CONTENTS

TOXICITY OF CERTAIN HERBICIDES IN SOILS
A. S. CRAFTS

STUDIES ON THE ACTIVATION OF HERBICIDES
A. S. CRAFTS and H. G. REIBER

MOVEMENT OF CARBON DISULFIDE VAPOR IN SOILS AS AFFECTED BY SOIL TYPE, MOISTURE CONTENT, AND COMPACTION
H. A. HANNESSON
STUDIES ON THE ACTIVATION OF HERBICIDES

A. S. CRAFTS AND H. G. REIBER
STUDIES ON THE ACTIVATION OF HERBICIDES
A. S. CRAFTS and H. G. REIBER

INTRODUCTION

Early in 1940 Chabrolin (1940) reported that sodium pentachlorophenate at a concentration of 1.5 per cent killed wild-radish plants. Used at a dosage corresponding to 20 kg per hectare, it was effective as a selective herbicide against certain annual dicotyledonous weeds in cereals. Later in the same year Hance (1940) claimed that sodium pentachlorophenate functions as an activator with common herbicides such as sodium arsenite and sodium chlorate.

Tests in 1941 by R. N. Raynor at this station failed to indicate activation when sodium pentachlorophenate was used with sodium arsenite and sodium chlorate. The solutions were sprayed on grasses (mostly *Hordeum murinum* L.) and mixed annual weeds. Under the semiarid conditions existing, no synergism could be noted. Sodium pentachlorophenate proved toxic and, in solution, spread well on the grasses. But whenever a given concentration of sodium chlorate or sodium arsenite was applied, with and without sodium pentachlorophenate, the total toxicity of each mixture was equal only to the sum of the toxicities of the separate ingredients. Our tests varied from those of Hance (1940). We compared sodium arsenite and sodium chlorate solutions with and without sodium pentachlorophenate—that is, the concentration of arsenite or chlorate was the same in the two solutions being compared. Hance, on the contrary, compared his "activated" solutions with a so-called "standard" formula containing a higher concentration of the herbicide being tested.

CONTROLLED EXPERIMENTS ON ACTIVATION

Because many variables are difficult to control in the field, the results of the above-described field tests were checked in the greenhouse. The testing method used has since proved valuable in comparing the relative merits of many chemicals as contact herbicides. Indicator plants (both crop plants and weeds) are grown in soil in no. 10 cans. When they are large enough for testing (usually 4 to 10 inches high), each can is placed on a turntable, and the spray solution is applied with an atomizer, using about 4 pounds of air pressure. The percentage injury is estimated daily until a constant condition is reached. By this method large numbers of cultures, seeded the same day and grown under the same conditions, can be treated in a short time, the type or concentration of spray solution constituting the chief variable.

In preliminary tests, sodium pentachlorophenate was about twice as toxic as sodium chlorate. In the first test on activation, a 1 per cent solution of sodium pentachlorophenate and a 2 per cent solution of sodium chlorate were...
Fig. 1.—Toxicity of sodium pentachlorophenate, sodium chlorate, and their combinations to *Brassica nigra*, *Amsinckia Douglasiana*, and *Centaurea solstitialis*. Sodium pentachlorophenate concentration, 1 per cent; sodium chlorate concentration, 2 per cent at full strength. Volume ratios for the combinations below each graph.
prepared. Since 10 ml of liquid was required to wet the cultures, a series was
designed to compare the toxicities of these two chemicals and their combina­
tions. These two solutions were used in the following proportions by volume:
10 : 0 ; 8 : 2 ; 6 : 4 ; 4 : 6 ; 2 : 8 ; 0 : 10.

Since the total volume of solution in each case was the same and the toxici­
ties were supposed to be approximately equal, any synergistic action should
show up as an increase in toxicity above the general level determined by the
two pure solutions. For purposes of comparison, the applications were made
at full strength, one-half strength, and one-fourth strength of the solutions.
Figure 1 shows the results. Each point on each curve represents an average
of four toxicity readings made 1, 2, 4, and 6 days after spraying.

Though the graphs of figure 1 do not give undisputed evidence of syner­
gism, one interesting feature should be noted. In every instance the toxicity
values of the pure chlorate solutions are appreciably lower than those of the
solutions containing 20 per cent sodium pentachlorophenate solution and 80
per cent sodium chlorate solution. Because this type of curve is characteris­
tic of synergism, it seems possible that some activation has occurred in this
experiment.

Graphs A, B, and C of figure 1, showing the results on black mustard (Bras­
sica nigra Koch) for full, one-half, and one-fourth-strength solutions re­
spectively, indicate that the concentration of sodium chlorate was not high
enough to give a horizontal line through the points. Evidently, under the
experimental conditions, sodium pentachlorophenate was three to four times
as toxic as chlorate.

The fluctuations in toxicity between the six solutions of each experiment
are inherent in the biological testing method. Though less uniform than desir­
able, comparison of results gives a measure of toxicity. Injury on fiddleneck
(Amsinckia Douglasi ana DC.) and yellow star thistle (Centaurea solstitialis
L.) was fairly comparable with that on black mustard.

For reasons to be explained later in this paper (p. 496), the ammonium salt
of pentachlorophenol is more toxic than the sodium salt. To determine whether
this increased toxicity would affect the outcome of the sort of experiment just
described, a second set of tests was run, using the ammonium salt. The same
concentrations were used as before, and the test plants were similar. Each
point on each curve is an average of 5 readings. Figure 2 presents the results.

Comparison with the graphs of figure 1 shows that, as expected, the ammo­
nium salt of pentachlorophenol is two or more times as toxic as the sodium salt.
This situation may be judged by comparing the B and E graphs (half strength
ammonium salt) of figure 2 with the A and D graphs (full strength sodium
salt) of figure 1. Because curves A and D of figure 2 lie within the 95 per cent
toxicity level through the four highest concentrations of ammonium penta­
chlorophenate, it seems that the concentration of this toxicant was too high
to give significant results in this type of test. Referring to figure 2, if curves
A and D are examined between the fourth and sixth points, if curves B and E
are examined between the third and sixth points, and if these are compared
with curve C, the significant parts of these curves are all seen to be essentially
straight lines; F is curved in the wrong direction to indicate activation. Hence
this set of experiments yields no evidence of synergism.
Fig. 2.—Toxicity of ammonium pentachlorophenate, sodium chlorate, and their mixtures to *Brassica nigra*, *Amsinckia Douglasiana*, and *Centaurea solstitialis*. Ammonium pentachlorophenate concentration, 1 per cent; sodium chlorate concentration, 2 per cent at full strength. Volume ratios for the mixtures below each graph.
To ascertain the effect of sodium pentachlorophenate upon arsenic toxicity, experiments were conducted with two different arsenic solutions. The first was a 0.2 per cent solution of chemically pure sodium arsenite. Since no analysis was given, the exact concentration of arsenic was not known. The second solution was 0.2 per cent \( \text{As}_2\text{O}_3 \) and was made up by mixing \( \text{As}_2\text{O}_3, \text{NaOH} \), and water in the proportions 4:1:3 by weight. This made a solution of sodium acid arsenite containing 50 per cent \( \text{As}_2\text{O}_3 \) by weight, which was diluted to 0.2 per cent. In each experiment sodium pentachlorophenate solution 0.2 per cent in concentration was used.

Figure 3 illustrates the results with the first solution mentioned above. The test plants were young carrot seedlings, nettle-leaf goosefoot (\textit{Chenopodium Murale} \text{L.}) and chickweed (\textit{Stellaria media} \text{[L.]} \text{Cyr.}). The curves are essentially straight lines. Figure 4 shows the results with the second solution, the test plants being common foxtail (\textit{Hordeum murinum} \text{L.}). Young carrot seedlings in the pots were all injured to such an extent (95 to 100 per cent) that their values were rendered useless. According to these curves, no synergism is shown by the arsenic and pentachlorophenate mixtures. On the other hand, these experiments show that salts of pentachlorophenol are extremely toxic chemicals. The sodium salt is somewhat more toxic than sodium arsenite on the \( \text{As}_2\text{O}_3 \) basis and at least three times as toxic as sodium chlorate when used as a contact spray. The toxicity of the ammonium salt of pentachlorophenol is even greater, being approximately twice that of the sodium salt.

One further experiment was conducted using a 0.2 per cent sodium pentachlorophenate solution, a sodium arsenite solution 0.2 per cent in \( \text{As}_2\text{O}_3 \), and a 0.4 per cent sodium chlorate solution. The three solutions were mixed in various proportions by volume and applied to cultures having young carrot seedlings and common foxtail. The carrots were completely killed in all cultures within 8 days and in all but one culture within 2 days. Results on the common foxtail plants are given in table 1.

Although the average toxicity values range from 21 to 35 per cent, there seems to be no definite pattern or trend. Again, evidence of synergism is lacking.

**ACTIVATION OF SUBSTITUTED PHENOL HERBICIDES**

\textit{Sodium Dinitro-o-cresylate}.—Sodium dinitro-o-cresylate was first used as a weed spray in France in 1933. It was applied experimentally in this country during the winter of 1937-38 by Westgate and Raynor (1940) and soon gained in popularity. At present, many thousands of acres of grain, flax, and onions are sprayed with Sinox* annually. About two years after its introduction here, experimenters found that the addition of ammonium sulfate or sodium bisulfate would greatly increase the toxicity of this organic herbicide. By using one of these relatively nontoxic salts, Harris and Hyslop (1942) increased the physiological action of sodium dinitro-o-cresylate in both intensity and rate. Immediately accepted by the trade, the practice of adding an activator to Sinox has become common.

Studies on the chemical mechanism of Sinox activation were started in

---

*Sinox is the trade name for a proprietary selective herbicide consisting of 30 per cent sodium dinitro-o-cresylate and 70 per cent water.
Fig. 3.—Toxicity of sodium pentachlorophenate, sodium arsenite, and their mixtures to carrots, Chenopodium Murale, and Stellaria media. Sodium pentachlorophenate concentration, 0.2 per cent; sodium arsenite concentration, 0.2 per cent at full strength. Volume ratios for the mixtures below each graph.

Fig. 4.—Toxicity of sodium pentachlorophenate, arsenic trioxide, and their mixtures to Hordeum murinum. Sodium pentachlorophenate concentration, 0.2 per cent; arsenic trioxide concentration, 0.2 per cent at full strength. Volume ratios for the mixtures below each graph.
December, 1942, and have been pursued intermittently since that time. Cultures of barley and flax with the weeds *Amsinckia Douglasiana* and *Brassica nigra* were used in the tests, and applications were made by means of the atomizer and turntable previously mentioned.

### TABLE 1

**Toxicity of Sodium Arsenite, Sodium Chlorate, and Sodium Pentachlorophenate on *Hordeum murinum*, When Applied in Various Proportions by Volume* (Total Volume Applied to Each Culture 10ml)

<table>
<thead>
<tr>
<th>Culture no.</th>
<th>Composition of solution, volume ratios</th>
<th>Average toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As$_2$O$_3$</td>
<td>NaClO$_3$</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>11</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>12</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>13</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>14</td>
<td>80</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>33$\frac{1}{2}$</td>
<td>33$\frac{1}{2}$</td>
</tr>
</tbody>
</table>

* Concentrations used were: sodium arsenite 0.2 per cent, sodium chlorate 0.4 per cent, and sodium pentachlorophenate 0.2 per cent.

### TABLE 2

**Relation of Activator Concentration to Toxicity of Sinox Solutions* on *Amsinckia Douglasiana* and *Brassica nigra**

<table>
<thead>
<tr>
<th>Activator concentration in weight</th>
<th>Toxicity of Sinox with ammonium sulfate to</th>
<th>Toxicity of Sinox with sodium bisulfate to</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><em>Amsinckia Douglasiana</em></td>
<td><em>Brassica nigra</em></td>
</tr>
<tr>
<td></td>
<td>per cent</td>
<td>per cent</td>
</tr>
<tr>
<td>0.000</td>
<td>14.1</td>
<td>12.5</td>
</tr>
<tr>
<td>0.025</td>
<td>93.3</td>
<td>78.0</td>
</tr>
<tr>
<td>0.050</td>
<td>93.3</td>
<td>86.8</td>
</tr>
<tr>
<td>0.075</td>
<td>93.3</td>
<td>92.1</td>
</tr>
<tr>
<td>0.100</td>
<td>93.3</td>
<td>92.6</td>
</tr>
<tr>
<td>0.150</td>
<td>93.3</td>
<td>90.8</td>
</tr>
</tbody>
</table>

* Sinox concentration was constant at 0.2 per cent. Activator concentration varied from 0.0 to 0.4 per cent.

In the first study, varying amounts of ammonium sulfate and sodium bisulfate were added to Sinox solutions, the concentration of the latter being constant throughout the series. Table 2 reports the results. The values given are the average toxicity of six successive readings made 1, 2, 4, 6, 8, and 10 days after spraying.

Each stock solution contained 4 grams of chemical to the liter of solution,
(except the highest concentration of activator, which was 30 grams per liter). All solutions were made up to a final volume of 12 ml per application.

As table 2 indicates, both salts used were very effective in increasing the toxicity of the Sinox solutions. Furthermore, in concentrations throughout the range one fourth to twice that of the toxicant, there was no significant change in toxicity. From table 2 one might conclude that the addition of one equivalent of the ammonium sulfate (66 gms) per mole of cresylate (198 gms) is sufficient to bring about full activation at this concentration of Sinox. The same reasoning applies fairly well to the sodium bisulfate.

If equivalent amounts of ammonium sulfate and Sinox will give full activation, then the ammonium salt of dinitro-o-cresol should be as effective as the activated sodium salt. On the other hand, if excess activator above the equivalent amount provides additional toxicity, then some other factor is involved. The range of concentrations must be such that toxicities through the middle of the range are included to obtain significant differences. To test this reasoning, the experiments reported in tables 3 and 4 were performed. Ammonium dinitro-o-cresylate solution was prepared at a concentration of 0.2 per cent. Sinox, ammonium sulfate, and sodium bisulfate solutions were 0.4 per cent in concentration. The solutions were mixed as indicated in the tables and were made up to a final volume of 8 ml for each application.
Although no significant differences appear in the higher concentrations, at the last two rates of application, that is, in the more dilute range, the ammonium dinitro-o-cresylate was somewhat less toxic than the activated Sinox solutions. The activators were in excess of equivalence in all solutions. Apparently, therefore, in this concentration range something other than an equivalent amount of ammonium ion is required for full activation of the dinitro-o-cresylate. Furthermore, sodium bisulfate forms a white precipitate which, when applied in suspension, produces a maximum toxicity. Judging from these observations, the activation of Sinox is the effect of the free acid, or of the acid produced by the hydrolysis of the ammonium ion, and not of ammonium ion itself. Subsequently it has been proved that ammonium sulfamate, aluminum sulfate, and even sulfuric acid will increase the toxicity and rapidity of Sinox action. Sodium sulfate had no effect. Apparently any chemical

**TABLE 5**

**TOXICITY OF SINOX AND AMENDMENTS TO CARROTS, Brassica nigra, AND Stellaria media**

<table>
<thead>
<tr>
<th>Chemical and concentration</th>
<th>Toxicity to Brassica nigra per cent</th>
<th>Toxicity to carrots and Stellaria media per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sinox at 0.2 per cent</td>
<td>64.6</td>
<td>20.0</td>
</tr>
<tr>
<td>Sinox at 0.2 per cent + NH₄OH at 0.05 per cent*</td>
<td>57.1</td>
<td>14.2</td>
</tr>
<tr>
<td>Sinox at 0.2 per cent + (NH₄)₂SO₄ at 0.2 per cent</td>
<td>89.3</td>
<td>83.8</td>
</tr>
</tbody>
</table>

* Sinox solutions containing NH₄OH above this concentration were toxic from the ammonia present.

that will provide hydrogen ions for the formation of dinitro-o-cresol in the spray solution will bring about activation.

Additional evidence on this problem is furnished by experiments in which ammonium sulfate and ammonium hydroxide were used in Sinox solutions. Table 5 shows the results.

As this table indicates, ammonium hydroxide repressed the toxicity of Sinox, whereas ammonium sulfate increased it. Since, furthermore, the parent dinitro-o-cresol dissolved in a nontoxic oil produces a solution fully as toxic, on a concentration basis, as does the activated sodium salt, undoubtedly the chemical mechanism of activation involves simply the provision of the free acid, dinitro-o-cresol, in the spray solution.

Table 6 presents data from a controlled laboratory experiment in which shoots of wild morning-glory (Convolvulus arvensis L.) were dipped in various solutions containing Sinox with ammonium sulfate, Sinox with ammonium hydroxide, plain Sinox, and ammonium dinitro-o-cresylate respectively. Readings of the pH values of all solutions were made with a glass electrode. After being dipped, the shoots were allowed to drain and then were set upright with their basal ends in tap water. Toxicity values as denoted by readings 1, 2, 3, 4, and 6 days after dipping are averaged in the last column.

Clearly, an alkaline reaction prohibiting the formation of the cresol in the Sinox solution reduces toxicity. The table shows a marked difference in toxicity of straight Sinox solutions and those containing the minimum amount
of activator, although the differences in pH are relatively small. This may be due to a buffering action which will be discussed later in detail (p. 498).

**Sodium Pentachlorophenate.**—If the fundamental behavior of all substituted phenol molecules is similar, it should be possible to activate sodium pentachlorophenate in the same way as Sinox. Table 7 presents data on toxicity tests with sodium pentachlorophenate, used alone or activated with aluminum sulfate, ammonium sulfate, and sodium bisulfate. Results are on *Chenopodium Murale* and *Centaurea solstitialis*. Toxicity readings were made 1, 3, and 8 days after treatment.

### Table 6
**Relation between pH Values and Toxicity of Cresylate Solutions to Convolvulus arvensis**

<table>
<thead>
<tr>
<th>Chemical and concentration, per cent</th>
<th>(NH₄)₂SO₄ Reaction of solution</th>
<th>Toxicity</th>
<th>Chemical and concentration, per cent</th>
<th>NH₄OH Reaction of solution</th>
<th>Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dinitro-o-cresylate (Sinox):</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>0.60</td>
<td>6.55</td>
<td>98</td>
<td>0.20</td>
<td>0.16</td>
</tr>
<tr>
<td>0.10</td>
<td>0.30</td>
<td>6.76</td>
<td>94</td>
<td>0.10</td>
<td>0.08</td>
</tr>
<tr>
<td>0.05</td>
<td>0.15</td>
<td>7.00</td>
<td>70</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>0.20</td>
<td>0.20</td>
<td>6.95</td>
<td>93</td>
<td>0.20</td>
<td>0.053</td>
</tr>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>7.08</td>
<td>86</td>
<td>0.10</td>
<td>0.027</td>
</tr>
<tr>
<td>0.05</td>
<td>0.05</td>
<td>7.25</td>
<td>73</td>
<td>0.05</td>
<td>0.014</td>
</tr>
<tr>
<td>0.20</td>
<td>0.066</td>
<td>7.03</td>
<td>94</td>
<td>0.20</td>
<td>0.018</td>
</tr>
<tr>
<td>0.10</td>
<td>0.033</td>
<td>7.20</td>
<td>86</td>
<td>0.10</td>
<td>0.009</td>
</tr>
<tr>
<td>0.05</td>
<td>0.017</td>
<td>7.34</td>
<td>62</td>
<td>0.05</td>
<td>0.005</td>
</tr>
<tr>
<td>Ammonium dinitro-o-cresylate:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>...</td>
<td>7.32</td>
<td>56</td>
<td>...</td>
<td>6.72</td>
</tr>
<tr>
<td>0.10</td>
<td>...</td>
<td>7.42</td>
<td>56</td>
<td>...</td>
<td>6.68</td>
</tr>
<tr>
<td>0.05</td>
<td>...</td>
<td>7.43</td>
<td>11</td>
<td>...</td>
<td>6.70</td>
</tr>
</tbody>
</table>

As these results show, sodium pentachlorophenate can be activated by any acid salt that does not tie the toxicant up in an insoluble compound. In fact, pentachlorophenol itself is more toxic than its sodium salt, its chief drawback being its low solubility. The pentachlorophenol reported in the footnote of table 7 was a micronized product, thoroughly dispersed in water by violent shaking before application. It produced a toxicity of 66.6 per cent to *Chenopodium Murale* and *Centaurea solstitialis*. This chemical is also soluble in oil to a concentration of about 8 per cent by weight. A solution containing 0.5 per cent pentachlorophenol in any oil of proper viscosity makes an excellent general contact herbicide. An emulsion containing 4 pounds of pentachlorophenol in 6 gallons of diesel oil, made up to 100 gallons with water and stabilized with 0.80 pound of Vatsol⁷ or similar wetting agent, has proved an inexpensive general contact herbicide. A spray machine with agitator is required for application, since the emulsion is not stable enough to stand for any length of time. The ammonium salt of pentachlorophenol proved as toxic as the activated sodium salt. In concentrations ranging between 0.25 and 0.50

---

⁷ Vatsol is a dioctyl ester of sodium sulfosuccinate; it is a wetting and emulsifying agent.
per cent by weight, it gives promise of being a practical selective herbicide. It may be produced at a low cost, and it does not have the objectionable yellow color of dinitro compounds.

**Other Substituted Phenols.**—During routine testing of a great many organic chemicals, comparisons have been made between sodium and ammonium salts. In all the tests conducted so far the ammonium salts have proved more toxic than the sodium salts, and a remarkable parallelism occurs between the relative toxicities of the ammonium salts in aqueous solution and the

---

**TABLE 7**

TOXICITY OF 1 PER CENT SODIUM PENTACHLOROPHENATE SOLUTION ALONE AND ACTIVATED TO CHENOPODIUM MURALE AND CENTAUREA SOLITARIA*

<table>
<thead>
<tr>
<th>Activator concentration in weight</th>
<th>Toxicity with $\text{Al}_2(\text{SO}_4)_3$ per cent</th>
<th>Toxicity with $(\text{NH}_4)_2\text{SO}_4$ per cent</th>
<th>Toxicity with $\text{NaHSO}_4$ per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>28.3</td>
<td>28.3</td>
<td>28.3</td>
</tr>
<tr>
<td>0.500</td>
<td>85.0</td>
<td>85.0</td>
<td>85.0</td>
</tr>
<tr>
<td>0.250</td>
<td>83.3</td>
<td>83.3</td>
<td>80.0</td>
</tr>
<tr>
<td>0.125</td>
<td>76.6</td>
<td>80.0</td>
<td>75.0</td>
</tr>
<tr>
<td>0.062</td>
<td>66.6</td>
<td>65.0</td>
<td>58.3</td>
</tr>
</tbody>
</table>

* A 1 per cent pentachlorophenol suspension in water produced a toxicity to the above weeds of 66.6 per cent.

The activation of substituted phenol herbicides has been proved beyond question and is being employed daily in the use of Sinox and similar spray materials. Furthermore, a logical chemical mechanism to explain such activation has been postulated.

Other cases of activation are less well substantiated. Data presented in this paper offer no evidence for activation of sodium arsenite solution by sodium pentachlorophenate.

When one compares the “activated” formula of Hance* (5 pounds $\text{As}_2\text{O}_3$, as sodium meta arsenite, 2 pounds sodium pentachlorophenate, 2 pounds sodium chlorate, and 2 pints of wetting agent per 100 gallons) with the unactivated formula (10 pounds $\text{As}_2\text{O}_3$ and 2 pints of wetting agent per 100 gallons), it seems evident, considering the toxicities of the separate ingredients, that a simple summation of the individual toxicities should approximately balance. If one were to add a pound of ammonium or aluminum sulfate to this formula, plus enough sulfuric acid to make it very slightly acid, activation of the pentachlorophenate should considerably increase its toxicity, as occurred in the experiments reported in table 6.

Concerning the activation of chlorate, the evidence is less clear. According to Dancaster (1942), several metallic salts that act as catalysts in oxidation processes increase the rate of killing by sodium chlorate as a contact herbicide.

* F. E. Hance. Private correspondence, 1941.
Vanadium pentoxide was the best of the group. Whether sodium pentachlorophenate would act in a like capacity is not known.

When one views the problem from the reverse angle, it seems possible that the sodium chlorate might be activating the pentachlorophenate. Decision on this matter, however, must await further research.

In studying the chemical mechanism of Sinox activation, one sees that reaction of the spray solution alone is not sufficient to control the process. Considering the results given in table 6, the differences in pH between the Sinox solutions with equivalent amounts of ammonium sulfate and sodium dinitro-o-cresylate and those with no activator are not significant; yet the activated solutions were much more toxic. The explanation comes in a consideration of the reaction on the plant. In case of the unactivated solution, the dinitro-o-cresol formed by the hydrolysis of the cresylate ion may be selectively absorbed by the plant. Such absorption, removing the cresol, results in further hydrolysis, as shown by the following equation

\[ \text{PO}^- + \text{H}_2\text{O} \rightleftharpoons \text{POH} + \text{OH}^- \]

where \text{PO}^- and \text{POH} are the substituted phenylate ion and phenol respectively. The increasing alkalinity of the solution thus limits the concentration of the phenol in the solution.

In the activated solution, containing either an acid salt (NaHSO_4) or an ammonium salt, the hydroxide ion produced combines with the acid or with the ammonium ion and thus allows further production of the cresol. Buffering may also be accomplished by addition of a strong acid or a strongly acid salt. In this case, when the pH goes below a value of about 5.2, a finely divided white precipitate of dinitro-o-cresol is formed; and as long as this solution remains saturated, activation is maintained.

It has been postulated that dinitro-o-cresol is more soluble than its salts in the plant cuticle, and therefore enters the plant more readily. The wide variety of plants responding to activated Sinox solution indicates, however, that something more fundamental is involved. Possibly the entrance of the toxicant into the protoplasm and its reaction with the protoplasm are somehow conditioned by its molecular state.

Since a Sinox solution remains activated in the region of neutrality, provided ammonium sulfate is present, it seems evident that activation is determined primarily, not by the concentration of dinitro-o-cresol in the solution, but by the selective absorption of its molecules by the plant. If the concentration were the only problem involved, one would expect activation to occur only in the region of pH 5.2 or below.

Two important practical applications may be derived from these chemical studies on Sinox activation. First, in order to insure maximum activation in the field, one may add an equivalent amount of ammonium sulfate (about 1 pound per gallon of Sinox) and then (using the cheapest source of acid available) acidify the solution until a slight precipitate occurs. For convenience sodium bisulfate is probably best, though sulfuric acid could be used. By this method the ammonium salt acts as a buffer, and the formation of a white precipitate serves as an indicator of the proper reaction. An alternative method would be to use acid alone, allowing the dispersed dinitro-o-cresol to
act as a buffer. If, however, acid in excess of the capacity of the cresol were added, the result might be a corrosive mixture that would ruin the spray rig. Another method would be to use several equivalents of ammonium sulfate. This would be somewhat more expensive.

The second point refers to the use of the ammonium salt of dinitro-o-cresol or any other substituted phenol herbicide. Conceivably, since such a small amount of toxicant is required, in extremely alkaline water the buffer capacity of the ammonium ion might be exceeded; the alkalinity would repress absorption. The addition of sodium bisulfate until the first appearance of the white precipitate would insure the treatment against failure.
LITERATURE CITED

Chabrolin, C.

Dancaster, E. A.

Hance, F. E.

Harris, L. E., and G. R. Hyslop.