einigen davon waren zwar schon bekannt, aber in geometrischen Bezieungen sehen sie noch nicht ganz rein aus.

Vier Isomere von *n*-Hexin-1-olen, die Ausgangsmaterialien für die Darstellung der *trans*- oder *cis*-Hexen-1-olen wurden in jeden Fällen von Acetylen aus über Acetylennatrium in flüssigem Ammoniak synthesiert. Besonders war diese Darstellungsmethode von 4- und 5-Hexin-1-ol in der Ausbeute bedeutend überlegen als die bisherige. 2-, 3- und 4-*trans*-Hexen-1-ol und 5-Hexen-1-ol wurden durch die 1 Mol. Hydrierung der entsprechenden *n*-Hexin-1-olen mit Natrium in flüssigem Ammoniak gewonnen, während 2-, 3- und 4-*cis*-Hexen-1-ol durch die 1 Mol. Hydrierung in Gegenwart von Palladium-Bariumsulfat bei −15° geliefert wurden. Diese Alkohole wurden über 3,5-Dinitrobenzoat gereinigt. Die Infrarotspektren von diesen Verbindungen gaben die verschiedenen interessanten Probleme.

The Chemical and Physical Properties of Talcs and Their Behavior on the Decompositon of EPN Dust Formulation. Chemical Studies on Organophosphorus Insecticides. VIII.
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Received July 30, 1959. *Botyu-Kagaku* 24, 156, 1959.

30. タルクの物理化学的性質が EPN 粉剤の経時変化に及ぼす影響 有機燐殺虫剤の化学的研究 第8報

佐藤六郎・久保博司（農林省農薬検査所）34. 7. 30 受理

前報で methyl parathion 粉剤の経時変化とその機構を検討したが，本報では更に，前報と同一の天然タルクを用いて EPN 粉剤を調製し，タルクの物理化学的性質と EPN 成分の分解との相関性を検討した．タルクの水分吸着能，塩基置換容量及び全塩基性は EPN の分解と深い関係を持つことが確認された．EPN の分解機構は methyl parathion の場合と同様，タルクの物理的吸着活性点の量とその塩基性に基因するものと推測される．

This report is an extension of our research for the degradation mechanism of organophosphorus insecticides in dust formulation. The relationship between the chemical and physical properties of talcs and the rate of decomposition of EPN in talcum dust have been investigated. The amounts of moisture sorbed, base exchange capacity and total basicity of talc had highly significant relation to the decomposition of the active ingredient. The degradation of EPN would proceed essentially by the same way as that of methyl parathion. The possible two dominant factors would be the amounts of electronegative active site and its chemical basicity.

In the previous paper[1] the relationship between chemical and physical properties of talcs and the rate of decomposition of the active ingredient of methyl parathion dust formulation had been investigated. The most reasonable mechanism for the storage decomposition of methyl parathion dust would involve a nucleophilic attack on the phosphorus atom by the base distributed over the negatively charged parts of cilica-magnesium complex. The present study was undertaken, furthermore, to determine whether similar evidence could be obtained in the case of EPN talcum dust.

Materials

We selected nineteen sorts of talcs out of the same sample that were used for the previous paper. The chemical and physical properties of these talcs were given in Table 1. The 1.5% EPN dusts were prepared by mixing these talcs with pure EPN in a porcelain bowl. The dust products were stored in a thermostat at 50°C. They were analyzed for active ingredient by measuring the amounts of liberated *p*-nitrophenol colorimetrically at 400mμ using Beckman DU type spectrophotometer. The rate of decomposition of the active ingredient was also

Table 1. Talcs, their chemical and physical physical properties and the rate of decomposition of 1.5% EPN in talcum dust

Code	Particle size (mesh)	Minig place	Producer	H_2O sorbed %	Base ex. cap me/100g	Total basicity me/100g	Total basicty me/100g	Decomp. (%)at50°C Days storage		
								7	14	28
A	150–	Manchuria	Asada	0.22	0.35	0.20	0.05	1.7	1.8	1.9
B	150–200	〃	〃	0.23	0.36	0.24	0.06	1.7	1.9	2.4
C	200–250	〃	〃	0.25	0.45	0.25	0.07	2.2	2.5	2.6
D	250–300	〃	〃	0.28	0.82	0.32	0.10	2.5	3.0	3.7
E	300–	〃	〃	0.40	0.98	0.46	0.15	3.9	5.0	6.0
F	150–	Gunma	〃	0.62	1.32	0.50	0.05	4.2	4.9	5.7
G	150–200	〃	〃	0.70	1.65	0.65	0.07	4.7	5.4	6.2
H	200–250	〃	〃	0.70	1.74	0.67	0.10	4.9	5.6	6.3
I	250–300	〃	〃	0.76	1.99	0.73	0.17	5.9	7.2	7.6
J	300–	〃	〃	1.00	2.40	0.83	0.23	6.4	7.8	9.5
M	200–250	Iwate 1	Kunimine	0.52	1.31	0.57	0.14	5.6	6.7	7.5
N	300–	〃	〃	0.61	1.45	0.67	0.15	5.7	7.2	8.8
R	200–250	–	Yukizirushi	0.57	1.07	0.47	0.12	4.2	5.0	5.7
S	250–300	〃	〃	0.47	1.11	0.50	0.15	4.3	5.5	6.0
T	300–	〃	〃	0.52	1.20	0.56	0.19	4.5	5.9	6.1
V	300–	–	–	0.68	1.63	0.82	0.14	6.1	7.5	8.6
W	200–250	Saitama	Kantobentonaito	0.55	0.95	0.64	0.10	3.9	4.8	5.7
Y	200–250	–	–	0.84	1.83	0.74	0.13	5.0	6.0	7.3
Z	300–	–	–	0.88	2.12	0.94	0.15	6.1	7.4	9.0

given in Table 1.

Results

Fig. 1, 2, 3 and 4 illustrate the correlation between the rate of decomposition of the active ingredient of 1.5% EPN dust and the chemical and physical properties of talcs used as carriers. In these figures normal alphabets show the sample for one week storage and alphabets with open circles are for four weeks storage. The correlation coefficients of ordinate *versus* abscissa were calculated for two groups of plots. The correlation coefficients (r) for one week storage are shown in right down side and those of four weeks are shown in up left side of each figure. The linear plots of Fig. 1. 2 and 3 confirm and extend the previous findings on the mechanism of degradation. The amounts of moisture sorbed (Fig. 1) and the base exchange capacity (Fig. 2) would indicate the amounts of chemically active site of accessible crystal lattice which would play one important role in the decomposition of EPN, while total basicity (Fig, 3) would indicate other chemical role of the active site. However, the total acidity seems to act rather little part in the reaction as shown in Fig. 4.

Discussion

The degradation of EPN dust will proceed essentially as same as that of methyl parathion dust. These two organophosphorus inseticides suffer degradation from the two dominant factors of talc. One is the factor concerning the physical contact and the other is the factor concerning the chemical basicity.

EPN is comparatively stable in dust formulation, although EPN is essentially more unstable against alkaline hydrolysis than methyl parathion[2]. The loss of EPN dust was only from half to one third comparing with that of methyl parathion dust.

The relative stability of EPN would be attributable to some factors as described below. One physical factor would be the disparity in vapor pressure as quoted from two literatures in Fig. 5[3,4].

This fact would cause slow diffusion of EPN

Fig. 1

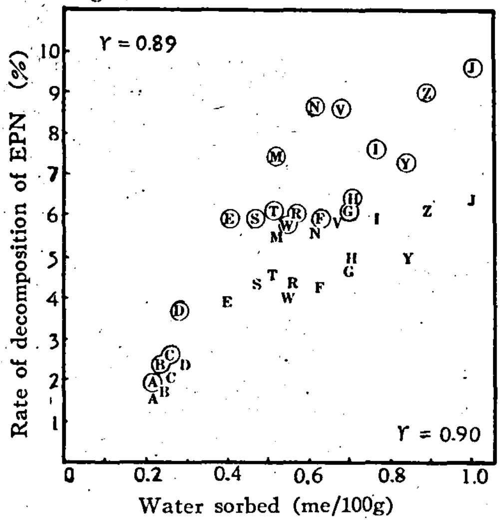

Fig. 2

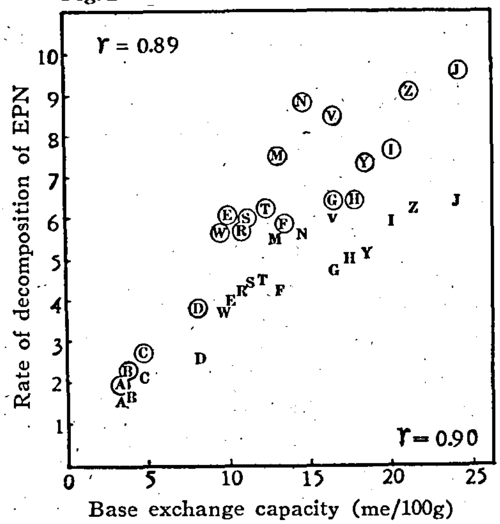

Fig. 3

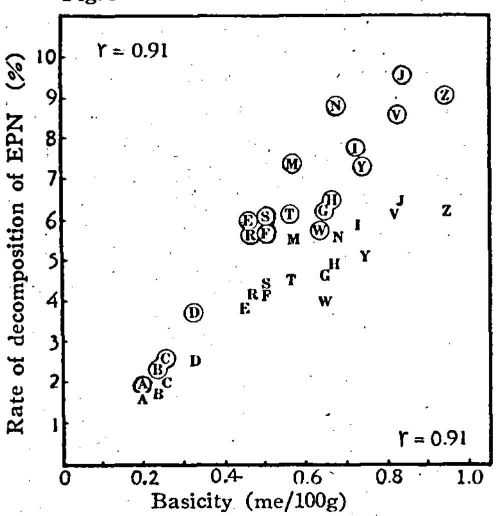

Fig. 4

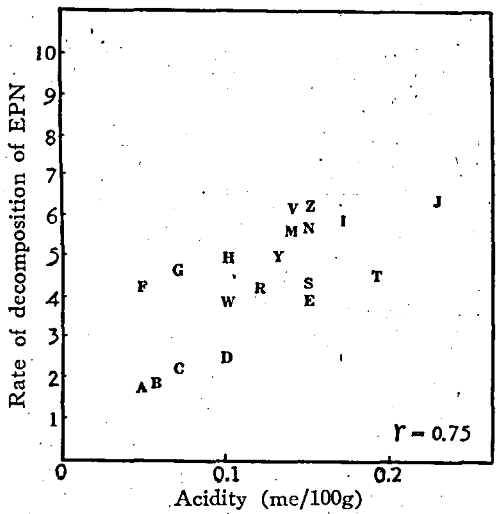

Fig. 1~4 The correlationship between the rate of decomposition of the active ingredient in EPN dust at 50°C and the amounts of moisture sorbed (Fig. 1), the base exchange capacity (Fig. 2), total basicity (Fig. 3), and total acidity (Fig. 4).

into the basic active site. Consequently the active ingredient could be maintained unaffectedly in dust. Another factor would be the bulky molecular structure of EPN (M.W. 323.2) comparing methyl parathion (M.W. 263.2) and its lipophile property with more aromatic configulation.

The data illustratd in Fig. 6 will give one of the evidences. EPN had low adsorbability (proportional to 80% of methyl parathion) on talc, accordingly physical accessible area on the chemically active site of talcum surface would be limited in the case of EPN.

The phosphorus moiety produced by degradation is hardly possible to elute with ethyl ether but considerably high amounts of phosphorus is apt to be fixed firmly on talc which could not leach with water and salt solution. This fact will give some supports to the mechanism illustrated in Fig. 7.

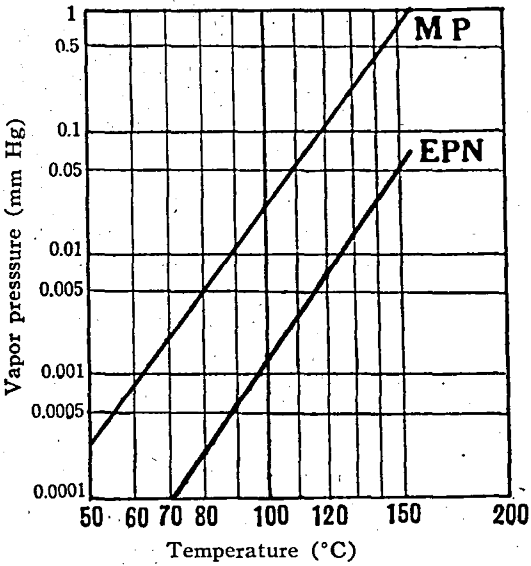

Fig. 5. Vapor pressure of EPN and methyl parathion

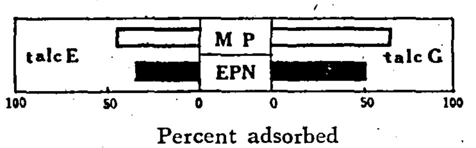

Fig. 6. Adsorption of EPN and methyl parathion on talcs when contacted 20 ml of 20 ppm esters in n-hexane solution with 5g of talcs.

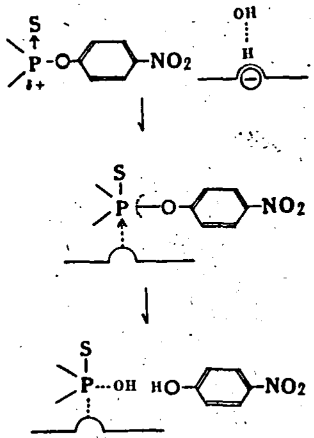

Fig. 7.

Acknowledgement

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The Chemical and Physical Properties of Clays and their Behavior on the Decomposition of Methyl Parathion Dust Formulation. Chemical Studies on Organophosphorus Insecticides. IX. Rokurō Satō and Hiroshi Kubo (Agricultiral Chemicals Inspection station, Ministry of Agriculture and Forestry, Kodairamachi, Tokyo) Received July 30, 1959. *Botyu-Kagaku* **24**, 159, 1959.

31. クレーの物理化学的性質がMethyl parathion粉剤の経時変化に及ぼす影響 有機燐殺虫剤の化学的研究 第9報 佐藤六郎・久保博司 (農林省農薬検査所) 34. 7. 30 受理

Methyl parathion 粉剤の経時変化とその機構を明らかにするため，18 種の代表的な天然クレーの化学的物理的性質，即ち水分吸着能，塩基置換容量，全塩基性，全酸度及び表面酸性等の特性を検討し，これらの性質と methyl parathion の分解との相関性を検討した。クレーの場合は幾つかの分解要因が交錯しているが，しかし常温に於て最も本質的な要因となっているものは塩基性である。クレーの酸性は高温に於て methyl parathion をより不安定な S-methyl isomer に異性化させる要因となっている。

This article reports the results of study on the degradation mechanism of methyl parathion in clay dust formulation. The reactions are found to be intermingled together