

and EPN have been studied in alcoholic alkali media and in Bordeaux mixtures. In alcoholic media the order of instability of organophosphate esters against alkaline hydrolysis is in agreement with the order of electrophilic character of the phosphorus atom. The change of solvent from less to more aqueous medium accelerates the hydrolysis reaction. In Bordeaux mixtures EPN turns to stable considerably. Cupric component increases the hydrolysis of methyl parathion but EPN is not greatly affected by it.

Acknowledgments

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The Chemical and Physical Properties of Talcs and their Behavior on the Decomposition of Methyl Parathion Dust Formulation. Chemical Studies on Organophosphorus Insecticides. V. Rokurō SATO and Hiroshi KUBO (Agricultural Chemicals Inspection Station, Ministry of Agriculture and Forestry, Kodairamachi, Tokyo) Received April 30, 1959. *Botyu-Kagaku* 24, 93, 1959.

20. タルクの物理化学的性質がメチルパラチオン粉剤の経時変化に及ぼす影響 有機磷殺虫剤の化学的研究 第5報 佐藤六郎・久保博司(農林省農薬検査所) 34. 4. 30 受理

メチルパラチオン粉剤の経時変化とその機構を明らかにする為、代表的26種の天然タルクの化学的物理的性質、即ち水分吸着能 (I)、アンモニア吸着能 (II)、置換性カチオン (Mg, Ca, Al, Fe) (III)、塩基置換容量 (IV)、全塩基性 (V)、全酸度 (VI)、及び表面酸性 (VII) 等の特性を検討し、これらの性質とメチルパラチオンの分解との相関性を検討した。I, II, IV, V はメチルパラチオンの分解要因と深い関係を持つことが確認された。メチルパラチオンの分解機構はキャリアーの表面に分布した電気的陰性に基づく吸着活性点による求核的反応とその塩基性に基因するものと推測される。

This report presents the relationship between the chemical and physical properties of talcs and the rate of decomposition of the active ingredient of methyl parathion in dust formulation. Various factors of diluents having effect on the decomposition of methyl parathion were investigated. The amounts of moisture sorbed (I), that of ammonia chemisorbed (II), that of some replaceable cations, e. g. Mg, Ca, Fe and Al (III), the base exchange capacity (IV), total basicity (V), total acidity (VI) and surface acidity (VII) have been measured on the various talcs commercially available for the dust formulation. The considerably high relationships were obtained between the data of I, II, IV and V and the rate of decomposition of methyl parathion. The results are consistent with the proposal that the reaction involves a nucleophilic attack to the phosphorous atom of methyl parathion molecule by the negatively charged points distributed over the active surface of talcs.

Introduction

In contrast to the extensive literatures dealing with the organophosphorus insecticides, very little is known yet concerning the behavior of carriers or diluents on the active

ingredient in dust formulation.^{1,2,3} During long storage severe decomposition of the active ingredient in some organophosphorus insecticides have been taken place actually. Especially the loss of the active ingredient in methyl parathion dust has become an serious industrial

problem to be clarified.

As talc is most generally used to make insecticidal dust formulation, we studied on the relationship between the various chemical and physical properties of talcs and their chemical actions on the active ingredient of methyl parathion dust.

Experimental

Materials

The carriers or diluents of various clay minerals were kindly supplied from many producers. We sorted out typical nine mineral carriers which were supposed to be predominantly composed of talc. Talcs were made into suspension with water and separated to several fractions through screens. Muddy fractions were filtrated on a Buchner funnel, air

dried for 16 hours. Thus twenty-six samples were prepared and assigned following coding alphabets as in Table 1. Before all experiments talcs were heated again to dry at 105° C for two hours.

Rate of Decomposition

The 1.5% methyl parathion dusts were prepared by impregnating above-mentioned talcs with acetonic methyl parathion solution, removing solvent by allowing to stand overnight and blending well. The dusts were put in the bottles and stored in a thermostat at 50° C. The rate of decomposition of the active ingredient of methyl parathion dust was determined by measuring the amounts of liberated *p*-nitrophenol colorimetrically at 400m μ using Beckman DU type spectrophotometer (Table 2).

Table 2. The rate of decomposition of 1.5% methyl parathion dust stored at 50° C. (percent)

Table 1.

Coding	Particle size	Mining place	Producer
A	150— (MES-1)	Manchuria	Asada
B	150—200	〃	〃
C	200—250	〃	〃
D	250—300	〃	〃
E	300—	〃	〃
F	150—	Gunma	〃
G	150—200	〃	〃
H	200—250	〃	〃
I	250—300	〃	〃
J	300—	〃	〃
K	200—300	Gifu	Chubukasseki
L	300—	〃	〃
M	200—250	Iwate I	Kunimine
N	300—	〃	〃
O	250—300	〃 II	〃
P	300—	〃	〃
Q	150—200	—	Yukizirushi
R	200—250	〃	〃
S	250—300	〃	〃
T	300—	〃	〃
U	200—300	—	—
V	300—	〃	〃
W	200—250	Saitama	Kantobentonaito
X	300—	〃	〃
Y	200—250	—	—
Z	300—	〃	〃

Code	Days storage						
	2	4	7	11	14	18	28
A	1.0	1.5	2.3	3.3	3.5	4.3	5.1
B	1.2	1.9	2.7	3.7	4.2	4.4	5.6
C	1.3	2.1	3.2	4.4	4.5	6.0	6.6
D	1.8	3.0	4.3	5.5	6.1	7.0	7.8
E	2.4	3.7	5.5	8.0	8.0	9.9	10.9
F	5.9	9.0	11.5	14.7	15.3	18.1	19.5
G	7.5	9.1	11.9	15.9	17.5	18.6	20.7
H	7.7	10.6	14.1	17.8	17.5	21.3	22.3
I	9.2	11.5	16.7	19.8	23.3	25.1	30.5
J	11.7	14.1	19.4	24.5	25.3	26.8	32.0
K	4.8	7.5	10.0	11.2	14.0	13.6	15.0
L	5.5	8.6	10.9	11.8	15.2	14.8	16.9
M	5.6	8.6	10.0	11.8	12.9	15.0	16.3
N	5.8	8.6	10.8	13.1	14.0	16.7	18.2
O	4.5	7.3	9.6	10.4	12.6	14.0	14.9
P	5.5	8.8	11.6	14.6	14.0	17.3	17.8
Q	3.3	5.8	7.6	10.1	10.4	12.3	13.4
R	3.4	5.7	7.3	10.2	—	11.3	13.4
S	3.4	5.6	7.6	—	10.7	12.5	14.3
T	4.4	6.5	7.9	11.4	11.8	14.5	15.9
U	5.4	8.4	10.6	13.1	13.9	15.6	17.6
V	6.3	9.6	12.0	14.8	15.1	17.6	20.0
W	3.9	6.6	8.7	10.6	10.9	12.9	14.0
X	4.4	6.9	9.4	11.7	12.6	14.6	17.2
Y	7.2	10.2	13.2	16.2	16.6	21.1	22.4
Z	8.2	12.4	16.8	18.7	21.8	23.7	26.4

Water Sorption

We determined the amounts of moisture adsorbed on the surface of talcs which might be one representative of the surface area where degradation of methyl parathion was taken place.

Two or three grams of samples were taken in the tared weighing bottle and weighed. They were adjusted to equilibrium in an atmosphere of 99% relative humidity by allowing to stand for 10 days at 30°C in a desiccator containing 3.3% H_2SO_4 and evacuated to 50 mm Hg. They were then dried to constant weight in an oven at 110°C. The lost weight was considered to be the adsorbed water on the surface of talc.⁴⁾

Ammonia Sorption

We expected that sorption of ammonia, a gaseous base, might provide some information on the physical surface area or the acid strength.

About one gram of talc was weighed and placed in the 30 ml test tube. Talcs were exposed to ammonia vapors for one week and then took the excess ammonia away in a large desiccator containing conc. H_2SO_4 for two weeks under vacuum (5 mm Hg) at room temperature. The amounts of ammonia uptaken on the dust by chemisorption were measured by the indophenol method.^{5, 6, 7)}

Three ml of 1.5N- H_2SO_4 was added into the test tube containing talc, heated in a water bath for about one hour to liberate ammonia with shaking from time to time and allowed to stand overnight. Three ml of 1.5N-sodium hydroxide-5% phenol mixture, 2 ml of saturated sodium bicarbonate solution and 3 ml of sodium hypochloride alkaline solution (10% NaOCl 2: 10% Na_2CO_3 1) were added. The content of the test tube should be shaken well all the time of the addition and filtered. Blue color of the filtrate was measured after 20 min. at 625 m μ using Beckman DU type spectrophotometer and compared the optical density with that of the standard ammonium solution.

Replaceable Cations

Some replaceable cations which were liberated from talcs by neutral normal ammonium acetate solution, e. g. Mg, Ca, Al and Fe were determined.

Carries were leached with 90 ml of the neutral normal ammonium acetate solution and after draining washed with 50 ml of neutral 80% methanol. The leachates were collected and made up to 100 ml with water⁸⁾.

A) Magnesium and Calcium

Magnesium and calcium were determined by titrating 20 ml of each leachate with N/100-E. D. T. A. at pH 10 using Eriochrom Black T as indicator^{9, 10)}.

B) Aluminum

The amounts of aluminum in the leachate were determined spectrophotometrically by using Stilbazo, which was recently discovered as a new specific colorimetric reagent by Kuznetsow^{11, 12, 13)}.

Ten ml of leachate was taken in a test tube. One ml of 10% ascorbic acid to reduce active ferric ion into ferrous, 5 ml of 0.4M-acetate buffer to adjust pH 5.65 and 2 ml of 0.08% Stilbazo reagent were added. The red color produced was measured after 10 min. spectrophotometrically at 520 m μ against reagent blank prepared by the same procedure and compared the optical density with that of the standard aluminum solution.

C) Iron

Ferric ion was determined by the complexometric titration with N/100-E. D. T. A. at pH 2.8 using Variamin Blue as indicator¹⁴⁾.

Base Exchange Capacity

The samples treated with above stated procedures were leached again with 90 ml of 10% potassium chloride solution. The leachates were made up to 100 ml with water. To the Kjeldahl flask 25 ml portions were transferred, distilled the ammonia into 5 ml of standard N/50- H_2SO_4 and titrated the excess acid with standard N/50-NaOH¹⁵⁾.

Basicity

The total base in talc was determined in the nonaqueous protogenic medium¹⁶⁾.

Two grams of sample was taken in the 100 ml Erlenmeyer flask and added 5 ml of acetic acid-acetic anhydride (5:1). Each suspension was then titrated with N/100- $HClO_4$ in acetic acid. Alphanaphtholbenzein was used as indicator.

Notable green color durable for 30 seconds was taken as the end point.

Acidity

The total acid in talc was determined in the nonaqueous basic medium^{17, 18}. Two grams of sample was taken in the 100 ml Erlenmeyer flask and added 5 ml of dimethylformamide. Each suspension was then titrated with N/50-sodium methylate in benzene. Thymol Blue was used as indicator. Notable blue color durable for 30 seconds was taken as the end point.

Surface acidity

The surface acidity was measured by Walling method¹⁹.

Results

The results obtained are summarized in Table

3. The rate of decomposition of the active ingredient of 1.5% methyl parathion dust formulations stored at 50°C is compared with the capability of water sorption of talcs as in Fig. 1.

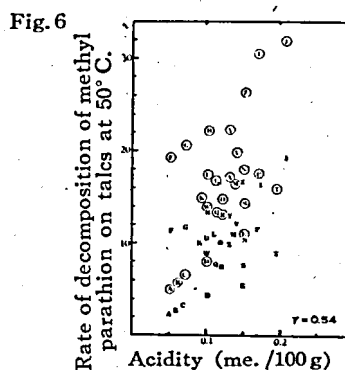
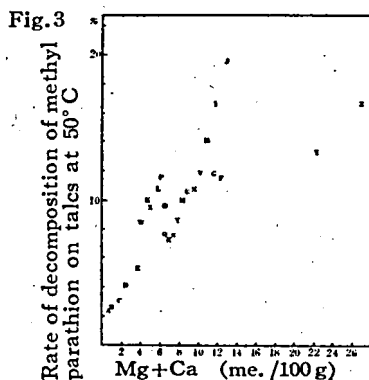
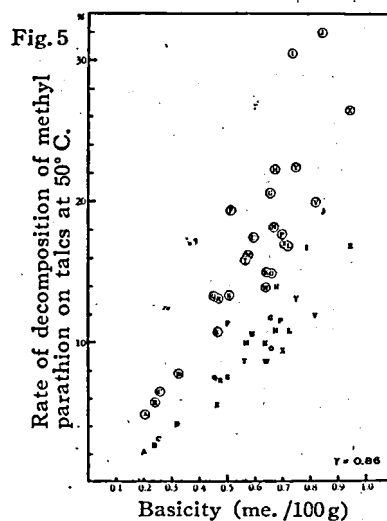
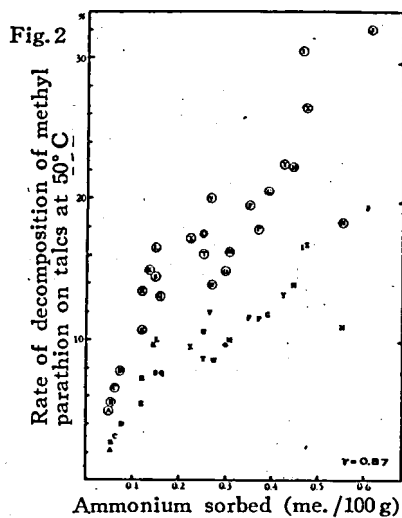
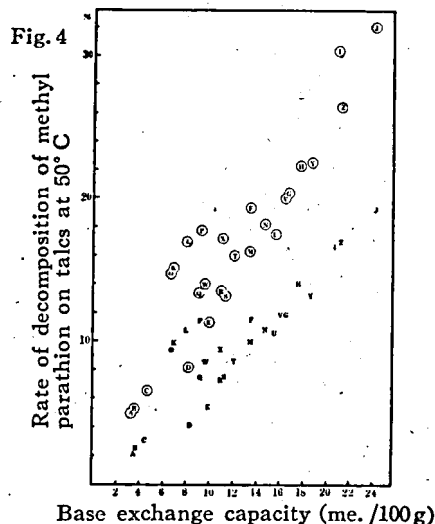
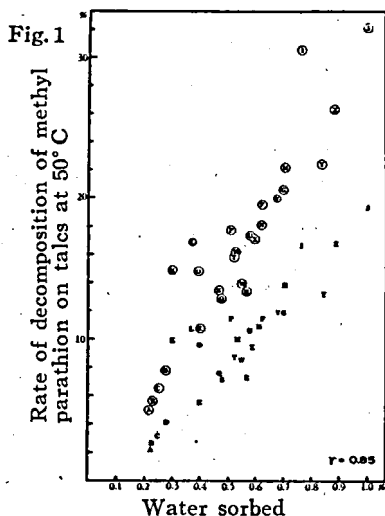
In this and the following figures, normal alphabets show the samples for one week storage, and alphabets with open circles are for four weeks. Considerably linear relationships are observed between them. The correlation coefficients are calculated to be 0.85 for one week and 0.83 for four weeks storage.

The amounts of ammonia chemisorbed on talcs have also high correlation with the rate of decomposition of methyl parathion as in Fig. 2. The correlation coefficients estimated are 0.87 for one week and 0.70 for four weeks storage.

Table 3. The chemical and physical properties of talcs.

Code	H ₂ O sorbed %	NH ₄ sorbed %	Mg+Ca me./100g	Al me./100g	Base ex. cap. me./100g	Total basicity me./100g	Total acidity me./100g	pKa
A	0.22	0.05	0.7	none	3.5	0.20	0.05	3.3-1.5
B	0.23	0.05	0.9	//	3.6	0.24	0.06	//
C	0.25	0.06	1.7	//	4.5	0.25	0.07	//
D	0.28	0.07	2.3	//	8.2	0.32	0.10	//
E	0.40	0.12	3.6	//	9.8	0.46	0.15	//
F	0.62	0.35	12.3	trace	13.2	0.50	0.05	//
G	0.70	0.39	11.6	//	16.5	0.65	0.07	//
H	0.70	0.44	10.8	//	17.4	0.67	0.10	//
I	0.76	0.46	11.6	//	19.9	0.73	0.17	//
J	1.00	0.61	12.8	//	24.0	0.83	0.23	//
K	0.30	0.14	4.5	0.04	6.8	0.64	0.09	3.3
L	0.37	0.15	5.7	0.05	7.8	0.72	0.11	//
M	0.52	0.31	8.2	trace	13.1	0.57	0.14	3.3-1.5
N	0.61	0.55	9.4	//	14.5	0.67	0.15	//
O	0.39	0.30	6.4	0.04	6.9	0.66	0.12	//
P	0.51	0.36	6.0	//	9.1	0.69	0.17	//
Q	0.47	0.16	6.7	trace	8.9	0.45	0.11	//
R	0.57	0.12	6.8	//	10.7	0.47	0.12	//
S	0.47	0.15	7.4	//	11.1	0.50	0.15	//
T	0.52	0.25	7.6	//	12.0	0.56	0.19	//
U	0.57	0.25	9.0	//	15.6	0.59	0.10	//
V	0.68	0.26	10.1	//	16.3	0.82	0.14	//
W	0.55	0.22	4.0	//	9.5	0.64	0.10	//
X	0.59	0.27	4.9	//	10.8	0.70	0.13	//
Y	0.84	0.42	22.3	//	18.3	0.74	0.13	//
Z	0.88	0.46	27.1	//	21.2	0.94	0.15	//

Fig. 1-6. The correlationships between the rate of decomposition of the active ingredient in methyl parathion dust at 50°C and the ammounts of moisture sorbed (Fig. 1). that of ammonia chemisorbed (Fig. 2), that of exchangeable magnesium and calsium (Fig. 3), the base exchange capacity (Fig. 4), total basicity (Fig. 5) and total acidity (Fig. 6).



Magnesium was found to be the most common and predominant cation replaceable with ammonium but the amounts of replaceable magnesium could not reasonably be attributed to the chemical activity of talc as in Fig. 3. The presence of exchangeable aluminum would indicate the existence of impurities with silica-alumina type. The talcs which contain detectable aluminum seem to show some tendency of plots to locate far out of linear groups such as sample K, L, O and P. This tendency suggests that aluminum complex in carrier might play other additional role in the chemical activity on the decomposition of methyl parathion.

We could not detect enough amounts of iron in exchangeable form.

The rate of degradation increased with increasing the base exchange capacity of talc as shown in Fig. 4. The correlation coefficients estimated are 0.86 for one week and 0.81 for four weeks storage.

The amounts of moisture sorbed, ammonia chemisorbed on surface and the capacity of exchangeable base would provide some information on the architecture and the chemically active site of the accessible crystal lattice.

The total basicity proved to have a potent influence on the degradation of methyl parathion in dust formulation. The same hydrolysis with alkali might be taken place on the surface of talc as in the basic solution. The linear plots of Fig. 5 indicate that the correlation coefficients are 0.86 for one week and 0.93 for four weeks storage.

However, the total acidity seems to act rather little part in the reaction as shown in Fig. 6. Plots are distributed over a wide range and have low correlation coefficients, $r=0.54$ for one week and 0.55 for four weeks.

No information could not be gained from the data of surface acidity tested by Walling color reagents.

Discussion

It is generally agreed that the hydrolysis of methyl parathion in alkaline solution proceed as shown in Fig. 7a.

On account of the electronegativity difference

between sulfur and phosphorus, phosphorus atom will carry a small positive charge and be the electrophilic center of the molecule²⁰.

Similar mechanism would be taken place on mineral carriers.

The most reasonable mechanism for the decomposition of the active ingredient of methyl parathion dust formulation on talc would follow the reaction scheme as proposed in Fig. 7b.

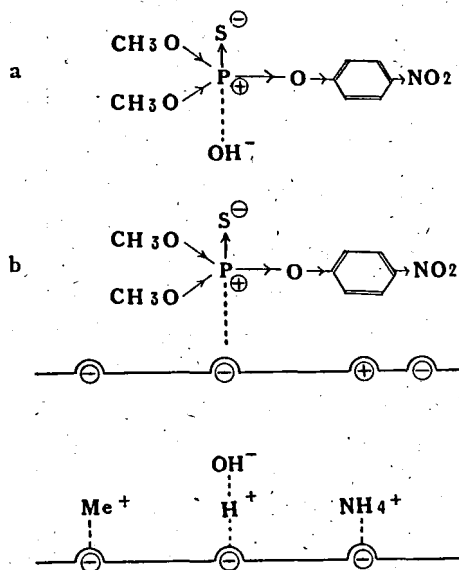
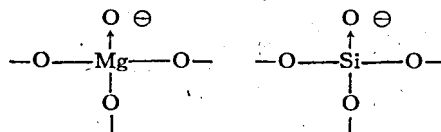


Fig. 7

The first stage of the reaction would involve the accession of the phosphorus atom to the negatively charged parts of talc which caused by isomorphic substitution of the positive ions (e. g. Ca and Al) for silicon in the crystal lattice²⁰ or caused by the broken bonds on crystal edges, e. g.



Such electronegative sites located on the surface of talc will be represented in some properties of talc such as sorption of moisture, chemisorption of ammonia or base exchange capacity.

The second stage of the reaction would involve the nucleophilic attack on the phosphorus atom by the base including the electron

donor defined by Lewis distributed over the active surface and disproportionation of methyl parathion molecule to separate *p*-nitrophenyl moiety. The total basicity of talc will be some representative of the chemical active site and will play an important role in this reaction.

Acknowledgement.

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21. Methyl parathion 粉剤の分解防止剤について 有機燐殺虫剤の化学的研究 第6報。後藤真康・牟田一郎・佐藤六郎 (農林省農薬検査所) 34. 4. 30 受理。

Methyl parathion 粉剤の分解防止剤を検索して, triphenylphosphate, 脂肪酸, アルコール, alkylbenzenesulfonate などが大部分のキャリアーに対し最も有効である事を見出した。又、これらの作用機構について検討した結果、これらはキャリアーの塩基性を中和し、キャリアーの活性点と考えられる電気的陰性部に吸着されることによりその活性をおさえ、又、混在する重金属や金属化合物の触媒作用を阻害する事によつて分解抑制作用を示すものと思われる。

Methyl parathion はこれを粉剤に製剤した場合、保存中に分解して効力を減ずる事は以前から知られていたが、その原因及び防止法については今日迄充分明かにされたとは云えない。我々は数年前よりこの問題について研究し、各種の重金属及びその塩が著しく分解を促進する事を報告し¹⁾、更に、キャリアー自体の

触媒作用、特にその塩基性が分解の重要な要因である事を明かにした²⁾。鹼物性キャリアーが主剤の分解を促進する事は pyrethrin, heptachlor 等においても知られているが、前者に対しては hydroquinone 等を³⁾、後者に対しては diethyleneglycol 等を⁴⁾ 粉剤に添加する事によつて主剤の分解を防止しうる事が報