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STABILITY OF INSECTICIDE FORMULATIONS

The Use of Stabilizing Agents to Decrease Decomposition of Malathion on High-Sorptive Carriers

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Decomposition of malathion when impregnated on certain mineral carriers has long been a problem in the pesticide industry. Theories concerning the causes of decomposition are reviewed and discussed. A comparison is made of the variability of catalytic activity of two high-sorptive carriers, an attapulgite and a montmorillonite. Comparative data are presented on rates of degradation on these carriers along with data on a few low-sorptive diluents. Comparative data are presented on the stabilizing efficiency of glycols, tall oil compounds, and other weak acids. Data indicate that tall oil compounds are slightly more effective in their stabilizing action than glycols. Use of tall oil as a stabilizing agent resulted in dust formulations that exhibited improved stability for short-term storage, although no additives have as yet been found to completely inhibit decomposition of malathion impregnated on the highly sorptive carriers studied, and under the test conditions used.

MUCH EFFORT has been expended on the development of satisfactory dust formulations of phosphate-type insecticides since the introduction of these toxicants. Because of the inherent instability of the phosphates (5, 16) and their susceptibility to decomposition by the catalytic activity of surfaces of various solids, the formulation of adequate dry-compositions has been difficult. This instability has been particularly evident on mineral carriers that exhibit high-sorptive capacity. This factor has resulted in the use of carriers with lower sorptive capacities, and other less attractive properties, as the bases for dusts. Malathion, a major product of this type, has been prepared on many low-sorptive-capacity carriers which give less decomposition, but demonstrate poor flowability and application characteristics.

To overcome this problem, considerable work has been carried out to determine the cause of malathion decomposition (5, 15, 16). As a result of these investigations, studies have been made on additives that might be used to correct mineral surface conditions connected with decomposition (7, 8, 12).

The present study was undertaken to obtain comparative data on the decomposition of malathion when impregnated on low- and high-sorptive carriers, and on the effect of various additives on decreasing malathion decomposition when impregnated on high-sorptive carriers.

Materials and Methods

The carriers used in this work are described in Table I. Some of the descriptions given in this table were taken from the work of Watkins and Norton (14).

Chemical analysis, differential thermal analysis, and x-ray diffraction data indicate that the bentonitic clay from northern Georgia is an extensively leached and altered montmorillonite, markedly deficient in bases and enriched in siliceous materials as a result of geological weathering.

Technical-grade malathion containing a minimum content of 95% of *O,O*-dimethyl dithiophosphate of diethyl mercaptosuccinate was the insecticide studied in this work. The stabilizing agents fell into two broad categories: glycols and tall oil additives. The

glycols included mono-, di-, tri-, and polyethylene glycols; propylene glycol; and alkyl ethers of mono-, di-, and triethylene glycols. The tall oil additives included crude and distilled whole tall oils and some carboxylic acids. The commercial additives tested are described in Table II. Materials were graded for possible use as deactivators, primarily because of their ability to stabilize malathion formulations on attapulgite.

The samples were formulated by first adding a solution or liquid blend of the stabilizing agent and malathion to the carrier while mixing in a Hobart mixer, then thoroughly mixing for 20 minutes. The mixtures were next passed through a hammermill twice, and then thoroughly blended on a roller mill for 30 minutes.

The compatibility of each of the carriers with malathion, or the effectiveness of a stabilizing agent, was determined by subjecting the formulated samples to accelerated decomposition conditions (elevated temperature). The samples were analyzed for malathion content before and after the accelerated test, and decompositions were calculated

as per cent of initial malathion content. Those stabilizing agents that showed any promise, as indicated by the accelerated test data, were also tested for stabilizing efficiency during room temperature storage.

The accelerated test condition used in this work was storage for 1 month at 40° C. The determination of the relationship between rate of degradation at room temperature and at elevated temperatures was not feasible, since the rate changes with the carrier and stabilizing agent. However, it is estimated that for 5% of malathion impregnated on attapulgite, degradation during 1 month of storage at 40° C. is equivalent to that occurring during approximately 3 months at room temperature.

In most of this work, the stability of 5% malathion dust was determined rather than that of 25% dust concentrates. It was believed that 5% materials would show greater sensitivity to the test variables than 25% formulas. However, it is theorized that decomposition data in a 25% dust concentrate can be directly related to that of a 5% dust; that is, approximately the same loss of malathion per unit of clay content can be expected from the concentrate as from the dilute dust, since clay is the limiting reactant in the decomposition reaction. Because of the higher clay content of the 5% dust, loss of malathion in the 5% dust will be higher, by a factor of 95/75, than in the 25% dust.

The analytical method used to determine the malathion content of formulated samples was provided by the American Cyanamid Co. (7). Malathion is decomposed by alkali in carbon tetrachloride-ethanol solution to sodium *O,O*-dimethyl dithiophosphate, sodium fumarate, and ethanol. The sodium *O,O*-dimethyl dithiophosphate is then converted to the cupric complex, which is soluble in carbon tetrachloride with formation of a yellow color. The color intensity is proportional to the concentration of the cupric salt of *O,O*-dimethyl dithiophosphoric acid, and is measured colorimetrically at 418 m μ , a maximum absorption peak, with a Klett-Summerson photoelectric colorimeter fitted with a KS No. 42 filter (400 to 465 m μ). The corresponding amount of insecticide is then ascertained by comparison with a standard curve prepared from known amounts of pure insecticide carried through the procedure.

Each of the malathion analyses was performed in duplicate. The reproducibility of the analyses was good—the relative mean deviation ranging from 10 to 20 parts per thousand for two, and in some cases three, analyses of a sample.

Differences in results of duplicate formulations were observed. When decomposition of malathion was high

Table I. Description and Properties of Carriers

| Carrier Identification | Description | Oil Absorption (ASTM D281-31) |
|--------------------------------|--|-------------------------------|
| A Attapulgite LVM ^a | Attapulgite mined in Georgia and Florida; processed by crushing, drying to low volatile matter, ^b grinding with size classification by air separation | 119 |
| B Attapulgite RVM ^a | As above, except dried to regular (intermediate) volatile matter ^b | 112 |
| C Kaolinite | Kaolinite mined in Georgia; refined by water washing to remove sand, mica and water-soluble salts; average particle size — 4.8 μ | 34 |
| D Kaolinite | As above, except average particle size — 1.5 μ | 35 |
| E Montmorillonite group | Extensively weathered and altered montmorillonite mined in Georgia; processed by crushing, drying to low volatile matter, and grinding to powder | 70 |
| F Diatomite | Diatomite mined in California; processed by dehydration of natural diatomaceous earth | 175 |
| G Kaolinite | Kaolinite mined in South Carolina; processed by drying, pulverizing, and refining by air-flotation, average particle size — less than 1 μ | 33 |

^a LVM = Low volatile matter (6-8% VM); RVM = Regular volatile matter (12-14% VM).

^b Volatile Matter is ignition loss, mostly water, driven off when material is heated at 1800° F.

(over 40%), reproducible results were difficult to obtain with duplicate samples. There may have been variation in the activity of the carrier used, although an attempt was made to eliminate this possibility in stabilizer work by using samples of the carrier from the same batch or lot for all formulations.

To eliminate possible variation in decomposition results, the effects of these following three impregnation methods were evaluated.

Method No. 1. The samples were formulated by adding the stabilizing agent (dissolved in a suitable solvent if necessary) to the carrier while mixing in a Hobart mixer and blending for 20 minutes. The malathion was then dripped into the mixture and blended for an additional 20 minutes.

Method No. 2. The samples were formulated by adding a solution (or dispersion) of stabilizer and malathion simultaneously to the carrier while mixing in a Hobart mixer. The formulation was then blended for an additional 20 minutes.

Method No. 3. In addition to the procedure in Method No. 2, the formulation was passed through a hammermill twice, and postblended on a roller mill for 30 minutes.

Because of the lack of reproducibility of decomposition results between duplicate samples, Method No. 1 and, subsequently, Method No. 2 had to be abandoned. Method No. 3 was used for the preparation of all samples described in this study.

To minimize the effect of small losses of ingredients through handling during sample preparation, fairly large samples were prepared (1 kg. or larger). Losses of malathion through volatilization could be serious if precautions were not taken.

Table II. Description and Sources of Commercial Additives

| Agent | Description |
|--------------------------------|---|
| Union Carbide Corp. | |
| Carbowax 200 | Polyethylene glycol polymer, molecular weight range 190-210 |
| Carbowax 400 | Polyethylene glycol polymer, molecular weight range 380-420 |
| Carbowax 4000 | Polyethylene glycol polymer, molecular weight range 3000-3700 |
| West Virginia Pulp & Paper Co. | |
| Liqro | Whole crude tall oil |
| Indusoil M-28 | Distilled tall oil |
| Tallene | Tall oil pitch |
| Liqrene | Tall oil pitch |
| Arizona Chemical Co. | |
| Acintol C | Whole crude tall oil |
| Acintol R | Tall oil rosin |
| Acintol D | Distilled tall oil |
| Acintol FA2 | Tall oil fatty acid |
| Acintol Heads 1112 | Tall oil heads |
| Acintol Heads 2122 | Tall oil heads |

In every run, the blended sample was immediately split and placed in a 1-quart jar, and two or more 2-ounce jars, fitted with screw-type caps. The sample in the 1-quart jar was reserved for the initial malathion analysis (and room temperature storage tests); the 2-ounce jars were placed in the oven at the elevated temperature. In some cases, samples were tested at 2 weeks, 1 month, and 3 months; an undisturbed jar was removed from the oven for each test. The jars were allowed to cool to room

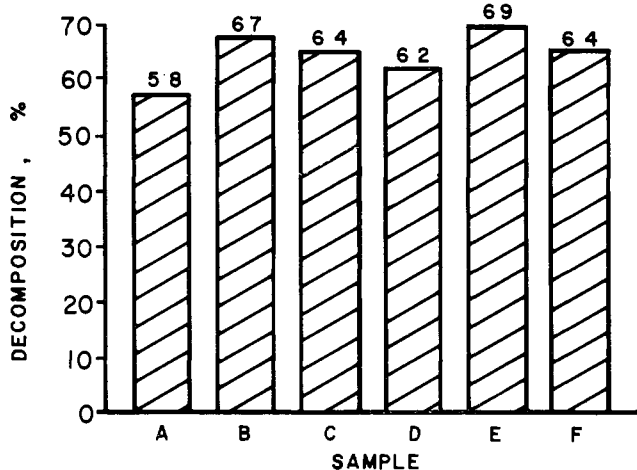


Figure 1. Decomposition of malathion 5% on attapulgite carrier—69, maximum; 64, average; 58 minimum

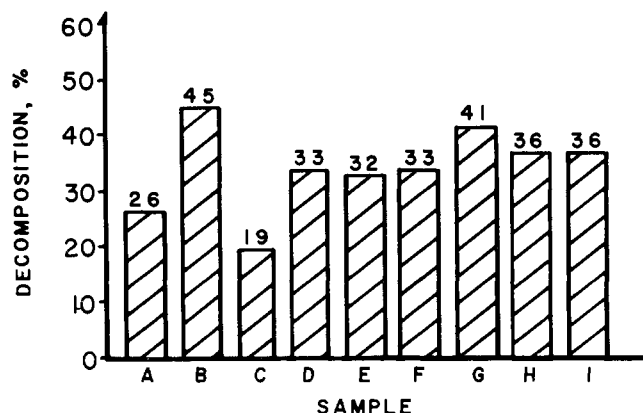


Figure 2. Decomposition of malathion 5% on montmorillonite carrier—45, maximum; 33, average; 19, minimum

Table III. Stability of 5% of Malathion on Various Carriers

| Carrier | Loss on Malathion When Stored at 40° C. for 30 Days, % |
|---|--|
| Attapulgite LVM | 64.1 (6) ^a |
| Attapulgite RVM | 46.9 (2) ^a |
| Montmorillonite (E) | 32.4 (19) ^a |
| Kaolinite (C) | 14.0 |
| Kaolinite (D) | 27.5 |
| Kaolinite (G) | 28.5 |
| Kaolinite (G), 3 parts — diatomite (F), 1 part | 17.4 |
| Kaolinite (G), 1 part — montmorillonite (E), 1 part | 63.6 (2) ^a |
| Kaolinite (G), 1 part — attapulgite LVM, 1 part | 71.0 (2) ^a |

^a Number of determinations included in average.

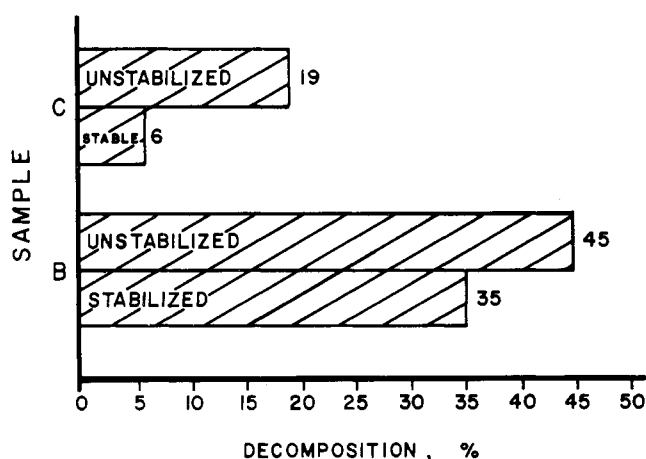


Figure 3. Decomposition of malathion 5% on montmorillonite carrier unstabilized and tall oil stabilized

temperature before removing samples for analyses. All initial analyses were conducted within 24 hours after the preparation of the dusts. The 2-ounce jars were placed in the oven at the same time a sample was removed from the 1-quart jar for initial analysis.

Malathion Decomposition on Carriers

Malathion is relatively stable in neutral or moderately acidic media (16). In the presence of moisture, the compound decomposes rapidly by base-induced hydrolysis (16). Almost all mineral carriers inherently possess one or more attributes, such as free moisture content, acid and base sites, and high surface area—properties that would provide ideal conditions for malathion degradation. Since the cited properties vary from carrier to carrier, it is reasonable to assume that rate of decomposition of impregnated malathion will also vary.

Comparative stability data for 5% malathion dusts using various carriers

are given in Table III. The results show that, of the samples tested, the attapulgite dusts were the least stable. These results substantiate the work of Yost *et al.* (15, 16). Approximately 64% decomposition was obtained during the accelerated test for LVM attapulgite (carrier A), whereas for RVM attapulgite (carrier B), there was approximately 47% decomposition. The decomposition value for montmorillonite (carrier E) was 32%, based on an average of 19 determinations. This will be discussed below. The kaolinites were less active than either the attapulgites or montmorillonite.

Table III also contains decomposition data for mixtures of a kaolinite (carrier G) with a diatomite (carrier F), a montmorillonite (carrier E), and an attapulgite (carrier A). The combination of kaolinite with diatomite as carrier gave the most stable dust of the three combinations tested. However, flowability measurements as conducted in our laboratories indicated that this type of

product exhibited very poor flow properties. Poor flowability was also demonstrated by dusts produced by using kaolinite as the sole carrier.

Figure 1 shows data for the decomposition of malathion impregnated on LVM attapulgite. The clay samples were collected from production runs over a 2-year period; the decomposition data reveal that the activity of the clay was reasonably constant. Figure 2 presents data of 19 determinations on nine samples of a given montmorillonite (carrier E) obtained at random throughout the country. The activity of this montmorillonite clay varied widely; the reason for this is unknown.

Use of Glycol as Stabilizer

On the surface of mineral carriers, there are acid sites whose strength can be correlated with the decomposition of certain chlorinated organic insecticides (2, 3, 6, 9-11). The surface acidity was measured by a method of

Table IV. Glycols and Glycol Derivatives as Stabilizing Agents for 5% of Malathion on LVM Attapulgit

| Additive, % | Loss of Malathion When Stored at 40° C. 30 Days, % |
|---------------------------------------|--|
| Ethylene glycol, 2 | 45.7 |
| Ethylene glycol, 5 | 46.2 |
| Diethylene glycol, 3 | 33.5 |
| Diethylene glycol, 5 | 38.9 |
| Diethylene glycol, 7 | 48.0 |
| Triethylene glycol, 3 | 29.6 |
| Triethylene glycol, 5 | 27.5 |
| Triethylene glycol, 7 | 22.8 |
| Carbowax 200, 3 | 51.8 |
| Carbowax 400, 3 | 40.9 |
| Carbowax 4000, 3 | 20.2 |
| Propylene glycol, 3 | 26.8 |
| Methyl ether of ethylene glycol, 3 | 40.2 |
| Butyl ether of ethylene glycol, 3 | 38.5 |
| Dibutyl ether of ethylene glycol, 3 | 30.9 |
| Methyl ether of diethylene glycol, 3 | 51.2 |
| Diethyl ether of diethylene glycol, 3 | 44.0 |
| Butyl ether of diethylene glycol, 1 | 51.0 |
| Butyl ether of diethylene glycol, 2 | 45.7 |
| Butyl ether of diethylene glycol, 3 | 48.7 |
| Dibutyl ether of diethylene glycol, 3 | 62.9 |
| Methyl ether of triethylene glycol, 3 | 50.6 |
| Ethyl ether of triethylene glycol, 3 | 28.5 |
| | 33.8 |
| | 44.8 |
| | 33.1 |

Table V. Tall Oil Derivatives and Carboxylic Acids as Stabilizing Agents for 5% of Malathion on LVM Attapulgit

| Additive, % | Loss of Malathion When Stored at 40° C. for 30 Days, % |
|-----------------------|--|
| Liqro, 5 | 40.3 |
| Liqro, 10 | 25.1 |
| Acintol D, 5 | 21.8 |
| Acintol FA2, 5 | 26.6 |
| Acintol R, 5 | 18.5 |
| Acintol C, 5 | 23.8 |
| Acintol Heads 1112, 5 | 25.9 |
| Acintol Heads 2122, 5 | 23.9 |
| Tallene, 5 | 25.3 |
| Liqrene, 5 | 26.9 |
| Pelargonic Acid, 5 | 46.2 |
| Stearic Acid, 5 | 48.8 |
| Indusoil M-28, 5 | 43.4 |
| | 46.7 |
| | 53.6 |
| | 51.9 |
| | 51.5 |
| | 52.8 |
| | 32.6 |
| | 31.9 |
| | 44.6 |
| | 45.7 |
| | 18.5 |
| | 20.7 |

Table VI. Indusoil M-28, 5%, as a Stabilizing Agent for 5% of Malathion on LVM Attapulgit

| Test No. | Loss of Malathion When Stored at 40° C. for 30 Days, % |
|----------|--|
| 161 | 21.6 |
| 182 | 28.8 |
| 197 | 21.8 |
| 199 | 18.5 |
| 203 | 25.3 |
| 282 | 22.0 |
| 283 | 28.5 |
| 300 | 20.7 |
| 301 | 25.0 |
| 302 | 21.8 |
| 303 | 22.8 |
| 335 | 21.6 |
| 336 | 23.4 |

Table VII. Indusoil M-28, 5%, as a Stabilizing Agent for 25% of Malathion on LVM Attapulgit

| Sample | Per Cent Loss of Malathion | |
|--------|----------------------------|---------------------|
| | Room temp., 6 mos. | Room temp., 12 mos. |
| 1 | 2.4 | 11.2 |
| 2 | 2.6 | 10.8 |
| 3 | 3.1 | 11.7 |
| | 3.0 | 11.8 |
| | 2.8 | 10.9 |
| | 2.8 | 10.8 |

Walling (13) and Johnson (4). This test is widely used today to determine the completeness of neutralization of acid sites for the impregnation of these insecticides. This acid-site theory has also been proposed as the cause of decomposition of some thiophosphate insecticides; namely, malathion, parathion, and methyl parathion. Oxygen-containing compounds, such as glycols, reduce surface acidity (6). Such compounds have been proposed for use as stabilizers in dry formulations for phosphate insecticides (12), although not on the basis of reducing acid sites. As will be shown below, merely neutralizing these acid sites by this technique does not completely eliminate the decomposition of malathion impregnated on attapulgit.

Table IV presents data on the stabilizing efficiency of mono-, di-, tri-, and polyethylene glycols; propylene glycol; and alkyl ethers of mono-, di-, and triethylene glycols. The results indicate that propylene glycol, Carbowax 200, and the butyl ether of diethylene glycol show the most promise of all the glycols and glycol derivatives tested.

It has been reported (6) and shown in this study that the use of 7% of diethylene glycol is capable of changing the surface acidity of LVM attapulgit from less than 0.8 to 3.3, as measured by the method of Walling (13). Table IV shows that the use of 7% of diethylene glycol does not completely eliminate

the malathion decomposition. These results indicate that either diethylene glycol did not decrease the surface acidity sufficiently to prevent decomposition, or causes other than, or in addition to, surface acidity are responsible.

Tall Oils as Stabilizers

Because of the limitations shown by the glycol-stabilizing approach, it was decided that other possible causes of thiophosphate decompositions would be re-examined to determine other potential remedies. Yost *et al.* (15, 16) reported the following inherent properties of malathion:

It is stable to light, but undergoes some decomposition when held at temperatures much exceeding room temperature.

It decomposes slightly when stored for prolonged periods in the presence of iron.

The presence of moisture and strong acids may induce chemical decomposition.

In highly alkaline media it hydrolyzes readily but it is quite stable in neutral or even somewhat acidic media.

Alkaline substances and divalent metal ions in general catalyze or induce decomposition.

Clay properties, other than surface acidity, which were likely to cause or support the decomposition of malathion were considered. The presence of moisture in a carrier increased the rate of decomposition, but removal by drying the carrier did not eliminate decomposition (16). An alkaline condition on the clay surface, as a cause of hydrolysis, is a possibility when the heterogeneous nature of adsorbent surfaces is realized. LVM attapulgit shows surface acidity values (H_0) of less than 0.8 (3) when dry, but when slurried in water, it exhibits a pH of 7.5 to 9.0. Metallic salts (calcium and magnesium) could possibly provide the alkaline condition on the clay surface. Therefore, an alkaline-site theory is proposed as a cause of decomposition of the P-S-C linkage by hydrolysis. The factors lending validity to this theory were checked by treating LVM attapulgit with a variety of agents which, because of their structure and active groups, would tend to interact with alkaline sites or free alkaline materials.

Over 100 different additives at various concentrations were investigated for their stabilizing effects. Of the additives investigated, the tall oil compounds showed the most promise, considering both cost and efficiency of stabilization. Table V presents stability data on some tall oil derivatives and carboxylic acids. These materials were tested in an attempt to determine which portion of the commercial tall oil mixture was stabilizing the malathion dusts. Accordingly, crude tall oils, distillation

heads, distilled whole tall oils, distilled tall oils with high rosin acid contents, and distilled tall oils with high fatty acid contents were tested. Of the materials tested, the most efficient and most economical stabilizers were: two distilled whole tall oils, Indusoil M-28 and Acintol D; and Acintol FA2, a distilled tall oil fatty acid. Stability data are presented in Table VI on 5% malathion dusts made with six different lots of LVM attapulgite using 5% of Indusoil M-28 as a stabilizing agent. Comparison of the stabilizing efficiency of Indusoil with diethylene glycol revealed that the lower-cost Indusoil was more efficient. However, as with glycols, the tall oil compounds did not completely inhibit the decomposition.

Treatment of LVM attapulgite with varying amounts (up to 8%) of Indusoil had no effect on the surface acidity as measured by the method of Walling (13). This would indicate that the mode of stabilization is other than the neutralization of surface acidity, as is indicated for the glycol deactivators (6, 12).

In Figure 3, data are presented on the stabilizing effect of Indusoil M-28 on 5% malathion dusts made with two different samples of the same montmorillonite (carrier E). Clay samples were chosen having low and high activity as indicated in Figure 2. Data in Figure 3 indicate that, although Indusoil was effective in decreasing decomposition of malathion with montmorillonite, com-

mercial use of this technique may not be feasible, since decomposition is unpredictable because of apparent variations in the montmorillonite activity. The activity of attapulgite is believed to be consistent enough to predict the extent of decomposition in a specified period. Overages of the insecticide can then be impregnated so that the product will meet the analysis guarantee.

Data are presented in Table VII on the stabilizing efficiency of Indusoil on 25% malathion-attapulgite dusts. Three different lots of attapulgite were used, and the samples were stored at room temperature (25° C.) for 6 and 12 months. Again, the data indicate that Indusoil is effective in reducing decomposition, and the extent of decomposition for a specified period of time is fairly consistent and predictable.

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INSECTICIDE-SYNERGIST ANALYSIS

Chromatographic Separation and Colorimetric Determination of Pyrethrins and Piperonyl Butoxide Mixtures

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THE INSECTICIDE referred to as pyrethrins is a mixture of four organic compounds (4), extracted from the dried flowers of *Chrysanthemum cineræfolium*. Piperonyl butoxide (3,4-methylenedioxy-6-propylbenzyl) (butyldiethylene glycol) ether is a synthetic organic compound used as a synergist for pyrethrins and similar compounds. Pyrethrins are used either alone or with piperonyl butoxide for the control of household and stored grain insects because of fast knock-down and relatively low toxicity to warm-blooded animals. The cost of pyrethrins sprays may be reduced with piperonyl butoxide since lower concentrations may

be used without loss of over-all insecticidal potency.

In the colorimetric determination of pyrethrins, color formation is inhibited by piperonyl butoxide. The reverse is true when determining piperonyl butoxide. The quantitative determination of pyrethrins in samples containing piperonyl butoxide has not been possible. High boiling hydrocarbons also interfere with the development of a clear-colored solution in the determination of pyrethrins or piperonyl butoxide.

Information in the literature suggests that pyrethrins may be separated from piperonyl butoxide by partition chromatography, but no one has suggested this as a method for separate determination.

Jones *et al.* (6) investigated the color-forming characteristics of piperonyl

butoxide as a methylene dioxyphenyl compound. Jones' method for the analysis of piperonyl butoxide, with some variations, was used in this experimental work. Other colorimetric methods available for the analysis of piperonyl butoxide are: Beroza's (2) method using chromotropic and sulfuric acids and Blum's (3) method using gallic and sulfuric acids. These can lead to charring and interferences when other organic compounds are present.

Piperonyl butoxide may be separated from certain other insecticides by partition chromatography (7). Samuel (7) used the Harris (5) procedure for the analysis of certain chlorinated hydrocarbon insecticides and found that only a few compounds would interfere. He used the Jones method for colorimetric measurement of piperonyl butoxide.

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