possibly with the larger molecular size of the carboxyacids—e.g., malathion monoacid, mol. wt. 302, compared with dimethyl phosphorothioate, mol. wt. 142.

It had been hoped to study fecal excretion in the dog, but the animals had to be fasted and were also disturbed by the restriction of the metabolism cage; thus dog X did not defecate during the whole of the control period.

In the rat, the fraction of chloroform-extractables (malathion plus malaoxon) was greatly increased in blood and in the whole animal; in the blood the malaoxon level was reduced. These observations parallel those of Seume and O'Brien for rat tissues in vitro. In the dog, the chloroform-extractable picture in blood was obscure: No conclusions could be drawn. The levels of total radioactivity of chloroform-inextractable metabolites in the blood were raised somewhat at first, but these effects had disappeared 10 hours after treatment.

These results do not permit a final verdict on the ultimate mechanism of potentiation. It appears certain that in vivo, as in vitro, carboxyesterase(s) is (are) inhibited by EPN. That this inhibition gives rise to an increase in malathion level has been shown only in the rat (for blood and whole animal). The rat results confirm the hypothesis of Seume and O'Brien (9) that there is an actual reduction of the concentration of malaoxon at the hypothetical target site and not an increased level, unless measurements on blood and the whole body are a very inaccurate reflection of events at the target site. If this is so, the effectiveness of EPN-potentiated malathion must be caused by an increased persistence of malaoxon at the target site, rather than an increased concentration. A final conclusion can be based only upon a more precise study of potentiation in vivo.

Acknowledgment

The authors are indebted to R. C. Herrin, Department of Physiology, University of Wisconsin, for providing the dogs and giving a great deal of his time to handling them; to Shirley DuBreuil and R. W. Young, American Cyanamid Co., Stamford, Conn., for providing the characterized malathion derivatives; and to G. D. Thorn, Pesticide Research Institute, London, Canada, for a sample of malaoxon. The skilled technical assistance of Claire Asselin and Judy Engel is gratefully acknowledged.

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INSECTICIDE DECOMPOSITION

Clay-Catalyzed Decomposition of Insecticides

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LARGE QUANTITIES OF INSECTICIDES are formulated in the form of dusts or wettable powders in which the toxicant is mixed with a finely ground, natural clay which dilutes the insecticide to concentrations suitable for agricultural use, and imparts the desirable properties of flowability and dispersibility to the dust. Various mineral clays (attapulgite, kaolinite, montmorillonite, etc.) are used as supposedly chemically inert diluents. Prior to these studies, it had been recognized that

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clay-diluted chlorinated insecticides occasionally decompose, sometimes becoming sufficiently hot to ignite spontaneously. Investigations (3) showed that the decomposition was promoted by the acid sites of the clay and that appropriate neutralization could reduce decomposition to negligible rates. Since the introduction and widespread use of clay-deactivators (3, 5) this problem of decomposition has virtually disappeared.

Early studies of the decomposition of dieldrin in solution showed that the reaction is catalyzed by mineral acids or even wet ferric chloride. Active clays were examined with indicator dyes and found to be surprisingly strong acids, especially when dry. Acidic diluents are shown to catalyze the decomposition of

DDT, aldrin, toxaphene, chlordan, dieldrin, heptachlor, Aramite, and endrin. Although these compounds have the carbon-chlorine bond in common, the decomposition reactions do not appear to involve only this bond. With the epoxidized insecticides (dieldrin and endrin), the epoxy group disappears and the formation of carbonyl groups is indicated by infrared studies. With endrin, the main product of decomposition has been identified as a ketone of unchanged molecular weight. A wide variety of diluents has been investigated but most of the work has been done with Velvex (a kaolinite clay) or Attaclay (an attapulgite clay).

Two experimental innovations were used extensively: indicator dyes to

Decomposition of insecticides occurs in wettable powders and dusts as a result of the catalytic action of the clay diluent. The heat evolved is occasionally sufficient to cause spontaneous ignition. Rates of reaction of these insecticides in the presence of various clay diluents increase with increasing acidity of the clay surface. Treatment of the clays with volatile organic bases or basic-acting substances, such as urea or hexamethylene-tetramine, reduces the acid strength and diminishes the rate of decomposition accordingly. Sodium clays are usually sufficiently neutralized with one molecule of the appropriate base for each sodium ion. Reaction rates were determined from data obtained by infrared analysis or bioassay of samples from isothermal storage, and by differential thermal analysis. With 25% concentrates the reactions were zero order, and half times of reaction decreased upon dilution with clay reaching a minimum at two molecules of insecticide per exchange ion.
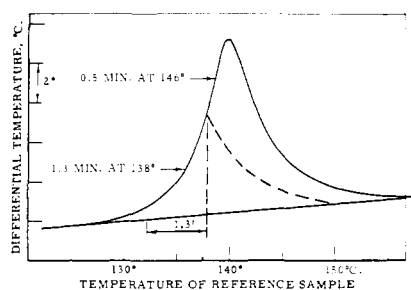

Figure 1. Exothermic peak obtained in differential thermal analysis of 25% dieldrin-Attaclay mixture

predict catalytic activity of acidic solids, and differential thermal analysis to measure reaction rates.

Experimental Methods

Acid Strength from Indicator Color Changes. The acid strength of a clay surface can be estimated with the method suggested by Walling (10) and extended by Benesi (1). This method consists of contacting separate samples of the clay under study with each member of a set of appropriate indicators (herein called Hammett indicators), and noting the resulting colors of the adsorbed indicators. If one indicator gives its acid color and a second its basic color when adsorbed on a given clay, the acid strength of that clay must lie between those of the two indicator acids.

The Hammett indicators used to estimate acid strengths of clay surfaces are listed in Table I. This class of indicators is used to estimate acid strengths of solid surfaces in terms of Hammett and Deyrup's H_0 scale (4), which can be considered an extension of the pH scale into media where hydrogen ion activity is no longer equivalent to its stoichiometric concentration.

Amine Titration. The method used to titrate clay surfaces is that developed by Benesi (2), who extended the method first employed by Johnson (6). It consists of measuring the amount of n-butylamine needed to neutralize the clay surface to each of the Hammett

Table I. Properties of Hammett Indicators

Indicator	pK_a	Basic Color	Acid Color
Phenylazonaphthylamine	+4.0	Yellow	Red
Butter yellow	+3.3	Yellow	Red
Benzeneazodiphenylamine	+1.5	Yellow	Purple
Dicinnamalacetone	−3.0	Yellow	Red
Benzalacetophenone	−5.6	Colorless	Yellow
Anthraquinone	−8.2	Colorless	Yellow

Table II. Properties of Insecticide Diluents

Diluent Name	Type	Surface Area, Sq. M./G.	% Loss on Dry-ing[a]	pH in Water[b]	H_0 As received[c]	H_0 Dried[a,c]
Velvex	Kaolinite	24	1.0	4.6	−3 to −5.6	−5.6 to −8
Barden	Kaolinite	...	...	...	−3 to −5.6	...
Pikes Peak	Montmorillinoid group	112	4.3	5.1	−3 to −5.6	−3 to −5.6
Rev dust	...	...	...	...	−3 to −5.6	...
Diluex	Attapulgite	125	7.0	9.5	+1.5 to −3	−5.6 (tr)
Attaclay	Attapulgite	126	5.9	7.2	+1.5 to −3	−5.6 (tr)
Celite 209	Diatomite	26	4.9	5.2	+1.5 to −3	+1.5 to −3
Celite 400	Diatomite	26	4.1	6.0	+1.5 (tr)	+1.5 (tr)
Pyrax ABB	Pyrophyllite	3	0.1	6.2	+1.5 (tr)	+1.5 (tr)
Talc	Talc	...	7.1	...	+3.3 (tr)	...
Hi-Sil 101	Silica	100	...	9.4	+3.3 (tr)	+3.3 to +1.5
CCC (CaCO₃)	Calcite	...	...	...	+3.3 (tr)	...

[a] Dried at 120° C. for 16 hours.
[b] pH of a 1% water suspension.
[c] tr represents transition color.

indicators in an inert solvent such as benzene. Clay surfaces are not uniformly acidic but, instead, give amine titers that continuously decrease with decreasing basicity of the Hammett indicators.

Reaction Rates by Differential Thermal Analysis. It was found that reaction rates could be measured rapidly and accurately by differential thermal analysis (DTA). The DTA apparatus used for most of the work consisted of the following principal parts: a nickel calorimeter block heated by a vertical, symmetrically wound furnace; a heating program control unit; a Photopen linear chart recorder used in conjunction with a galvanometer, connected in series with the platinum vs. platinum-rhodium differential thermocouple to record differential temperatures; and a Brown Electronik recorder connected

to an iron vs. constantan thermocouple to record the block temperature. The sample (containing the insecticide) of about 1 gram was pressed firmly into a hole in the nickel block and a reference sample of the diluent under study was pressed into another hole symmetrically located in the block. Junctions of the differential thermocouple were inserted into the center of each sample and the block was sealed with a metal cap. The nickel block was inserted into the furnace and heated at a constant heating rate—about 4° C. per minute for most studies. The differential thermocouple junctions were opposed in series to give a chart reading of differential temperature. If heat were given off or taken up by decomposition of the insecticide, it was registered as a deflection of the pen.

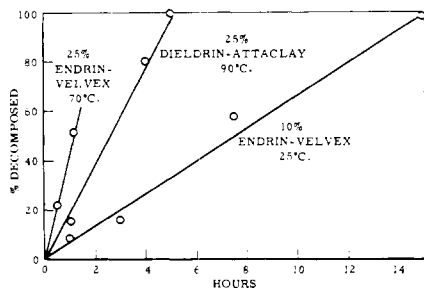The interpretation of the DTA chart can lead to determination of the heat,

Figure 2. Time dependence of decomposition of dieldrin or endrin, showing zero-order characteristics

Figure 3. Temperature dependence of half time of decomposition of 25% dieldrin or endrin in mixtures

rate, and order of reaction (7). A typical DTA chart is reproduced in exact shape in Figure 1, and illustrates the determination of half times of decomposition. The heat of reaction, proportional to the area under the curve, was determined by calibration with clay-naphthalene mixture, using the known heat of fusion of naphthalene (36 cal. per gram). The inflection point of the heating curve occurs near the maximum and the cooling curve is the relaxation curve for the hot sample (as obtained with naphthalene-clay mixtures). By reference to Kissinger (7), it can be seen that these features distinguish a zero-order reaction. A slight rounding of the very top of the peak occurs in Figure 1 because in that particular sample, as is explained later, the order is zero for the first 80% of the reaction and increases during the last 20%. The half time of reaction was determined graphically as indicated in Figure 1.

Because most reactions were zero order, the top of the heating curve represents the end of the exothermic reaction. At higher temperatures the curve is purely a cooling curve and its shape is determined by the heat transfer coefficient from the sample to the block. The half time of reaction was obtained by shifting the cooling curve until it bisected the area (dashed curve). The time from this intersection to the peak (or to the start of the temperature rise) is the half time of reaction, and the temperature of reaction is the average temperature over the period (average temperature of the reference sample plus the differential temperature).

Isothermal Decomposition Rates.
To obtain temperature coefficients for predicting storage stabilities, it was necessary to measure reaction rates at lower temperatures. Small sealed samples were stored at various controlled temperatures for periods of weeks or months and the rate of decomposition was determined by infrared analysis (5) of the toxicants after chromatographic extraction with solvents. In studies with Aramite, toxicant concentrations were determined by bioassay with the two-spotted spider-mite, *Tetranychus telarius* (L.), using Aramite as the standard.
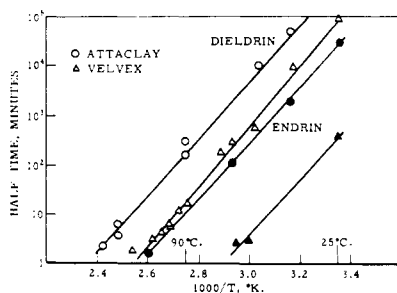
Materials

Unless otherwise specified, the toxicants used in this study were commercial grade materials and are referred to by common or trade names. Some measurements were made with the recrystallized active compounds of aldrin, dieldrin, and endrin. The composition and purity of these samples were as follows: recrystallized aldrin (99.3%) containing 99.3% of 1,2,3,4,10,10-hexachloro-1,4, 4a,5,8,8a - hexahydro - 1,4 - *endo, exo*-5,8 - dimethanonaphthalene (abbreviated HHDN); recrystallized dieldrin (99.9%) containing 99.9% of 1,2,3,4,-10,10 - hexachloro - 6,7-epoxy - 1,4,4a,-5,6,7,8,8a - octahydro - 1,4 - *endo,exo* - 5,8-dimethanonaphthalene (abbreviated HEOD); recrystallized endrin (98.3%) containing 98.3% of 1,2,3,4,10,10-hexachloro-6,7,-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo,endo*-5,8-dimethanonaphthalene.

The mineral diluents (mostly clays) are also referred to by common or trade name. Their descriptions, together with a list of properties which include surface areas and surface acidities, are given in Table II.

The H_0 values listed (Table II) give upper and lower limits of the H_0 of the strongest acid sites on the clay surface. As examples, a clay having an H_0 between $+1.5$ and -3.0 gives a purple color with benzeneazodiphenylamine and a yellow color with dicinnamalacetone; an H_0 of $+1.5$ (tr) not only means that benzeneazodiphenylamine gives a transition color (brown or orange), but that butter yellow gives a red color and dicinnamalacetone a yellow color.

It is interesting to note that there is poor correlation between H_0 values and the pH values listed in Table II. For example, Diluex gives an alkaline reaction in water even though it is strongly acid to Hammett indicators and, as will be shown later, is highly active for insecticide decomposition. There is an obvious explanation for the above discrepancy. The H_0 values are a measure of the strongest acid sites on the clay surface. However, the pH value of a clay-water suspension is the result of hydrolyses of all portions of the clay

surface. In the case of a clay like Diluex (which contains 7% magnesium oxide) one can visualize a process whereby alkaline portions of the surface produce more than enough OH^- to neutralize the H^+ originating from the acidic portions of the surface.

Kinetics of Dieldrin and Endrin Decomposition

Clay-toxicant mixtures containing 25% of dieldrin or endrin were used for the detailed kinetic studies, and most of these measurements were made with Attaclay (an attapulgite clay) or with Velvex (a kaolinite clay).

Heats of Decomposition. With DTA measurements, the heat of decomposition of the 25% concentrates was about 33 cal. per gram for either technical dieldrin or endrin on Attaclay or Velvex. The heats of decomposition of 25% concentrates of recrystallized dieldrin (HEOD) and recrystallized endrin were about 36 cal. per gram which corresponds to 144 cal. per gram of toxicant or 55 kcal. per mole.

Order of Reaction. The order of reaction is best illustrated with measurements of decomposition during isothermal storage (Figure 2). Here it is shown that dieldrin or endrin, when mixed with various diluents, decomposes at a constant rate independent of the concentration of undecomposed material. This is a zero-order reaction which indicates that the reaction occurs on sites that are completely covered by reacting molecules.

The reaction mechanism probably involves vaporization of the solid toxicant, diffusion through air spaces to the clay particle, diffusion through pores within the clay particle, adsorption, reaction to produce less strongly adsorbed products, desorption, and diffusion of the products away from the clay surface. Because the vapor pressure of toxicants at the temperature of the reaction is very low $(10^{-3}$ mm. of mercury for endrin at $25°$ C.), it seemed possible that diffusion might limit the above process. However, a calculation of diffusion rates (11) indicated that even for the most active system (endrin on Velvex) the time of diffusion is negligible compared to the time of reaction.

The number, n, of molecules of toxicant per acid site is given by

$$n = \frac{10^8 W}{MS(100 - W)}$$

where W is the weight % of toxicant; S, the micromoles of acid sites per gram of clay; and M, the molecular weight of the toxicant. For a 10% endrin-Velvex mixture, $n = 11$. Thus, for a reaction time of 840 minutes, the average residence time on the acid sites was about 75 minutes.
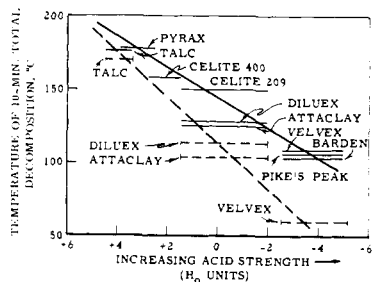
Figure 4. Effect of acid strength of carriers on stability of 25% endrin or dieldrin dust concentrates

– – – and carrier names on left for endrin
——— and carrier names on right for dieldrin

Table III. Reaction Rates of Dieldrin with Pure Kaolinites

Cation	Cation Concn., μMoles/G.	Total Acidity,[a] μMoles/G.	H_0	$t_{1/2}$ by DTA Min.	$t_{1/2}$ by DTA ° C.	$t_{1/2}$ at 65° C., Min.
Natural	. . .	25	−3 to −5.6	3	110	400
H⁺	. . .	24–31	−5.6 to −8	2	90	30
NH₄⁺	24	. . .	−3 to −5.6	3	102	150
Na⁺	26	19–22	−3 to −5.6	2	114	400
Ca⁺²	15	10–20	+1.5 to −3	1.5	115	330
Al⁺³	8	10–12	−5.6 to −8	3	87	30

[a] By butylamine titration.

Effect of Temperature. Rates of decomposition of 25% dieldrin-Velvex, dieldrin-Attaclay, endrin-Velvex, and endrin-Attaclay mixtures were determined over a wide range of temperatures by isothermal storage, and also at more elevated temperatures by DTA measurements. These have been correlated by the Arrhenius relation:

$$k = \frac{1}{2t_{1/2}} = Ae^{-E/RT}$$

where $t_{1/2}$ is the half time of the reaction; A, the frequency factor; and E, the activation energy. This relation is illustrated in Figure 3 in which log $t_{1/2}$ is plotted as a function of $1/T$. The slope is $E/2.303R$; A can be calculated from the temperature of the intercept (log $t_{1/2} = 0$).

The results shown in Figure 3 cover an unusually wide range of reaction rates, from half times of 1 to 100,000 minutes, yet the straight lines of the Arrhenius relation fit the data very well. The frequency factor, A, appears to depend mainly on the clay. With endrin and dieldrin on Attaclay A is $10^{11.1}$ and $10^{11.4}$, respectively, while on Velvex A is $10^{13.1}$ and $10^{13.4}$, respectively.

The diagrams allow prediction of intermediate rates and temperatures, and illustrate the use of DTA measurements to predict storage stabilities for any system where A is known. The values of A for Attaclay and Velvex are nearly the same for endrin and dieldrin; if they are the same for these clays with other toxicants, then the rate of decomposition at any temperature can be determined by a single DTA measurement.

Effect of Acidity of Diluent. Dieldrin and endrin were mixed with a number of different diluents covering a wide range of acidity and each mixture was subjected to DTA measurements. The results are shown in Figure 4 where the temperature causing a half-time decomposition of 5 minutes is shown as a function of the H_0 of the diluent. A range of H_0 values is shown for each diluent; this is the best estimate (based on amine titration data) of the actual H_0 values of the stronger acid sites of the diluents as used in these

experiments. This figure illustrates the marked effect of the acidity of the diluent on the rate of decomposition. Higher temperature for a 10-minute decomposition denotes greater storage stability. The effect of the H_0 of the diluent on half time may be expressed by d log $t_{1/2}/dH_0 = 0.3$ to 0.4 for dieldrin and d log $t_{1/2}/dH_0 = 0.4$ to 0.5 for endrin.

Effect of Exchangeable Cations. Many natural clays have about 1 μmole of cation exchange site for every square meter of surface. Kaolinites with 25 square meters per gram of surface have 25 μmoles of exchangeable cations per gram of clay, and attapulgites with 125 square meters per gram of surface have 125 μmoles per gram. Most natural clays used for agricultural diluents have sodium ions in the exchange sites. Although hydrogen ions can be put into the exchange sites, hydrogen clays are not stable and are not found to any extent in nature.

The effect of different cations on the H_0 value and catalytic activity of kaolinites was determined with samples of Velvex prepared in several pure ionic forms (8): H⁺, NH₄⁺, Na⁺, Ca⁺², and Al⁺³ (Table III). Natural clay and sodium kaolinite appear identical in H_0 values and catalytic activity. The hydrogen kaolinite and the aluminum kaolinite are more strongly acidic and are much more active catalysts, promoting tenfold faster rates of reaction.

Catalytic Activity of Neutralized Clays

Because dieldrin and endrin formulated with neutral diluents, such as talc or calcium carbonate ($H_0 \geqq +3.3$), decompose much more slowly than when formulated with acidic diluents, such as kaolinite ($H_0 \cong −5.60$) or attapulgite ($H_0 \cong −3$), it was of interest to compare the catalytic activity of talc with kaolinite neutralized to $H_0 = +3.3$. The catalytic activities were found to be approximately the same. A wide variety of bases can be used to neutralize the acidity of clays, but the maximum H_0 attainable and the amount of base needed to attain any given H_0 value differ with each base and with each diluent.

Population of Acid Sites in Various Diluents. By means of the previously described titration of acid sites with butylamine in benzene (amine titer), the number of acid sites per gram of clay has been determined for Velvex, Diluex, Attaclay, and Wyoming Bentonite (Figure 5). The amine titer at any point on these curves represents the number of acid sites, expressed in millimoles per gram of clay, having a strength equal to or greater than the H_0 value at that point. The length of the vertical lines indicates the experimental uncertainty of the titration measurement. The total number of acid sites per unit surface of each of these clays is about 1 μmole per square meter, the exchange capacity.

Kinetics of Decomposition on Neutralized Clays. The neutralized Velvex or Attaclay formulations of dieldrin and endrin were so stable that rates could not be measured at ordinary storage conditions. The heats of reaction with neutralized clays at elevated temperatures are generally greater than with unneutralized clays. This increase might be interpreted as a reaction of the decomposition products with the base; such a secondary reaction would tend to reduce the neutralizing effect of the base and cause the rate of reaction to increase during course of decomposition. However, no such increase has been observed. The further decomposition of the primary decomposition products may be the reason for the greater heats at the elevated temperatures.

The decomposition reactions remain zero order, as is illustrated in Figure 6 where the solid line represents zero order and a dashed line first order for comparison. The temperature dependence of reaction rate was found to be governed again by the Arrhenius equation, in which the frequency factor, A, was the same as found with the unneutralized clays, but in which the neutralization increased the activation energies, E. Figure 7 shows a fan of Arrhenius relations for 25% endrin on Attaclay in which the solid lines represent changes in E for various neutralizing treatments, all drawn at constant A ($10^{11.1}$). Maximum and minimum activation energies are labeled. As is shown, the effectiveness of a neu-
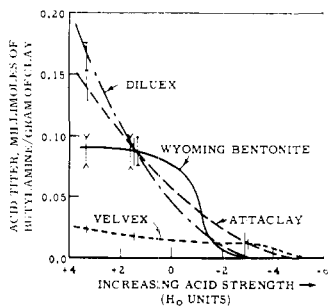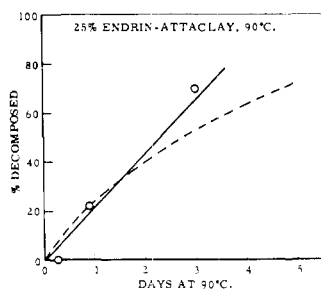
Figure 5. Acidity of clays dried at 120° C.

Figure 6. Time dependence of decomposition of 25% endrin-Attaclay mixture

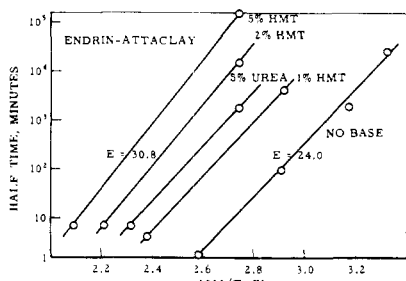Attaclay neutralized with 2.5%·urea and 2.5% NH₄HCO₃
—— Zero order
— — — First order

Figure 7. Temperature dependence of 25% endrin-Attaclay mixtures with added bases
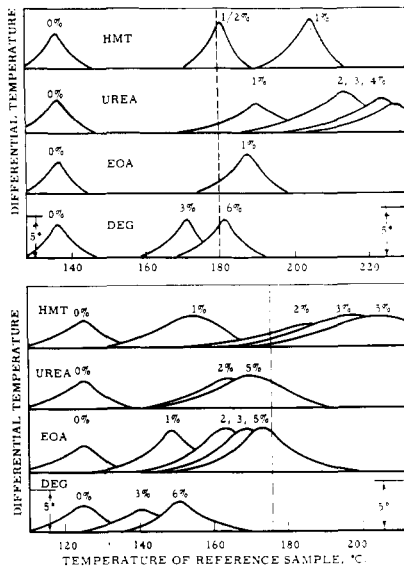

Figure 8. DTA results for neutralization

Top.   Of 25% dieldrin-Attaclay mixtures
Bottom.   Of 25% endrin-Attaclay mixtures

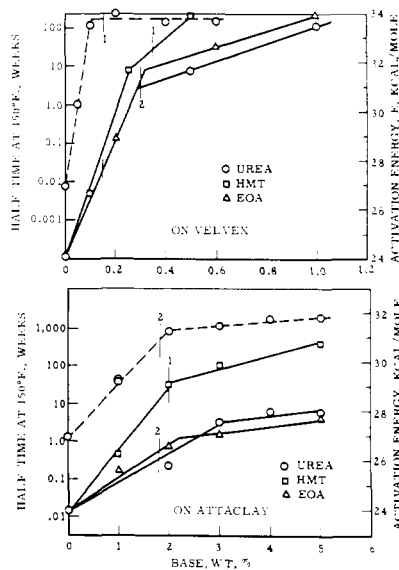Figure 9. Dependence of storage stability on concentration of added base

— — — Dieldrin
—— Endrin

Figure 10. Effect of dieldrin concentration (inside circles) on storage stability at 150° F. calculated from DTA measurements

tralizing treatment may be expressed by the increase of the activation energy, E.

Comparison of Various Neutralizers. A wide variety of bases have been tested, including inorganic bases, nitrogen bases, and oxygen bases (including water). Some require application in water slurry and some may be sprayed in liquid form on the diluent, while volatile solids can be mixed with the clay and the neutralization accomplished through diffusion of the vapor.

Inorganic bases such as sodium hydroxide are moderately effective, slowing the reaction of dieldrin on Velvex at 100° C. from a half time of 8 minutes to 25 weeks. However, this treatment is effective only if the clay is neutralized when suspended in an aqueous slurry. Merely adding the same amount of sodium hydroxide in water (10 wt. % of the clay) does not slow the reaction but does increase the heat of reaction. Another disadvantage of the sodium hydroxide treatment is that, though all exposed surfaces may be neutralized, subsequent grinding exposes new surfaces as acidic as the fresh clay; this makes a sodium hydroxide treatment impractical commercially.

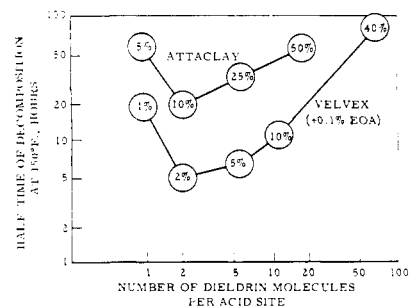Figure 8, top, shows the original DTA charts for decomposition of 25% dieldrin-Attaclay mixtures with various neutralizers, illustrating the effect of change in concentration of bases. The stabilizing effect of neutralizers is shown by the shift of the peaks to higher temperatures as the concentration of neutralizer is increased. The three nitrogen bases [hexamethylenetetramine (HMT), urea, and ethanolamine (EOA)] are much more active than an oxygen base [diethylene glycol (DEG)] (9), and HMT is definitely more active than the other nitrogen bases. The vertical dashed line shows the DTA peak temperature which indicates a 20-week half time of decomposition at 150° F. (65.5° C.). All peaks to the right of this line indicate a greater storage stability than this arbitrary standard.

Figure 8, bottom, shows DTA data for 25% endrin-Attaclay mixtures. The decomposition temperatures are much lower because of the greater reactivity of endrin. In this case HMT stands out clearly as being much more effective than urea or ethanolamine, and is the only base giving peaks to the right of the critical stability line. Other strong nitrogen bases, such as cyclohexylamine and dicyclohexylamine, were as effective as ethanolamine, but it took 3% of the weakly basic aniline to give the same results as 1% of these stronger bases.

Figure 9 shows the reaction times at 150° F. of 25% endrin or dieldrin mixtures with Velvex or Attaclay to illustrate the effect of concentration of various bases. The corresponding activation energies, E, are also shown, so that rates of decomposition at any temperature may be calculated for these compositions. A regular increase in stability is obtained on adding more base until a critical level is reached, after which further addition of base increases the stability only slightly. The changes in slope generally correspond to some stoichiometric ratio of molecules of base to acid sites. For urea on Velvex with dieldrin, the change of slope is at 16 μmoles of urea per gram of clay, which corresponds to one urea molecule for each strongly acid site. With HMT and endrin on either Attaclay or Velvex, the change of slope also occurs at one molecule of HMT per acid site (vertical lines in Figure 9). On the

other hand, for urea with dieldrin on Attaclay, or urea and ethanolamine with endrin on either clay, the change of slope comes at two molecules of base per acid site. This is evidence that the decomposition reaction takes place only on the acid sites in the clay.

Estimation of Neutralization by H_0 Measurements. Earlier, in Figure 4, the relation between the H_0 of unneutralized diluents and their catalytic activity was shown to be fairly reliable. However, the same relation is not as reliable with neutralized clays, for, although the same slope fits the data, the scatter of points is much broader. Perhaps the organic bases have some influence on the performance of the indicator dyes. It appears that an H_0 value in excess of $+3.3$ for neutralized clays is not necessarily an indication of a 20-week half time of decomposition at 150° F.

Commercial Storage Problems

Calculation of Isothermal Decomposition Rates. In the previous section it was shown that the rates of decomposition of 25% dust concentrates at various temperatures could be calculated with the Arrhenius equation, using the half time of reaction as a measure of the rate of decomposition. However, with compositions containing less toxicant, the half time of reaction is shorter because n, the number of toxicant molecules per acid (or exchange) site, is less. For example, a 25% dieldrin-Velvex concentrate $(n = 33)$ may be stabilized with urea so that half the dieldrin decomposes in 140 days at 150° F. (total decomposition in 280 days); this amounts to an average reaction time (t_r) of a dieldrin molecule on an acid site of 8.5 days, where $t_r = 2t_{1/2}/n$. The same reaction time occurs in a 4% dieldrin dust containing the same clay. As here there are only four molecules of dieldrin per acid site, however, the time for half-decomposition (2 molecules per site) would equal 17 days as compared with 140 days for the 25% concentrate.

The decrease of half times of decomposition with decrease in n is shown in Figure 10 to occur only in compositions where n is large and average reaction times (t_r) are independent of dieldrin concentration—i.e., true zero-order kinetics result. However, when n approaches unity, the values of t_r and $t_{1/2}$ increase. At low concentrations $(n<1)$, all of the toxicant is adsorbed onto acid sites and no more solid dieldrin remains as a reservoir to keep the dieldrin vapor at saturation. Consequently, the thermodynamic activity and chemical reactivity of the adsorbed dieldrin decline rapidly as n decreases below unity. Under these conditions, t_r increases rapidly during the reaction and

the order of reaction increases. (Inhomogeneity of composition can also result in an apparent increase in both half times and order of reaction.)

The steep increase in half times $(t_{1/2})$ as n decreases below 2 is illustrated in Figure 10 with data from DTA measurements. Thus, half times of reaction decrease on dilution to a minimum and then increase on further dilution. The toxicant concentration of the minimum (where $n = 2$) depends largely on the concentration of acid sites of the clay diluent. This is further illustrated by isothermal storage data at 195° F.; a tenfold decrease in $t_{1/2}$ occurs upon diluting a 25% dieldrin-Velvex concentrate $(n = 33)$ to a 2% dust $(n = 2)$, whereas a sevenfold increase in $t_{1/2}$ occurs upon diluting a 25% dieldrin-Attaclay concentrate $(n = 6)$ to a 2% dust $(n = 0.4)$.

"Spontaneous" Decomposition in Commercial Storage. The above calculations of rates are made for isothermal decomposition of the mixture. However, if the mixtures are stored in large bags, drums, or bins, the evolution of heat resulting from a very slow rate of decomposition can warm up the center of the mixture to temperatures well above that of the outside air and the rate of decomposition increases. In separated 50-pound bags, the rate of cooling of the interior by conduction of heat to the outside is about 0.1 cal. per gram of mixture per day per degree centigrade difference in temperature between the center and surface of the bag. Under such conditions, heat evolution in the center of 0.2 cal. per gram per day can be controlled by conduction, but if the heat evolved from the reaction reaches 0.3 cal. per gram per day the center of

Table IV. Storage Stability of 25% Dieldrin Dust Concentrates in Fifty-Pound Bags at 150° F.

Carrier	Base	After 1 Week Calcd.	After 1 Week Exptl.	After 8 Weeks Calcd.	After 8 Weeks Exptl.
Attaclay	None	100	100	100	100
Attaclay	5% urea	0.05	0	0.4	0
Attaclay	5% NH$_4$HCO$_3$	0.6	0	5	0
Attaclay	1% NH$_3$, 4% H$_2$O	...	0	...	0
CCC, 95% / Hi-Sil 101, 5%	None	...	0	...	0
Phosphodust	None	...	0	...	0
Pyrax ABB	None	0.2	0	2	0

(% of Dieldrin Decomposed at 150° F.)

Table V. Stability of Field-Strength Dieldrin or Endrin Dusts on Unneutralized and Neutralized Diluents

Decomposition of Toxicant, Wt. %, When Stored for

Type of Diluent	Deactivator, Type and Amt.[a]	Toxicant[b]	14 Days at 130° F. Exptl.	14 Days at 130° F. Calcd.	10 Months at 75° F. Exptl.	10 Months at 75° F. Calcd.
Calcium carbonate	0	Dieldrin	0	...	0	...
	0	Endrin	0	...	...	...
Talc[c]	0	Dieldrin	10–90	13	0–20	<1
	Urea, 1%	Dieldrin	0–3	...	...	...
	HMT, 0.5%	Endrin	0	...	...	...
Pyrophyllite	0	Dieldrin	20	13	0	<1
	Urea, 1%	Dieldrin	2	...	...	...
	0	Endrin	>95	70	...	...
	HMT, 0.25%	Endrin	0	...	...	...
Kaolinite	0	Dieldrin	>95	100	60–100	100
	Urea, 1%	Dieldrin	4	<1	...	...
	HMT, 1%	Endrin	0	<1	5	<1
Attapulgite	0	Dieldrin	90	75	...	...
	Urea, 1%	Dieldrin	0–4	2	...	...
	HMT, 4%	Endrin	4–17	<1	0–3	<1
	HMT, 5%	Endrin	0–4	<1	...	...
Diatomite	0	Dieldrin	>95	70	45	60
	Urea, 1%	Dieldrin	2	...	...	...
	HMT, 3%	Endrin	12	...	...	...
	HMT, 4%	Endrin	2	...	...	...
Montmorillonite	0	Dieldrin	>95	...	10–50	...
	Urea, 1%	Dieldrin	>95	...	3–50	...
	Urea, 3%	Dieldrin	0	...	...	...
	HMT, 3%	Endrin	3–60	...	...	...
	HMT, 5%	Endrin	0–6	...	...	...

[a] Amount of deactivator is expressed as weight % of diluent replaced.
[b] Toxicant concentration was 1 to 5% in all cases.
[c] "Soapstone" from Valley Chemical Co., Greenville, Miss.

Table VI. Quantities of Urea or HMT Necessary to Stabilize Dieldrin and Endrin Field-Strength Dusts

Carrier, Trode Name	Urea Required for Dieldrin Dusts, Wt. %	HMT Required for Endrin Dusts, Wt. %
CCC	0	0
Flo-Float	0	0
Kaluent	0	0
Tobacco dust diluent	0	0
Slaked lime	0	0
Hi-Sil 233	0	5
Silene EF	0	. . .
Celite 209	1	3
Clear Lake talc	0	0.25
Sierra White talc	1	0.25
Southwest talc	1	0.5
Mil-Slip talc A	1	0.5
Mil-Slip talc B	1	0.5
Frianite M-3X	1	0.5
Diacron	1	2
Diluex	1	5
Attaclay	1	4
Carriclay	1	. . .
Pyrax ABB	1	0.25
Pyro clay	1	0.25
Phosphodust	1	1
Dusting sulfur	1	0.25
Natka clay	1	1
Tako clay	1	1
Barden AG clay	1	1
Extender clay	1	1
Velvex	1	1
FF absorptive clay	2	3
Rev dust	3	5
Pikes Peak clay	3	5
Dilu-Dust	3	. . .

Table VII. Rates of Decomposition of Various Insecticides as Measured by DTA

Toxicant	Carrier	Base	Measured $t_{1/2}$ Min.	°C.	$t_{1/2}^a$ at 150° F.	E^a	h^b
25% aldrin[c]	Velvex	None	3	150	3 weeks	31.5	120
	Velvex	0.1% urea	>20	240	>10 years	>38	. . .
	Attaclay	None	4	199	2 years	30.5	145
	Attaclay	0.2% urea	6	228	>10 years	32.5	155
25% toxaphene	Velvex	None	8	120	13 hours	29.3	28
	Velvex	1% urea	10	153	15 weeks	32.0	80
	Attaclay	None	6	158	5 weeks	28.2	84
25% chlordan	Velvex	None	6	109	11 hours	28.2	37
	Velvex	1% urea	9	161	35 weeks	32.6	68
25% heptachlor	Attaclay	None	5	140	5 days	27.0	43
25% DDT	Velvex	None	2.5	143	8 days	30.3	100
	Velvex	1% urea	5	193	10 years	34.5	56

[a] Estimated by assuming A to be $10^{11.4}$ and $10^{13.4}$ for Attaclay and Velvex, respectively.
[b] Calories evolved per gram of toxicant (by DTA).
[c] 99.3% pure HHDN.

the bag will heat up slowly for a while and then in a day or two it will heat very rapidly until all of the toxicant is decomposed. This results from the fact that the rate of cooling by conduction rises linearly with temperature, while the rate of heating due to the reaction rises exponentially with temperature.

Effect of Moisture. In the preceding section on rates of decomposition, all clays were dried for 1 day at 90° to 110° C. before testing. Rates of decomposition are slower on clays containing more adsorbed water, so the rates predicted by the previously described calculations are rates expected only for dry, active clays. Indicator dyes show that clays with H_0 values of −5.6 can be neutralized to about +1.5 by water vapor alone. The neutralization with water vapor is neither sufficiently complete nor permanent for safe storage conditions.

Because of the considerable effect of water on rates at temperatures below 100° C., isothermal storage behavior cannot be correlated except for systems with dry clay. However, in most DTA measurements the water is driven off and the results correlate with those for dry clay.

Experiments with 50-Pound Samples. Fifty-pound batches of 25% dieldrin dust concentrates were formulated with various diluents and deactivators as shown in Table IV and these were stored in multiwall bags placed inside open steel drums in a constant-temperature room at 150° F. The dieldrin content was determined periodically by infrared analysis. For purposes of comparison, Table IV has both experimental and calculated values for the amount decomposed; the agreement is satisfactory.

Stabilization of Field-Strength Dusts. Dusts of the type used in crop-dusting (containing 1 to 5% of toxicant) were prepared with a variety of carriers, deactivators, and with both dieldrin and endrin (Table V). Samples were stored at 130° F. in pint Mason jars and analyzed for toxicant concentration by infrared analysis. Calculated amounts of decomposition are shown for comparison with the experimentally determined values. For the purpose of calculation, it was assumed that, except with attapulgite, zero-order kinetics apply in this range, and the frequency factor, A, of the Arrhenius relation is the same for talc, pyrophyllite, kaolinite, and diatomite.

Table V shows that some of the diluents which are only slightly acidic (talc, pyrophyllite, diatomite) nevertheless require neutralization with bases for formulation with dieldrin or endrin as field-strength dusts. An arbitrary level of safe storage stability of 5% decomposition in 2 weeks at 130° F. has been adopted for field-strength dusts instead of the 150° F. for concentrates. The quantities of urea or hexamethylenetetramine necessary to stabilize dieldrin and endrin field-strength dusts made with various carriers are shown in Table VI.

Decomposition and Stabilization of Other Toxicants

The generality of the clay catalysis of decomposition reactions in pesticidal dusts or dust concentrates has been demonstrated with a number of other toxicants. Table VII shows the rates of decomposition at the elevated temperatures obtained in DTA measurements. It is useful to compare the estimated half times of reaction at 150° F. Without bases, the rates of decomposition are seriously high for chlordan, toxaphene, heptachlor, and DDT. The use of urea to inhibit decomposition is highly effective in all cases. The decomposition of Aramite, determined by bioassay of 25% dusts containing Velvex or Attaclay stored at 65° C., was quite parallel. Rates of decomposition were faster than with the above pesticides, faster on Velvex than on Attaclay, and subject to the deactivating influence of urea. Urea-neutralization of Velvex, Barden, or Attaclay carriers in 25% Aramite concentrates increased decomposition times 10- to 100-fold. Yaffe (12) has recently discussed the need of stabilizing Aramite formulations.

Effect of Bases on Other Properties. Investigation of formulations with and without added bases showed that urea and hexamethylenetetramine have no deleterious effect from the standpoint of insecticidal activity (by bioassay), phytotoxicity, grindability, and compatibility with common wetting and dispersing agents.

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PHYTOTOXICITY OF HERBICIDES

Reduction of 3-Amino-1,2,4-triazole Phytotoxicity in Tomato Plants

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The phytotoxicity of 3-amino-1,2,4-triazole was studied using tomato plants to determine the efficacy of selected compounds in reducing growth and chlorophyll toxicities. When the concentration of 3-AT was $1 \times 10^{-4}M$, equimolar solutions of certain purine precursors simultaneously applied caused a reduction of 3-AT growth inhibition; but this did not occur when all concentrations were five times this amount. Adenine, hypoxanthine, and guanine and their ribosides acted like the purine precursors. Riboflavin, FMN, and FAD reduced not only 3-AT growth inhibition at $5 \times 10^{-4}M$, but also the inhibition of chlorophyll formation. A hypothesis of the mechanism of 3-AT phytotoxicity is presented.

THE compound 3-amino-1,2,4-triazole (3-AT), also known as aminotriazole and Amitrol, is an effective defoliant and herbicide. Green plants, treated with sublethal dosages of 3-AT, manifest toxic effects in two ways—growth of embryonic tissues is inhibited, and leaves developed after treatment with 3-AT are devoid of chlorophyll. In addition, albinistic leaves in several species lack chloroplasts (16, 18). Thus, it may be concluded that 3-AT mainly affects developing rather than mature tissues.

Evidence related to the biochemical mechanism is limited. Possibly, the interaction of 3-AT with several metals to form stable complexes is responsible for the toxicity symptoms; however, Hall, Johnson, and Leinweber (6) found that plants inhibited by 3-AT were not benefited by treatment with excess metal ions.

The structural similarity between 3-AT and pyrrole makes it attractive to speculate that the phytotoxicity of 3-AT is in some way related to porphyrin or porphyrinlike substances. In support of this hypothesis, Heim, Appleman, and Pyfrom (7) and Pyfrom, Appleman, and Heim (16) have shown that crystalline catalase activity and catalase activity of

plants treated with 3-AT are depressed. Likewise, Margoliash and Novogrodsky (12) have shown that 3-AT causes a complete inhibition of crystalline preparations of liver and erythrocyte catalase in the presence of hydrogen peroxide. On the other hand, Bogorad (1), in his studies on the enzymatic synthesis of porphyrins from porphobilinogen (PBG), found that 3-AT up to $5 \times 10^{-3}M$ had no adverse effects on a system containing PBG and porphobilinogen deaminase.

The present report provides further evidence concerning the biochemical effect of 3-AT inasmuch as the 3-AT phytotoxicity was reduced by appropriate physiological compounds.

Procedure

Chemicals. Technical grade 3-amino-1,2-4-triazole was supplied by the American Cyanamid Co. and was recrystallized twice before use. 4-Aminoimidazole (4-AI) was prepared in aqueous solution according to the method of Rabinowitz (17).

Biological Assay. The effect of 3-AT on plants was studied by the observation of growth and chlorophyll development of the apparent first leaf of tomato plants subsequent to treatment of the growing tip of the plant with 3-AT and other compounds. Tomato plants, Lycopersicum esculentum Mill. var. Bonny Best, were grown in the greenhouse at 60° to 85° F. in vermiculite watered periodi-

cally with a complete nutrient solution (8) until the plants had reached the 8- to 12-leaf stage.

The growing tips of plants at this stage were treated with various chemical solutions. To accomplish this, the apparent third leaf was excised and a powder funnel was fitted around the terminal 3 cm. of the plant by means of a split rubber stopper sealed to the stem with anhydrous lanolin. The terminal leaflets of the apparent first and second leaf were removed to afford a higher proportion of juvenile tissue for treatment and to provide well defined points from which growth measurements could be made (Figure 1). With such an arrangement, the growing tip and the first two leaves could be totally submerged in the desired solution for a given period, at the termination of which the solution could be siphoned away. After treatment, the plants were maintained under normal greenhouse conditions.

The period of time during which the plant tip was exposed to the 3-AT solution is designated in this paper as treatment time. The inhibition of growth caused by treatment with $10^{-4}M$ 3-AT rapidly approached a value of about 50% for a treatment time of 12 hours. When the effect of two compounds on the same plant was tested, they were applied simultaneously in the same solution, as experience indicated that the inhibition caused by treatment with 3-AT could be partially reduced merely by an im-

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