

The Effect of chemical and physical properties of Korean talcs on the decomposition of Malathion in dust formulations

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Introduction

Numerous organic phosphorus insecticides have been prepared since the first discovery of Tetraethyl pyrophosphate as an insecticide. Parathion, Malathion, E.P.N. Diazinon and Dipterex have come into wide use because of their powerful killing action upon insects.

A dust formulation of an insecticide has many advantages over an emulsified preparation and many of the organic phosphorus insecticides have also been prepared in powder form. The dust formulation, however, has a disadvantage in that some of the active ingredient will be decomposed during its storage. Storage temperature and moisture content of the malathion dust formation were found to be important in determining the degree of decomposition of the ingredient. (1). Matsumoto (1, 2.) also found out that the adsorbed hydrogen ion was important in the decomposition. In expressing the effectiveness of various carrier materials, he used surface acidity. If the surface acidity expressed in term of pH is greater than pKa., the degree of decomposition is greatly reduced. Similar works concerning the effectiveness of hydrogen ion upon the decomposition of malathion and other organic phosphorus insecticides were published elsewhere. (4, 8, 11)

To explain the effect of hydrogen ion upon the decomposition Matsumoto (3) inferred to the acid-base hydrolysis, because a decomposition of organic phosphorus insecticides was known to be hydrolysis reaction itself, and that the decomposition is greatly effected by

hydrogen ion.

Cation exchange capacity of carrier materials has also received an attention. Sato (9, 10) found out that the decomposition is great when ever any material with high cation exchange capacity is used as a carrier. From his results and from the difference in the electronegativity between adjacent P and S in a organic phosphorus insecticide molecule, he proposed a decomposition mechanism of organic phosphorus insecticides. According to him, the decomposition is first induced by an adsorption of P atom toward electronegative spot on a carrier material. (5, 6, 7.)

The present authors tried to investigate the factors which may be responsible in determining the degree of decomposition of malathion in dust formulation prepared with Korean talcs, which became widespread use in Korea. Since talcs may not have high cation exchange capacity, Amberlite CG-120, a cation exchange resin, was also used to observe the effect of negative charge upon the decomposition.

Experimentals

Materials:

Malathion sample, technical grade, was obtained from American Cyanamid Co. The sample contained 95% malathion.

Talcs were obtained directly from four different mines in Korea. The mines were Chung ju, Chun ju, Tan yang and Ye san.

Amberlite CG-120, a cation exchange resin was obtained from Rohm and Haas Co,

Penn. U. S. A. The resin has $-\text{SO}_3\text{H}$ as an active group and particle size was from 100 to 200 mesh.

Methods:

Talc samples were ground to fine powders with Ball mill. The prepared powder was allowed to pass through 250 mesh sieve, and the finer particles were used for the experiment. Beside the powders as prepared as above, the hydrogen saturated form was also prepared with 1N-HCl. Excess acid was washed out with water.

Amberlite CG-120 obtained from the company has Na^+ as exchangeable ion, To see the effect of adsorbed H^+ and Mg^{++} which is supposedly the most abundant in talc, the saturation of the resin with HCl and MgCl_2 was carried out.

The dust formulations of malathion were prepared with the above mentioned original talcs, hydrogen saturated talcs, Na^+ -Amberlite, H^+ -Amberlite and Mg^{++} -Amberlite. In each dust formulation, the concentration of malathion was 2.5 %. Following symbols will be used for each sample.

TAM } original talc powders. A. B. C. D.
 TBM }
 TCM } represent different talc powders
 TDM } from different mines

HTAM } Hydrogen saturated forms of
 HTBM } A. B. C. D.
 HTCM }
 HTDM }

H-RM.....Hydrogen saturated Amberlite
 CG-120

MgRM.....Magnesium "

NaRM.....Sodium "

The malathion contents in the preparations were determined by officially adopted method in Korea. (12, 13)

Times of determination after preparation of the dust formulations were 1, 2, 3, 8, 16 and 31 days.

Water adsorption capacity of the carriers was obtained by the difference in weight of the samples between oven-dry weight and that

which equilibrated with 3.3% H_2SO_4 in a desiccator. (6, 15)

Specific surface was measured by total ethylene glycol retention method (14). Particle size distribution, exchangeable Ca^{++} , Mg^{++} , Na^+ and K^+ , pH and phosphate fixing capacity of the carriers were determined by the usual methods (12, 14, 16, 17, 18).

Result and Discussion

The results of the decomposition study with time are shown in Figure 1.

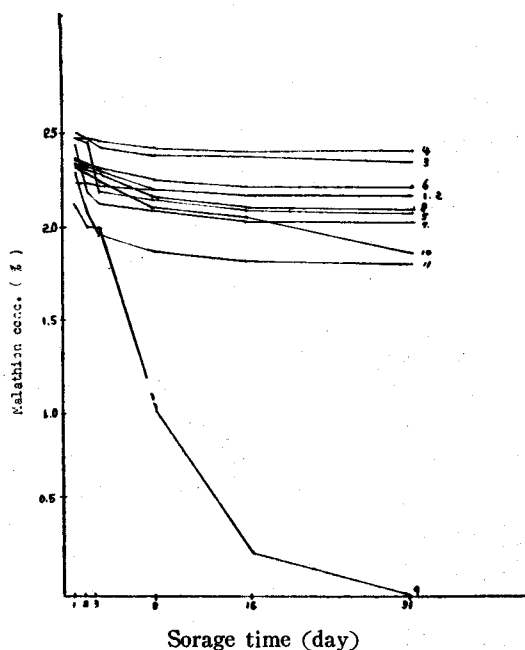


Fig. 1. The amount of malathion left in the dust formulations at various storage time. (storage temp. 26°C)

In the figure the ordinate represents the amount of malathion left in the formulation and the abscissa represents the time.

It is seen from the figure that the amount of malathion decomposed increases with time. The rate of the decomposition, however, decreases with time. This is readily seen from the fact that about 50% of the total decomposed malathion in a month has decomposed within 8 days. This result suggests us that the decomposition may be proportional to the amount of undecomposed malathion in the preparation. A

trial to see whether the decomposition actually is a first order reaction has been attempted. The result, however, indicated the reaction is much more complicated than was thought.

By Comparing between original and H⁺-saturated talcs, it can be readily recognized that the decomposition was greatly accelerated by the presence of hydrogen ion. This hydrogen ion effect was also remarkable even the resin was used. The resin, which has higher cation exchange capacity than the talcs, decomposed greater amount of malathion than the talcs in every case irrespectve of the forms of adsorbed cations.

Comparison among different forms of resin

also indicates that the hydrogen ion really has great effect upon the decomposition. It is surprising to note that none of the malathion is left after a month in the hydrogen saturated Amberlite CG-120. The magnesium saturated resin showed greater ability to decompose the malation than sodium saturated resin. It is just unknomn why such defference actually took place. No work concerning the difference between alkali and alkaline earth cations inabilityty to decompose malathion has been published. This point may require further study.

The physico-chemical properties of the talcs together with final amount of malathion decomposed are listed in Table 1.

Table 1. Some physical properties and the amount of malathion decomposed by the talcs and resin.

Sample	Amount of Malathion decomposed(%)	Moisture adsorbability (%)	PH	Specific surface (m ² /g)
TAM	8.51	3.71	8.80	915.0
TBM	4.44	2.33	8.65	63.6
TCM	7.33	2.73	9.00	522.3
TDM	5.12	2.17	8.44	340.0
HTAM	17.87	2.27	6.20	1095.0
HTBM	7.78	3.8	6.12	85.5
HTCM	17.87	2.43	4.20	506.7
HTDM	12.63	2.44	6.27	348.0
HRM	100.00	65.50	3.53	0
MgRM	21.89	65.60	5.50	0
NaRM	23.22	61.30	5.30	0

The moisture adsorption capacities of the samples as shown in the second column of the table indicate that there is almost no difference among the talcs. The slight difference among the samples may be attributed to some unknown cause, since the amount of moisture adsorbed does not seem to coincide between original and hydrogen saturated forms.

The pH of the original talcs are around 8.5

-9.0. The sample D had the lowest pH and C has the highest. The pH of hydrogen saturated talcs had much lower values than those of original forms. The difference among the hydrogen saturated forms is also noticed. The sample C which had the highest pH in natural state had the lowest value if saturated with hydrogen ion. On the other hand the saturation of D with hydrogen brought the slightest

change in pH from its natural state. In every case, the resin had the lowest pH, and especially the hydrogen saturated from had the lowest pH among all.

The result of specific data as shown in the fourth column indicate that there are great differences among the samples. There are slight difference in the specific surface due to saturation of the talcs with hydrogen ion, however, this slight difference doesn't seem to affect over-all pattern of specific surface of the samples. It is seen that the sample A had the greatest specific surface and C the next. The sample B had least specific surface and this area corresponds to about 1/15 of the sample A. It is interesting to compare the order of specific surface data with that of the per cent malathion decomposed.

Particle size distribution as shown on the next columns indicate that the sample A which had the highest specific surface had highest colloid content while the sample B had least.

General decreasing order of colloid content of the talcs is identical with that of specific surface data if only the original forms were compared. However, for the hydrogen saturated talcs, the order has changed a little. The sample C had higher colloid content than that of sample A if saturation of hydrogen is carried out. It is just uncertain what made these slight differences. It might be due to incomplete dispersion of samples before analysis or it might be due to dissolving power of acid treatment. It may also be due to coagulating power of hydrogen ion since in the samples A and B, the hydrogen saturation caused increases in the 300 mesh fraction while reverse was true for sample C. The difference in such change due to hydrogen saturation should receive more attention.

The exchangeable cations present in the talcs were listed in Table 2. On the last column of the table the sums of these cations are listed.

Table 2. Exchangeable ions of the natural and hydrogen saturated talcs.

Sample	Exchangeable cation (me/100g)				Total Exchangeable cation(me/100g)
	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	
TAM	0.68	0.26	1.05	0.39	2.38
TBM	0.62	0.26	0.11	0.26	1.25
TCM	0.68	0.79	0.49	0.01	1.96
TDM	0.91	0.53	0.68	0.01	2.13
HTAM	4.08	3.16	0.42	0.13	8.46
HTBM	1.09	2.76	0.49	0.67	5.02
HTCM	5.61	2.63	0.27	0.09	8.61
HTDM	1.90	1.78	0.32	0.01	3.81

For the natural samples, calcium ion seems the dominant form even though the presence of magnesium can not be neglected. By saturation of these samples with hydrogen ion greatly increased the "exchangeable" ions. For every sample, the increases in calcium and magnesium ions are noticeable due to saturation with hydrogen ion, and this tendency was

especially noticed for sample A and C. It is just uncertain whether cation exchange capacity of the samples actually increased by saturation of hydrogen ion or whether these ions are present in equilibrate dialyzate. No method to differentiate between adsorbed and free cations seems to be available at this moment.

It is interesting to compare between the total "exchangeable" cations and the amount of malathion decomposed. The sample A and C which decomposed great amount of malathion

had high content of the exchangeable cations.

The amount of phosphate fixed by the samples at various time intervals are shown in Table 3.

Table 3. The amount of phosphate fixed by the talcs and resin at various time intervals, (p. p. m. of P content)

Sample	5 min.	30 min.	1h.	2 hrs.
TAM	1.175	1.57	1.75	1.57
TBM	0.62	0.7	0.75	1.25
TCM	0.75	1.175	1.175	1.25
TDM	0.94	1.00	1.25	1.37
HTAM	0.87	0.94	1.00	1.87
HTBM	1.37	1.50	1.57	1.67
HTCM	0.62	0.75	1.37	1.87
HTDM	0.75	0.94	1.87	1.87
H-RM	0.50	0.70	0.75	0.94
Mg-RM	0.75	0.82	0.94	0.94
Na-RM	0.20	0.25	0.32	0.62

There are some differences among the samples irrespective of whether they are saturated with hydrogen or not. Generally, within a short period, the sample A and C fixed relatively great amount of phosphate than the other two, however, the differences among the samples diminished with time of contact between phosphate and the samples. The treatment of the samples with hydrogen generally decreased the capacity except sample B for which the same treatment increased the capacity. On the other hand, as the contact time became long, the capacity for these samples increased over that of the original samples. It is just unknown why these phenomena took place. The phosphate fixing capacity was determined in hope of finding out the magnitude of the positive charges and relative concentration of some cations which are supposedly responsible for removal of phosphate anion from solution. No difference among the samples seems to exist

as far as the phosphate fixing capacity is concerned.

To better understand the factors which may be responsible for decomposition of malathion the correlation analysis of the physical properties with the amount of malathion decomposed after 31 days of storage was carried out. The correlation analyses are shown in Table 4.

Table 4. The correlation coefficients between the physical properties of the carriers and the amount of malathion decomposed.

Sample	Exchangeable cation	Colloid content	Specific surface
Original talc	0.75	0.93	0.96
H ⁺ Saturated talc	0.79	0.91	0.83

It is seen from the table that some of the physical properties had very good correlation coefficients with the amount of malathion

decomposed. Especially noticeable physical properties were colloid content, specific surface and pH. The relation between colloid content and specific surface can well be understood, since the higher is the colloid content, greater would be the specific surface.

The above correlation analysis if properly interpreted, indicates that the colloid content and pH of the medium are the two most significantly related physical states that govern the amount of decomposition of malathion.

Conclusion

From the experimental results and correlation analysis, the factors which are responsible for the decomposition of malathion and mechanism involved in the process can be postulated as follows.

The colloid content and specific surface are the most significantly correlated physical properties studied. Since it is known that colloids have negative charges on the surface and the reaction of decomposition takes place at the interface, the results of correlation analysis can readily be interpreted as due to the reaction involving the adsorption of a malathion molecule upon negatively charged surface. The process of adsorption is schematically shown in Fig2.

The first stepwise reactions of the decomposition may involve the induced polarization or formation of activated state of a malathion molecule due to electric field of the negatively charged colloid. Since it is known that there is a difference in the electronegativity between adjacent P and S atoms, (P:2.5, S:2.1) it is natural to assume that the P atom will be positively charged relative to S under the influence of negative field due to colloids.

Since the separation of electric charge within a malathion molecule took place, the next step will be the ion-dipole interaction between charged colloid and the molecule.

As the result of shifting of electron clouds which might occur due to interaction, an weakening of the bonds between sulfur and adjacent atoms will result. If hydrogen ion is present nearby, the separation or beaking-up of a malathion molecule into succinate and phosphate moieties might occur.

Final stable forms after the breaking-up will be O,O-Dimethyl dithio phosphate, fumaric acid and ethanol. These end products will be identical with those of a malathion hydrolyzate caused by alcoholic- KOH solution.

From the postulated mechanism, it will be readily understood that the rate of decompos-

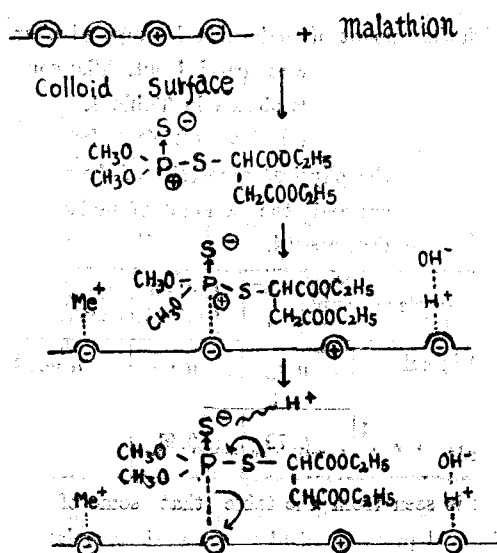


Fig. 2 The process of adsorption and decomposition of malathion in dust formulation.

ition will be accelerated by the presence of hydrogen ion in consistent with the experimental observation.

Summary

The decomposition of malathion in dust for mulations prepared from four Korean talcs as carriers during storage period has been studied.

Amberlite CG-120, a cation exchange resin which has higher cation exchange capacity than talcs, was also used as a carrier in hope of finding out the effect of nagative charge upon the decomposition of malathion. Besides the original talc powders obtained directly from the mines, the hydrogen ion saturated forms were also used as carriers for comparisonal study. The saturated ions for the resin were hydrogen, sodium and magnesium.

As the physical properties of the talcs, colloid content, water adsorption capacity, PH, specific surface, phosphate fixing capacity and exchangeable cations were determined, and these properties were correlated with the amount of the decomposition. Following results were obtained from the experiment.

1. The malathion in the talc in dust was found to decompose around 10-15% of the total within a month. About 50% of the decomposition that took place after a month was found to occur within a week.
2. The resin which has higher cation exchange capacity than the talcs was highly effective in the decomposition of malathion compared with the talcs.
3. In every case the saturation of the exchange complexes with hydrogen ion greatly accelerated the decomposition of malathion.
4. The most highly correlated physical properties with the decomposition were colloid content and specific surface of the talcs.
5. The water adsorption and phosphate fixing capacities of the talcs were found not to correlate with the amount of malathion decomposed.

From the experimetal results it was conclu-

ded that the active negative spots on the colloidal talcs or the resin attract the electro-positive phosphorus atom in a malathion molecule thereby inducing the decomposition easier. The presence of hydrogen ion nearby might cause a catalytic effect in the decomposition of malathion.

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要約

한국산 Talc 4종을 증량제로한 Malathion粉劑의 저장시의 분해를 연구하였다. 분해인자를 규명하기 위하여 Talc보다 양이온 교환능력이큰 양이온 交換樹脂 a-Mberlite CG-120을 비교試料로 택하고 이들에게 H⁺를 포화시킨것과 原광대로의 것 과에서 Malathion의 분해를 調査하였다. 樹脂는

원래의 Na^+ 型外에 Talc에 第一량다고 인정되는 M^{++} 를 포화시킨것도 사용하였다. Talc의 물리적 성질로서 Colloid含量, 水分吸着能, pH 比面면적, 인산固定능력및 치환성 양이온등을 조사하여 이들과 Malathion의 분해올과를 비교하였다. 다음과 같은 결과를 얻었다.

1. Malathion은 보통 Talc粉劑에서 10~15%가 1개월 동안에 분해가 되며 約1주일 동안에 1개월 분량의 半이 분해되었다.
2. 양이온 교환능력이 큰 수지는 Talc보다 분해를

더욱 많이 일으킨다.

3. 수소이온을 포화시키면 Malathion의 분해량이 증가한다.
4. 분해량은 Talc의 물리적 성질중 Colloid함량이 및 比표면적이 큰것에서 많은 것으로 나타났다.
5. 水分吸着能및 인산고정능력과 Malathion의 분해량과는 本실험관관계가 없는 것으로 나타났다 실험결과로써 Malathion의 분해는 증량제의 陰의 荷電點이 P의 원자에 作用하여 일어나고 또한 그때 수소이라는 결론을 내렸다.