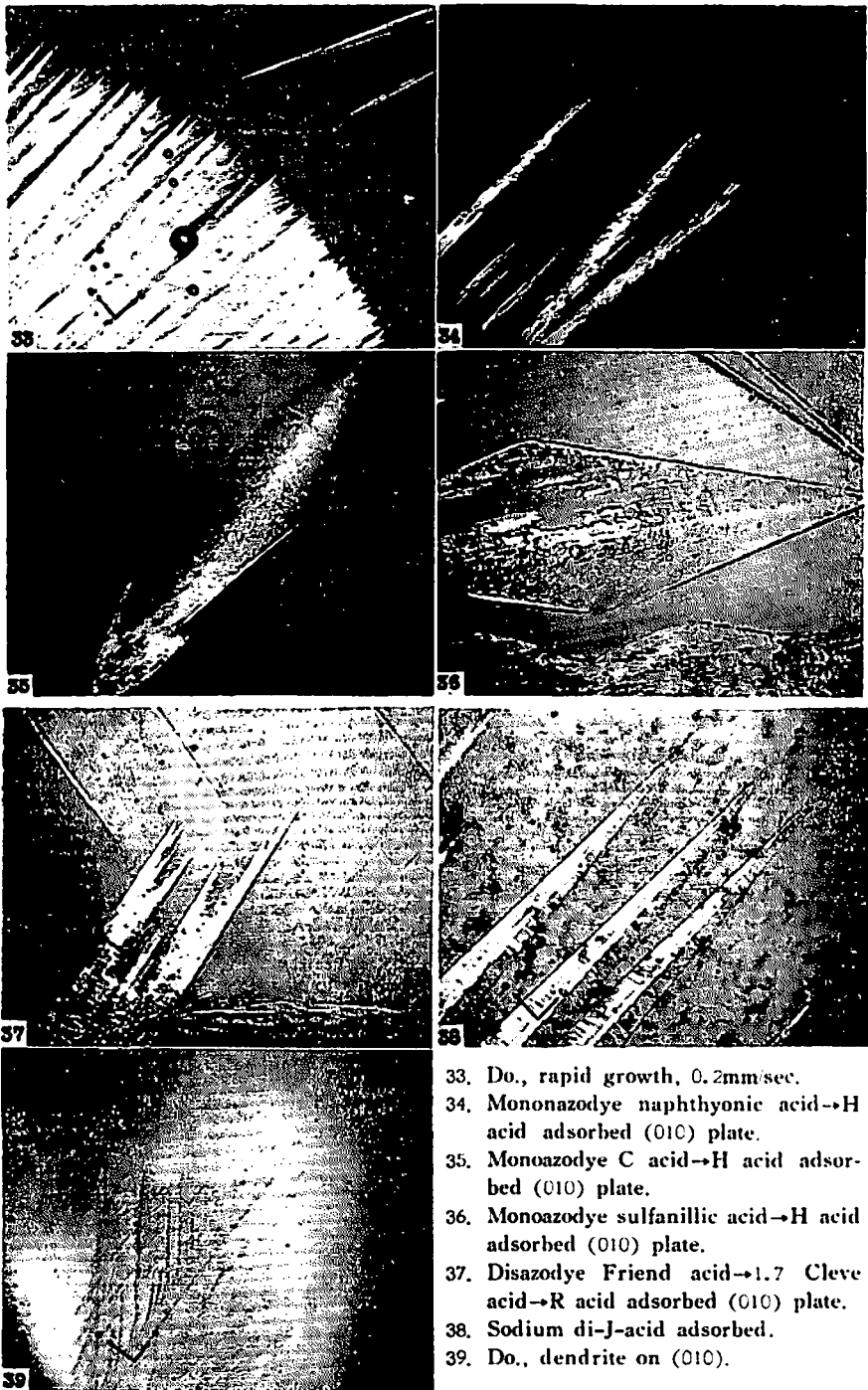
28. Monoazodye Amaranth adsorbed strap-shaped-crystals, crossed nicol.

29. Do.

30. Do., needles.

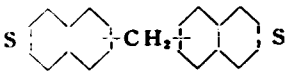
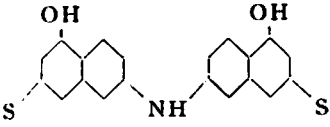
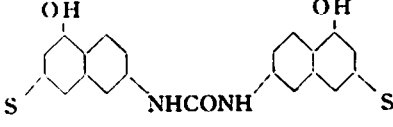
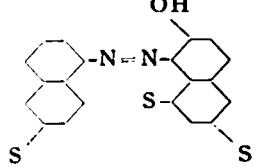
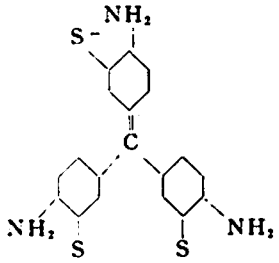
31. The needles make (010) lath.

32. Monoazodye 1.6 Cleve acid→G acid adsorbed (010) plate.



33. Do., rapid growth, 0.2mm/sec.
 34. Mononazodye naphthyonic acid→H acid adsorbed (010) plate.
 35. Monoazodye C acid→H acid adsorbed (010) plate.
 36. Monoazodye sulfanillic acid→H acid adsorbed (010) plate.
 37. Disazodye Friend acid→1.7 Cleve acid→R acid adsorbed (010) plate.
 38. Sodium di-J-acid adsorbed.
 39. Do., dendrite on (010).

Table 2. Crystal habit modifying substances, second group.

Class	Name	Formula**	Effect	Critical conc.
Alkyamine	n-Hexylamine	$C_6H_{13}NH_2$	lathy or platy (010)	2
Anionic surfactant	Sodium dinaphthyl-methane difulfonate		lathy or platy (010)	0.01
Dye-intermediate	Sodium di-J-acid		lathy (010)	
do	Sodium carbonyl-J-acid		lathy (010)	
Monoazo-dyes	Sodium 1,6-Cleve acid →G acid		fibrous or platy (010)	0.005
Triphenyl-methane dyes	Acid magenta		lathy or platy (010)	0.005

** S · SO₃Na

4-2. Discussion.

As it is shown in the tables habit modifying substances are primary alkylamines, alkylsulfates, alkylarylsulfonates and aromatic sulfonates. Their active groups are only the sulfonate, sulfate and primary amine, though they are found out from many organic substances. The fact that these active groups have a certain similarity in the shape and size to nitrate ion and ammonium ion which are constituents of ammonium nitrate crystals, reminds us the mechanism of the adsorption of dye ions by growing alum crystals proposed by W. G. France⁴⁾, that is: "The foreign ion or molecule may actually replace an ion in the crystal lattice, especially if there is an identity or close

similarity in the size and shape of an active group in the foreign ion with that of the ion it replaces."

Modifiers of the first group are nearly linear molecules having one active group on a terminal, whereas the second group are rather flat molecules having more than two active groups. As to the latter, which give (010) habit crystals, position of the active groups has quite specific effect on the habit modification, slight difference of it sometimes makes the modifying power invalid.

Though they are classified surface active agents, dye-intermediates or dyes, the habit modifying effect seems to have no connection with their original functions but to have with their molecular structures.

Habit modification with foreign substance like dyes comes from change of relative grow rate of the crystal faces caused by adsorption of the substance. The substance adsorbed on the surface of the crystal may exercise different effects, and the adsorbed face and developed face are not always the same. Such a circumstance is explained as follows. If the substance adsorbed strongly and in high surface concentration it may prevent further growth of the crystal. When the adsorption takes place on certain surfaces, they develop. In this case the foreign substance exists on the surface of the deve-

loped faces. If the surface concentration is not so high as to prevent later growth, or the substance is weakly adsorbed and it is easily expelled from the newly formed layer, it may leave distortion, dislocation or kink spot on the host crystal. Then these disorder may act as active spots from which crystal growth starts. In this case adsorbed faces grow rapidly and in consequence the edge plane developed, i. e. the adsorbed face and developed face are different. Adsorption of dye is concerned adsorbed face is tinted with the dye, then these circumstances are obvious.

Table 3. Crystal habit modifying effect of alkylamines.

Name	Formula	Effect	Critical conc.
methylamine	CH_3NH_2	no	
ethylamine	$\text{C}_2\text{H}_5\text{NH}_2$	no	
i-propylamine	$\text{C}_3\text{H}_7\text{NH}_2$	no	
n-butylamine	$\text{C}_4\text{H}_9\text{NH}_2$	no	
i-butylamine	$\text{C}_4\text{H}_9\text{NH}_2$	no	
i-amylamine	$\text{C}_5\text{H}_{11}\text{NH}_2$	no	
n-hexylamine	$\text{C}_6\text{H}_{13}\text{NH}_2$	lathy (010)	2
laurylamine	$\text{C}_{12}\text{H}_{25}\text{NH}_2$	fibrous	0.001
stearylamine	$\text{C}_{18}\text{H}_{37}\text{NH}_2$	fibrous	0.001
benzylamine	$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$	no	
diethylamine	$(\text{C}_2\text{H}_5)_2\text{NH}$	no	
dimethyl laurylamine	$\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_2$	no	
dimethyl stearylamine	$\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_2$	no	
lauryl trimethyl ammonium chloride	$[\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3]\cdot\text{Cl}$	no	
stearyl trimethyl ammonium chloride	$[\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3]\cdot\text{Cl}$	no	

5. Habit Modifiers.

5-1. Alkylamines.

Alkylamines are one of the most effective habit modifiers. Some of them shows critical effective concentration of habit modification as low as 0.001%. As it is shown later the alkylamine modified crystal has the best quality for AN-FO. Acetic salts of alkylamines having carbon number of 10~20 have been patented as anticaking agents for ammonium nitrate.⁵⁾ The mechanism of it is explained as a lowering in the surface tension of ammonium nitrate solution

and formation of oily surface films on the crystal.⁶⁾ The former is irrational from the reason that there are many surface active agents which depress the surface tension of the solution but few is effective for the prevention of the caking. It may be due to the formation of oily surface films by adsorption of alkylamine onto the surface of the crystal. Anticaking tendency of the modified ammonium nitrate crystal will be discussed later.

5-1-1. Alkylamines Tested.

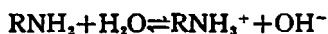
Habit modifying effect of various alkyl-

amines are tested as beforementioned. The results are shown in table 3. It is shown that primary alkylamines having more than 6 carbons are effective. As to secondary amines we can not say for certain owing to the small number of examples, they seem to be ineffective. Tertiary amines and quaternary ammonium salts are ineffective. Acetates of amines show the same behavior as original amines.

5-1-2. Properties of Alkylamines.

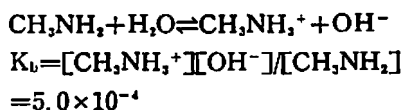
For discussing the mechanism of adsorption of alkylamines we have to know the properties of the substance. Alkylamines and ammonia are considered to be intimately related chemical compounds. Their molecular structure is verified to be a pyramid having a nitrogen atom for its apex by electron diffraction, dipolemomentum and x-ray diffraction of the crystal.

Aliphatic amines are stronger base than ammonia, and they dissociate according to the equation.



Dissociation constants are,

methylamine



n-propylamine

$$K_b = 4.7 \times 10^{-4}$$

i-propylamine

$$K_b = 5.3 \times 10^{-4}$$

n-butylamine

$$K_b = 4.1 \times 10^{-4}$$

i-butylamine

$$K_b = 3.1 \times 10^{-4}$$

n-amylamine

$$K_b = 4.4 \times 10^{-4}$$

i-amylamine

$$K_b = 5.0 \times 10^{-4}$$

cf. $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

$$K_b = 1.75 \times 10^{-5}$$

It is proved that the N atom of ammonium ion and quaternary ammonium salt takes tetrahedron structure which corresponds to the C atom of methane molecule. Dissociated amine salt is possible to take the same structure. Schematic models of the ions

are illustrated in Fig. 2 in which size of the atoms is expressed by van der waals diameter.

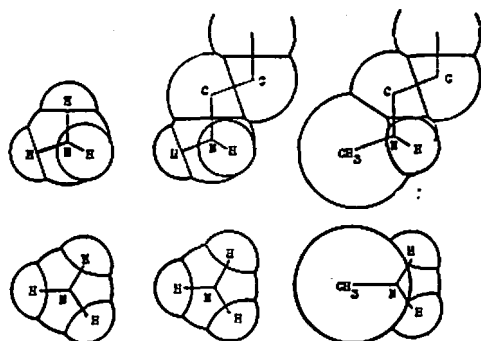


Fig. 2 Schematic Models of Amines and Ammonium Ion.

(a) ammonium ion (b) ionized primary amine (c) ionized secondary amine

5-1-3. Discussion

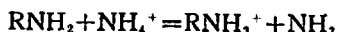
Habit modification with alkylamines seems to be caused by adsorption of ionized amines. Ammonium ion and ionized amine have the same unit charge, and have the same structure and dimensions on a certain direction. Therefore the ionized amine can be adsorbed electrostatically in place of ammonium ion. This idea is supported by the fact that the quaternary ammonium salts, tertiary amines and secondary amines do not show any effect. Their structures are similar to that of primary amine, but hydrogen atoms of latter are replaced by an alkyl group or groups. As a result of that their structures become so big that they cannot replace the ammonium ion.

Soluble salts of alkylamine, e. g. salt of acetic acid dissociate according to the equation:



and resulted ionized amine RNH_3^+ acts as a habit modifier. In the case of free alkylamine it removes a proton from an ammonium ion which exists much in the solution of ammonium nitrate, as it is a stronger base than ammonia, and almost all of alkyl-

amine molecules are ionized* according to the equation:



Thus the free amine and salts of amine act in the same way.

Summary

Habit modifiers for ammonium nitrate have been found out from many organic substances. They are classified into two groups. The first ones are nearly linear molecules having one active group on a terminal, and they give fibrous or dendritic crystals elongated along the c axis. The second ones are rather flat molecules having more than two active groups, and they give (010) plate or lath. These modifiers are adsorbed on the growing surfaces of ammonium nitrate crystals. Then the relative grow rate of the crystal faces are effected and the habit is modified. Effective groups for adsorption are alkylamine, sulfate and sulfonate. These active groups have a certain similarity in the shape and size to nitrate ion or ammonium ion which are constituents of ammonium nitrate, and are possible to replac one of the constituents.

* Dissociation of alkylamine in ammonium soln. is shown as follows. Dissociation constant of alkylamine is:

$$K_1 = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]} = 6 \times 10^{-4}$$

and that of ammonia is:

$$K_2 = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 2 \times 10^{-5}$$

combining these

$$[\text{OH}^-] = K_1 \frac{[\text{RNH}_2]}{[\text{RNH}_3^+]} = K_2 \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \dots (1)$$

The habit modifying effect of alkylamines have been discussed. Primary alkylamines having hydrocarbon chaine of more than 6 carbons are effective. The adsorption is effected by ionized amine group. In the ammonium nitrate aqua solution free amine and soluble acid salt of it act in the same way.

Acknowledgement

I wish to express my thanks to Professor S. Yamamoto of Tokyo University and Dr. K. Hino, Chief, Explosives Research Section, Nippon Kayaku Co. Ltd. for suggesting this investigation as well as for constant guidance in the course of the work.

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Let the concentration of alkylamine added be C_1 mol/l, that of ammonia C_2 mol/l and dissociation of amine x , then,

$$[\text{RNH}_2] = C_1(1-x), [\text{RNH}_3^+] = C_1x, [\text{NH}_3]$$

$$= C_2x, [\text{NH}_4^+] = C_2 - C_1x,$$

substituting these, equation (1) is written

$$K_1 \cdot C_1(1-x)/C_1x = K_2 \cdot C_2x/(C_2 - C_1x)$$

In a practical condition $C_1 \approx 10^{-2}$, $C_2 \approx 10$, then we get $x \approx 1$.

硝安の結晶癖変化に関する研究

(第二報) 晶癖変化性物質概観及アルキルアミン類

土屋能男

硝安の晶癖を変化させる物質を多くの有機化合物中より見出した。これは二種に大別することができる。第一は一端に一個の官能基を有する線状分子で繊維状晶又は樹枝状晶を与え。第二は二個以上の官能基を有する平面状分子で(010)板状晶を与える。これらの作用は生長しつつある結晶の表面に対する吸着であつて、それにより結晶面の相対的の生長速度が影響を受け晶癖が変化する。吸着に関与する基はアルキルアミン、サルフェート、スルフォネートであり、これらは

硝安を構成するアンモニウムイオン、硝酸イオンのいづれかと構造上の類似性を有し、それらに置き代つた形で静電的に吸着すると思われる。

次に各種のアルキルアミンの晶癖効果を検討した。効果を有するものは第一級アルキルアミンで炭素数6以上の炭化水素鎖を有するものである。吸着は解離アミンによるのであつて遊離アミンも、塩もその作用機構は同一と考えられ、実験では全く同一の結果を示した。