The Chemical and Physical Properties of Talcs and Their Behavior on the Decomposition of EPN Dust Formulation. 

Chemical Studies on Organophosphorus Insecticides. VIII

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Kyoto University
Einigen davon waren zwar schon bekannt, aber in geometrischen Beziehungen sehen sie noch nicht ganz rein aus.


30. ク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 有機磷殺虫剤の化学的

研究 第8報 佐藤六郎・久保博司（農林省農業試験所）34. 7. 30 受理

In the previous paper the relationship between chemical and physical properties of tales 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 silica-magnesium complex. The present study was undertaken, furthermore, to determine whether similar evidence could be obtained in the case of EPN talcum dust.
Table 1. Tales, their chemical and physical properties and the rate of decomposition of 1.5% EPN in talcum dust

<table>
<thead>
<tr>
<th>Code</th>
<th>Particle size (mesh)</th>
<th>Minig place</th>
<th>Producer</th>
<th>H₂O sorbed ex. cap % me/100g</th>
<th>Total basicity me/100g</th>
<th>Total basicity me/100g</th>
<th>Decomp. (%) at 50°C Days storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>150-</td>
<td>Manchuria</td>
<td>Asada</td>
<td>0.22</td>
<td>0.35</td>
<td>0.20</td>
<td>0.05</td>
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<tr>
<td>B</td>
<td>150-200</td>
<td></td>
<td></td>
<td>0.23</td>
<td>0.36</td>
<td>0.24</td>
<td>0.06</td>
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<tr>
<td>C</td>
<td>200-250</td>
<td>V</td>
<td></td>
<td>0.25</td>
<td>0.45</td>
<td>0.25</td>
<td>0.07</td>
</tr>
<tr>
<td>D</td>
<td>250-300</td>
<td>V</td>
<td></td>
<td>0.25</td>
<td>0.62</td>
<td>0.23</td>
<td>0.10</td>
</tr>
<tr>
<td>E</td>
<td>300-</td>
<td></td>
<td></td>
<td>0.40</td>
<td>0.98</td>
<td>0.46</td>
<td>0.15</td>
</tr>
<tr>
<td>F</td>
<td>150-</td>
<td>Gunma</td>
<td></td>
<td>0.62</td>
<td>1.32</td>
<td>0.50</td>
<td>0.05</td>
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<tr>
<td>G</td>
<td>150-200</td>
<td></td>
<td></td>
<td>0.70</td>
<td>1.65</td>
<td>0.65</td>
<td>0.07</td>
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<tr>
<td>H</td>
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<td>V</td>
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<td>1.74</td>
<td>0.67</td>
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<td>1.99</td>
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<td>J</td>
<td>300-</td>
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<td></td>
<td>1.00</td>
<td>2.40</td>
<td>0.83</td>
<td>0.23</td>
</tr>
<tr>
<td>M</td>
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<td>Kunimine</td>
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<td>1.31</td>
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<tr>
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<td></td>
<td>0.61</td>
<td>1.45</td>
<td>0.67</td>
<td>0.15</td>
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<tr>
<td>R</td>
<td>200-250</td>
<td>V</td>
<td>Yukizirushi</td>
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<td>0.12</td>
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<td>V</td>
<td></td>
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<td>1.11</td>
<td>0.50</td>
<td>0.15</td>
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<tr>
<td>T</td>
<td>300-</td>
<td>V</td>
<td></td>
<td>0.52</td>
<td>1.20</td>
<td>0.56</td>
<td>0.19</td>
</tr>
<tr>
<td>V</td>
<td>300-</td>
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<td>W</td>
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<td>Saitama</td>
<td>Kantobentonaito</td>
<td>0.55</td>
<td>0.95</td>
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<td>0.10</td>
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<tr>
<td>Y</td>
<td>200-250</td>
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<td>0.84</td>
<td>1.83</td>
<td>0.74</td>
<td>0.13</td>
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<td>Z</td>
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<td></td>
<td>0.88</td>
<td>2.12</td>
<td>0.94</td>
<td>0.15</td>
</tr>
</tbody>
</table>

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 tales 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 insecticides 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. 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. 157.
Fig. 1-4 The correlation 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).

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The data illustrated 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.
Acknowledgement

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

References

4) Suwanai, Nogyo Gijutsu Kenkyuo Hokoku, 1, C-7 and 2, C. -9.


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 有機耕作
虫剤の化学的研究 第9報 佐藤六郎・久保博司（農林省農業検査所）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、ならびに水分吸着性、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、これらの特性と methyl parathion の分解との相関性を検討した。クレーの場合は数つかの分
解要因が交錯しているが、しかし常温下において最も本質的な要因となっているものは塩基性である。
クレーの酸性は高湿下において 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