

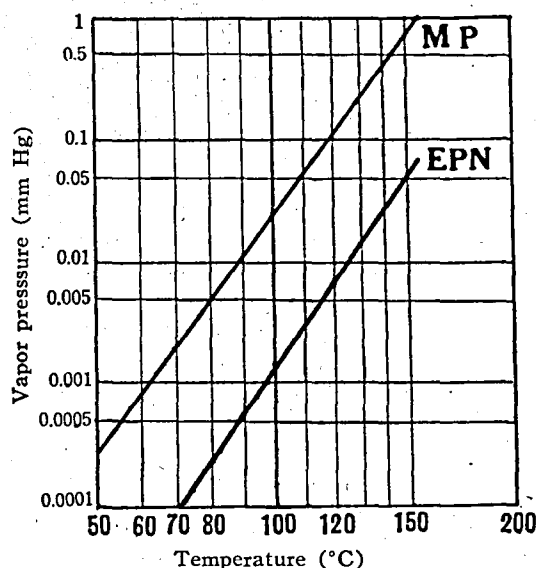


Fig. 5. Vapor pressure of EPN and methyl parathion

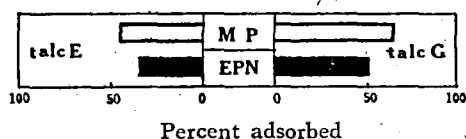


Fig. 6. Adsorption of EPN and methyl parathion on talcs when contacted 20 ml of 20 ppm esters in n-hexane solution with 5g of talcs.

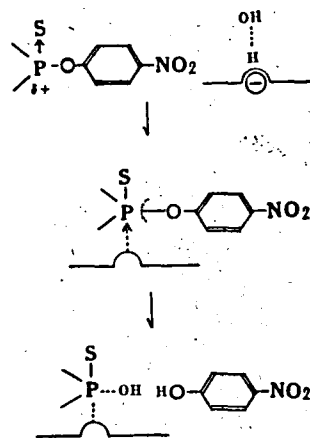


Fig. 7.

Acknowledgement

We are most grateful to Mr. Kengo Ogawa for his technical assistance.

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- 1) R. Sato, and H. Kubo., *Botyu-Kagaku*, **24**, 93 (1959).
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- 3) Gerhard Schrader, *Monographien zu Angew. Chem. und Chem. Ingen. Tech.* Nr. **62**, 53 (1952).
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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 SATO and Hiroshi KUBO (Agricultural 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

in the case of clay. However, the main features of mechanism are the same as stated in the previous papers. The most substantial and predominant factor of degradation at room temperature would be attributable to the basicity of clay. The acid character of clay due to the present hydrogen ion would cause the catalytic isomerisation of methyl parathion to the unstable S-methyl isomer at higher temperature.

The storage decomposition of methyl parathion and EPN dust prepared with talcs has been studied previously in this series. And the chemical and physical properties of talcs have been compared with the rate of decomposition of the active ingredient.

The present investigation was undertaken to obtain the extensive informations about the storage decomposition of methyl parathion on clay.

The so-called "clay" is widely used as the carrier of various pesticides. Clay is practically defined as a disperse system of mineral fragment of hydrated aluminum silicate, which is derived by weathering of an aluminous mineral and has not a definit chemical composition. From the modern concepts of mineralogy, clay comprises three main groups, namely, the kaolin group, the montmorillonite group and the illite group. The clay commercially available in Japan is random mixtures of several types of clay minerals.

Materials

Various commercial clays were kindly supplied from many producers. We selected eighteen clays and divided into two groups (dry process group, from A to I and wet process group from J to R) as given in Table 1. These samples which we used in this experiment belonged mainly to the kaolin group but contaminated more or less with quartz, mica and montmorillonite.

Rate of Decomposition

The 1.5% methyl parathion dusts were prepared by mixing clays with pure methyl parathion in a porcelain bowl. The dust products were placed in tightly stoppered bottle and stored in thermostats at 50°C and 30°C. They were analyzed for the active ingredient spectrophotometrically. The rate of decomposition of the active ingredient was given in Table 2.

Table 1. Materials

Coding	Mining place	Producer	Processing
A	Nagano Pref.	Asada	Dry process
B	//	—	//
C	//	Kantobentonaito	//
D	//	//	//
E	//	//	//
F	Hyogo	Nihonkogyo	//
G	//	—	//
H	Saitama	—	//
I	Tochigi	Oonuki	//
J	Okayama	Okayama-clay	Wet process
K	//	//	//
L	//	//	//
M	//	Shinagawa-clay	//
N	//	—	//
O	—	Yoshinaga Sangyo	//
P	Hyogo	—	//
Q	Ishikawa	Hattori Kogyo	//
R	—	—	//

Chemical and Physical Properties

The amounts of water sorbed, the base exchange capacity, total basicity, total acidity and surface acidity were measured according to the method as described in the previous paper¹⁾.

Results and Discussion

In order to make the results explicit, the data in Table 2. were illustrated in Fig. 1, 2, 3 and 4. In these figures normal capital letters show the sample for one week storage at 50°C and those with open circles are for two weeks storage at 50°C. The small letters correspond to the samples stored three weeks at 30°C.

The present results differ in some ways from those obtained in the case of talc. In the case of clay the reaction is so complex that the mechanism could not be explained in a single

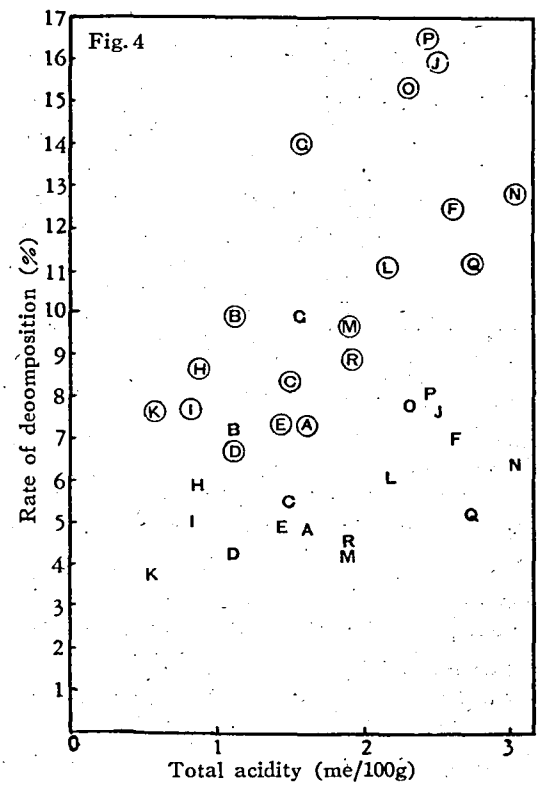
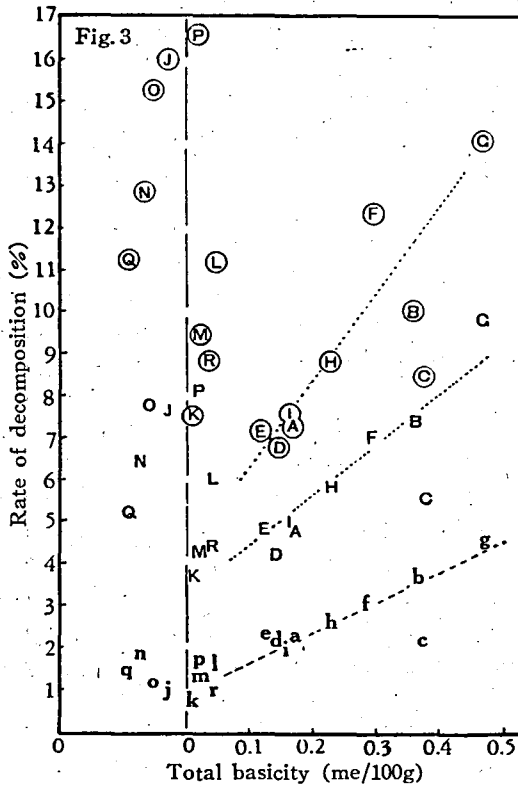
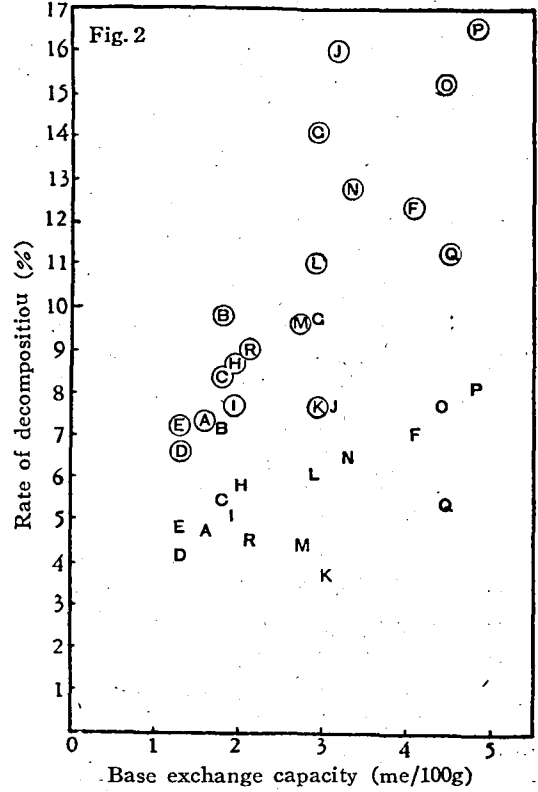
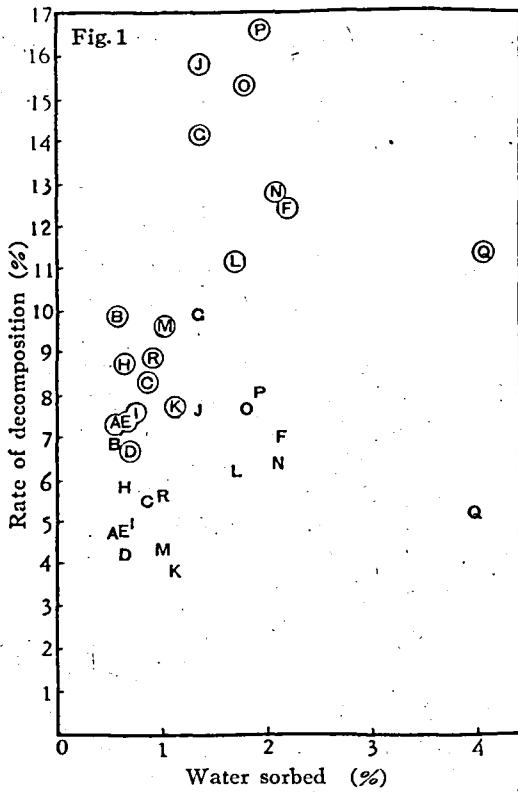


Fig. 1~4. The relationship between the rate of decomposition of the active ingredient in methyl parathion dust at 50°C and the amounts of moisture sorbed (Fig. 1), the base exchange capacity (Fig. 2), total basicity (Fig. 3) and total acidity (Fig. 4).

Table 2. Some of the chemical and physical properties of clays and their effect on the decomposition of methyl parathion dust formulation.

Code	Water sorbed %	Base ex. cap. me/100g	Total basicity me/100g	Total acidity me/100g	pKa	Rate of decomp. (%)		
						at 50°C	30°C	3 weeks
						1	2	
A	0.56	1.6	0.17	1.61	1.5-3.0	4.8	7.3	2.3
B	0.55	1.8	0.36	1.11	∥	7.2	9.9	3.7
C	0.88	1.8	0.37	1.48	∥	5.5	8.4	2.2
D	0.65	1.3	0.14	1.12	∥	4.2	6.7	2.3
E	0.61	1.3	0.12	1.43	∥	4.9	7.3	2.5
F	2.15	4.1	0.29	2.60	∥	7.0	12.4	3.1
G	1.32	2.9	0.47	1.57	∥	9.9	14.1	4.5
H	0.43	2.0	0.23	0.87	∥	5.9	8.7	2.6
I	0.68	1.9	0.16	0.82	∥	5.0	7.7	2.1
J	1.34	3.1	0	2.50	∥	7.7	16.0	1.0
K	1.07	3.0	0.01	0.58	∥	3.7	7.6	0.9
L	1.67	2.9	0.04	2.14	∥	6.1	11.1	1.7
M	1.00	2.8	0.03	1.90	∥	4.5	9.6	1.4
N	2.12	3.3	0	3.00	∥	6.4	12.8	1.9
O	1.75	4.4	0	2.30	∥	7.8	15.3	1.3
P	1.94	4.8	0.02	2.42	1.5	8.1	16.6	1.7
Q	4.16	4.5	0	2.72	1.5	5.2	11.2	1.5
R	0.90	2.1	0.03	1.92	1.5-3.0	4.5	8.9	0.9

feature.

To make the matter more complicated, the chemical and physical characteristics of clays were converted to some extent by adding chemicals during wet process. Particularly, the value of total basicity and acidity were disturbed considerably by wet processing. We could not measure detectable amounts of base in some of wet processed clay.

No significant informations could not be gained from the data of water sorption. The base exchange capacity and total acidity seemed to have slight correlation with the rate of degradation.

The total basicity had high correlation with the degradation of methyl parathion, especially at low temperature as shown in Fig. 3.

Although the clays which were manufactured by wet process by acid solution denatured their apparent basicity, those manufactured by natural dry process displayed considerable linear correlation between basicity and the rate of degradation even at 50°C.

The most substantial and predominant factor

of degradation would be attributable to the basicity of carrier.

As mentioned in Table 2, clays exhibit rather acidic character than basic. This acidity is caused by the known tendency of the aluminum atom to acquire a pair of electrons. To the authors it is apparent that the presence of such Brönsted acid in clay is not a foremost common mechanism for the decomposition of methyl parathion at room temperature. The most probable mechanism of Brönsted acid would be isomerising reaction of methyl radical by proton transferring action as illustrated in Fig. 5. We could ascertain considerably high amounts of S-methyl isomer in clay stored at 50°C by paper chromatography. Clays which had highly acidic properties are found to be highly catalytically active to the conversion of methyl parathion into Smethyl isomer, which would undergo hydrolysis or other secondary degradation more easily than methyl parathion.

In order to confirm the effect of acidity and basicity on the decomposition of methyl parathion, the acidity and basicity of clay No.

Table 3 The effect of acidity and basicity of clay on the decomposition of the active ingredient of 1.5% methyl parathion dust

Clay treated with (ml/100g)	Decomp. (%) of methyl parathion stored at 50°C for 2 weeks	Total acidity	Total basicity
N-(NH ₄) ₂ S ₂ O ₈ 20	8.9	3.4	0.44
// 10	7.4	2.0	0.46
None —	7.3	2.8	0.46
N-NaCl 10	9.9	0.7	0.84
// 20	11.4	0.6	1.23
// 40	13.8	0.6	3.58

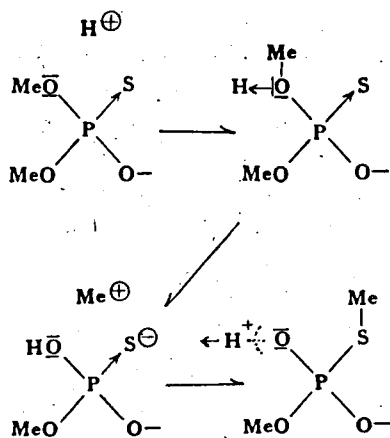


Fig. 5.

A was altered by adding ammonium persulfate and sodium chloride respectively and by igniting at 800°C for two days. And the decomposition rate of 1.5% methyl parathion dust prepared from the treated clays was determined. The data are given in Table 3.

It appeared reasonably to conclude that the basicity of clay contribute substantially to the degradation of methyl parathion.

Acknowledgement

We are most grateful to Mr. Kengo Ogawa for his technical assistance.

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- 1) R. Sato, and H. Kubo, *Botyu-Kagaku*, **24**, 93 (1959).

Reaction of Methyl Parathion with Phenylmercuric Acetate, II. Chemical Studies on Organophosphorus Insecticides. X. Ichirō MURA, Sinkō Goro, Rokurō SATO (Agricultural Chemicals Inspection Station, Ministry of Agriculture and Forestry, Kodairamachi, Tokyo) Received July 30, 1959. *Botyu-Kagaku* **24**, 163, 1959 (with English résumé, 168).

32. Methyl parathion と酢酸フェニル水銀との反応について (その2) 有機燐殺虫剤の化学的研究 第10報 牟田一郎・後藤真康・佐藤六郎 (農林省農薬検査所) 34. 7. 30 受理

Methyl parathion は有機溶媒中で有機水銀化合物と反応する。従ってこの混合粉剤の定量に際しては、有機溶媒抽出操作中に2化合物間に反応が起るため、正確な methyl parathion の含量が得られない。この場合 HCl を含む溶媒を使用すればこの反応が停止され、正確な定量値が得られる。この方法によって珪石粉剤中の methyl parathion の経時変化を測定した結果、30°, 50° いずれの保存に於ても同様に当量反応的に methyl parathion が分解されることを知った。Chloroform を抽出溶媒として HCl 滴定法により珪石粉剤中の有機燐水銀 (phenylmercuric acetate を添加した場合) の経時変化を測定した結果、PMA は O,O-dimethyl O-phenylmercuric thionophosphate に変化し、その残存する量は4週後では 69% (30°), 50% (50°) であった。更にペーパークロマトグラフ法により p-nitrophenyl acetate, O,O-dimethyl O-phenylmercuric thionophosphate を検出し、珪石粉剤中ではこれらの化合物が中間生成物として存在することを証明した。従って珪石粉剤における methyl parathion, phenylmercuric acetate の分解機構は中