Phenthoate appeared to dissipate by first order and fit the line described by $\ln y = -0.024t + \ln 130$ with $r = 0.88$ and $t_{1/2} = 29$ days. The highest phenthoate level found was 180 ppm. Although Figure 15 shows that oxon levels increased over the entire 60-day period sampled, the correlation for the line ($r = 0.69$) is poor. The maximum oxon level encountered was 30 ppm for one sample.

Air. Two polyurethane foam plug samples were placed under a lemon tree located in the center of a plot treated by low volume in the 1978 application. Since the low volume treated trees always have the highest levels of dislodgeable foliar residues, it was thought that these trees would yield the most insecticide vapors. Phenthoate concentrations collected 3, 4, 5, 6, 7, and 10 days postapplication (Oct 6, 1978) between 9 and 11 a.m. were 10, 5.5, 3.8, 3.4, 5.1, and 0.75 $\mu g/m^3$, respectively. The data fit the line described by $\ln y = -0.32t + \ln 24$ with $r = 0.91$ and $t_{1/2} = 2.2$ days. The dislodgeable foliar residues were dissipating with $t_{1/2} = 3.5$ days for this plot. Due to the very small treatment plots involved, the data are only crude estimates of insecticide levels present in the air.

Repetition of the air sampling under an orange tree located in the center of a 1979 plot treated with a dilute spray at 7.5 lb of AI (1500 gal)$^{-1}$ acre^{-1} indicated only 3 $\mu g/m^3$ on day 3 postapplication and less than 2 $\mu g/cm^2$ thereafter.

ACKNOWLEDGMENT

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Degradation of Diazinon Encapsulated with Starch Xanthate

Donald Trimnell,* Baruch S. Shasha, and William M. Doane

The degradation of diazinon encapsulated with starch xanthate (SX) cross-linked by various reagents was studied under accelerated aging conditions at 70 °C in the presence and in the absence of reported stabilizers. Stability of diazinon was unchanged by most of these stabilizers. Acidity from the decomposition of SX-encapsulated diazinon decreased the stability. Stability was increased by adding water, keeping the xanthate degree of substitution low, increasing the diazinon loading, and adding alkaline substances to neutralize acidic decomposition products. Calcium oxide was particularly helpful in stabilizing the preparations.
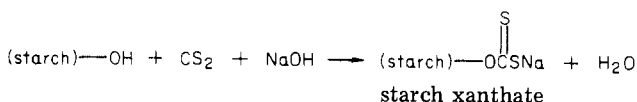
Diazinon [O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate] is an organophosphorus insecticide with low soil persistence (Getzin and Rosefield, 1966). This compound is widely used in agriculture; however, due to its short persistence, treatments with the compound must be repeated periodically during the growing season to maintain effective control (Sethunathan and Pathak, 1972). By formulating diazinon in suitable polymeric matrices, it has been possible to apply diazinon in a granular form having greater persistency and effectiveness (Langbridge, 1963). Formulations that keep the pesticide where applied not only improve effectiveness but also reduce environmental pollution (Balassa, 1973; Nelson and Whitlaw, 1972).

An effective matrix used in this laboratory for encapsulating pesticides is starch xanthate (Shasha et al., 1976). Evaluation of starch matrix containing diazinon revealed that this formulation is more stable than the unencapsulated technical product (Feldmesser et al., 1976; Doane et al., 1977). The encapsulating material is based upon starch, and hence it is nonpersistent in the environment.

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Starch xanthate is prepared by treating a slurry of starch and carbon disulfide in water with aqueous sodium hydroxide as follows:

$$\text{(starch)}\!-\!\text{OH} + \text{CS}_2 + \text{NaOH} \longrightarrow \text{(starch)}\!-\!\overset{\overset{\text{S}}{\|}}{\text{O}}\text{CSNa} + \text{H}_2\text{O}$$

starch xanthate

The xanthate is cross-linked either by oxidative coupling with hydrogen peroxide or sodium nitrite to the xanthide [(starch)—OC(=S)SSC(=S)O—(starch)] or by salt coupling using ferric chloride or sulfate.

Acid is required for the couplings, and both acetic and sulfuric acids have been used to adjust the pH to 5 or below. During oxidation with ferric salts, some acid is generated spontaneously and the reaction is complex. When these couplings are carried out on an intimate mixture with diazinon, the diazinon becomes entrapped as small cells in the cross-linked matrix. Control of pH is essential during the encapsulation to ensure good entrapment and particle firmness. The coupled starch xanthate containing diazinon is air-dried and stored for subsequent application. However, various preparations have been found to decompose upon storage for several months or years at ambient temperatures.

The purpose of this work was to determine the cause of this instability and to produce a more stable formulation. Variables of the encapsulation procedure such as amount of xanthate, method of cross-linking, diazinon concentration in the particles, particle size, moisture, salts, acidity, and various additives were studied and related to diazinon content as a function of time.

Some additives known for their stabilizing effects upon diazinon were included in several formulations. Known additives include glycols such as butoxypoly(propylene glycol) (Granett and Shea, 1955) and poly(ethylene glycol) (Ohmori et al., 1972), ammonia (Godfrey and Morrill, 1963), and ammonia generators such as urea (Ohmori et al., 1972), chlorinated hydrocarbons (Hornstein et al., 1955), quinones (Imperial Chemical Industries, Ltd., 1974), epoxides (Imperial Chemical Industries, Ltd., 1974), metal acetylacetonates (Pemberton, 1975), poly(vinyl alcohol) (Ozawa et al., 1974), poly(vinylpyrollidone) (Ozawa et al., 1974), cellulose ethers (Ozawa et al., 1974), and cyclodextrins (Yamamoto et al., 1976).

EXPERIMENTAL SECTION

Diazinon MG8 [8 lb of active ingredient (a.i.)/gal, 87%], 14G (14% a.i. on ground corn cob), and diazinon decomposition products, 4-ethoxy-2-isopropyl-6-methylpyrimidine, 4-(ethylthio)-2-isopropyl-6-methylpyrimidine, triethyl phosphorothioate, and 2-isopropyl-6-methyl-4-pyrimidinol were generously supplied by Ciba-Geigy Corp. Starch was modified pearl no. 3005 containing 12% moisture, from Corn Products Corporation International. Vikoflex 9010 (epoxidized methyl linseedate) was obtained from Viking Chemical Co., Carbowax 400 [a poly(ethylene glycol] was from Union Carbide Chemicals Co., and acetylacetone (practical) was from Eastman Kodak Co. The latter was used for the preparation of aluminumtris (acetylacetonate) (Biltz, 1904). Cross-linking agents included hydrogen peroxide (30% aqueous, Mallinckrodt, Inc.), sodium nitrite (Merck & Co., Inc.), and ferric chloride and ferric sulfate (Fisher Scientific Co.).

Gas–liquid chromatography (GLC) was performed by using an F & M Model 810 with hydrogen flame ionization detection. The column consisted of 6 ft $\times$ $^1/_8$ in. o.d. stainless steel tubing packed with 80–100-mesh Gas-Chrom Q coated with 3% Silar 5CP. Column temperature was

170 °C and helium flow was ~20 mL/min. Solvent methanol was used as the internal standard and injections were 1 μL. Ascendant peak heights from the base line corresponding to the diazinon peak in standards and unknowns were used in all calculations.

Diazinon standards containing 0.1–0.4% diazinon were prepared from a 1% solution using 1.15 g of Diazinon MG8 in 100 mL of methanol. Aliquots of 1–4 mL were diluted to 10 mL with methanol. Concentrations of diazinon in unknown samples were determined relative to a standard curve made from these standards. Standards were found to be stable for at least 1 week at room temperature.

Starch Xanthate (SX). Starch xanthate of degree of substitution (DS) 0.10 was prepared by treating a suspension of 90 g of starch in 500 mL of water with carbon disulfide (6 mL) and a solution of sodium hydroxide (10 g) in water (194 mL). The mixture was covered and stored for 1 h at room temperature or overnight at 5 °C. For DS 0.17, 10 mL of carbon disulfide and 10 g of sodium hydroxide were required, and for DS 0.33, 20 mL of carbon disulfide and 20 g of sodium hydroxide were required. Xanthate levels were calculated from sulfur analyses of the cross-linked products.

Cross-Linking. SX was cross-linked with mixtures of oxidant or iron salt and acid as follows. (a) *Hydrogen Peroxide–Acetic Acid.* SX (200 g), DS 0.33, was cross-linked by portionwise addition of a solution of 8 mL of acetic acid and 5 mL of 30% hydrogen peroxide in 100 mL of ice water. (b) *Hydrogen Peroxide–Sulfuric Acid.* SX (200 g), DS 0.10, was cross-linked by portionwise addition of a solution of sulfuric acid (3.1 g) and 30% hydrogen peroxide (1.5 mL) in 100 mL of ice water. for a DS level of 0.17, 3.1 g of sulfuric acid and 2.5 mL of hydrogen peroxide were required; for DS 0.33, 6.2 g of sulfuric acid and 5.0 mL of hydrogen peroxide were used. (c) *Sodium Nitrite–Acetic Acid.* SX (100 g), DS 0.10, was cross-linked by portionwise addition of a solution of acetic acid (3 mL) and sodium nitrite (0.5 g) in 100 mL of ice water. For a DS level of 0.17, 3 mL of acetic acid and 0.75 g of sodium nitrite were required; for DS 0.33, 6 mL of acetic acid and 1.5 g of sodium nitrite were used. (d) *Sodium Nitrite–Sulfuric Acid.* SX (100 g), DS 0.10, was cross-linked by portionwise addition of a solution of 2.5 g of sulfuric acid and 0.5 g of sodium nitrite in 100 mL of ice water. (e) *Ferric Chloride–Acetic Acid.* SX (200 g), DS 0.10, was cross-linked by portionwise addition of a solution of acetic acid (4 mL and 40% aqueous ferric chloride, 4.1 mL) in 50 mL of ice water. For a DS level of 0.17, 4 mL of acetic acid and 5.7 mL of 40% aqueous ferric chloride were required; for DS 0.33, 8 mL of acetic acid and 11.2 mL of 40% aqueous ferric chloride were used. (f) *Ferric Sulfate–Acetic Acid.* SX (200 g), DS 0.17, was cross-linked by portionwise addition of 4 mL of acetic acid and 7 g of ferric sulfate in 100 mL of ice water. (g) *Ferric Sulfate–Sulfuric Acid.* SX (100 g), DS 0.10, was cross-linked by portionwise addition of a mixture of 0.5 g of sulfuric acid and 2.5 g of ferric sulfate in 50 mL of ice water. When the ferric sulfate was increased to 3.5 g, no sulfuric acid was necessary.

Encapsulation. Diazinon MG8 and SX were mixed thoroughly. Brief stirring of the xanthate in a blender increased its fluidity and facilitated the mixing with diazinon. The cross-linking agent and acid were added portionwise with continuous mixing until solidification took place and the pH fell to 5 or below. Continued stirring broke the solid down to particles from which water could be expressed. After 5 min, the particles were filtered through cheesecloth on a Büchner funnel by using suction

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Table I. Effect of Water and Diazinon Concentration upon the Stability of SX-Encapsulated Diazinon at 70 °C[a]

	diazinon lost, %		
variable	7 days	14 days	21 days
water[b]			
control	25	55	83
20% water	19	37	53
diazinon concn[c]			
5	33	59	77
10	23	45	59
15	18	36	53

[a] SX DS 0.33, H_2O_2-HAc coupling. [b] Air-dried capsules as control and admixed with 20% (w/w) water; prepared by using 10 mL of diazinon/200 g of SX. [c] mL of diazinon/200 g of SX.

and a rubber dam to remove most of the water. The resulting cake was broken up in a blender, sieved to pass 12 mesh, and air-dried overnight to a constant weight. The dried particles were in the 14–35-mesh range. They were stored in plastic bags for subsequent stability studies in accelerated aging tests at 70 °C.

Typically, additives were introduced by adding them in the dry state to the air-dried capsules. Small amounts of liquid additives adsorbed well onto the dried capsules, and solid additives adhered to the capsules after adding a small amount of vegetable or mineral oil. If the capsules contained some adhering diazinon, the solids adsorbed well without adding oils. Certain solid additives such as calcium oxide were effective not only when admixed but also when placed in permeable packets adjacent to the capsules.

Analyses. Duplicate encapsulated samples of 50–200 mg were pulverized with four 2-mL portions of absolute methanol and filtered by mild suction through a medium fritted glass filter. The pulverized solid was washed with methanol, and the total filtrate and washings were made to 10 mL in a volumetric flask for diazinon analysis by gas chromatography. Kjeldahl analyses performed on residual solids showed less than 0.2% N.

Stability Studies. Samples containing diazinon were sealed in glass pressure flasks and kept at 70 °C for accelerated aging tests. Diazinon content was determined weekly by extraction and gas chromatography of aliquots of the extract. The pH of the pulverized material in an aqueous slurry was determined periodically.

Efficiency of Encapsulation. Percent efficiency of encapsulation was determined from the weight yield of the capsules and percent diazinon in the freshly prepared samples:

$$\% \text{ efficiency} = \frac{\% \text{ diazinon in capsules} \times \text{weight yield}}{\text{weight of diazinon taken} \times 0.87}$$

RESULTS

Efficiency of encapsulation of diazinon was 80–95% with encapsulated products containing up to 40% active ingredient. Accelerated aging at 70 °C progressively decomposed the diazinon while the pH of aqueous suspensions of the products fell from about 5 to 2.5 and a yellow-orange color appeared as decomposition took place.

The gas chromatographic peak attributed to diazinon had a retention time of 4 min, but it was small or absent in decomposed products. New peaks attributed to 4-ethoxy-2-isopropyl-6-methylpyrimidine and 4-(ethylthio)-2-isopropyl-6-methylpyrimidine appeared, having retention times of less than 1 min. A reported major decomposition product (Margot and Gysin, 1957), 2-isopropyl-6-methyl-4-pyrimidinol, was not detected due to its low volatility (mp 173 °C). No decomposition product seemed to have

Table II. Effect of Xanthate DS and Coupling Method upon the Stability of Encapsulated Diazinon at 70 °C

		diazinon lost, %		
xanthate DS	coupling method	7 days	14 days	21 days
0.10	H_2O_2-H_2SO_4[a]	0	100	100
0.17	H_2O_2-H_2SO_4[a]	7	100	100
0.33	H_2O_2-H_2SO_4[a]	92	100	100
0.10	$NaNO_2$-HAc[b]	0	23	100
0.17	$NaNO_2$-HAc[b]	6	79	100
0.33	$NaNO_2$-HAc[b]	4	62	100
0.10	$FeCl_3$-HAc	0	15	89
0.17	$FeCl_3$-HAc	0	20	88
0.33	$FeCl_3$-HAc	9	86	100

[a] 10 mL of diazinon/200 g of SX. [b] 5 mL of diazinon/100 g of SX.

Table III. Influence of Carbonates, Urea, and Additive Packets upon the Stability of SX-Encapsulated Diazinon at 70 °C

	diazinon lost, %		
additive	7 days	14 days	21 days
control[a]	10	41	84
sodium bicarbonate[b]	17	19	35
magnesium carbonate[b]	11	15	21
calcium carbonate[b]	11	12	68
urea[c]	22	29	51
control[d]	0	76	90
anhydrous copper sulfate packet[e]	17	100	100
drierite packet[e]	4	93	100
silica gel packet[e]	4	55	100
alumina packet[e]	7	43	100
calcium oxide packet[e]	8[f]	10[f]	14[f]

[a] SX DS 0.10; $Fe_2(SO_4)_3 \cdot nH_2O$-H_2SO_4 coupling; 5 mL of diazinon/100 g of SX. [b] 0.5 g added as a solution or slurry to moist capsules prior to drying. [c] 3.0 g added as for footnote b. [d] SX DS 0.10; H_2O_2-H_2SO_4 coupling; 10 mL of diazinon/100 g of SX. [e] Packets contained 1.0 g of substance/2.0 g of control. [f] Average of four runs.

the same R_f as diazinon. Duplicate analyses usually agreed to within ±5%.

The influences of water and diazinon concentration upon the stability of encapsulated diazinon are summarized in Table I. Water added to the dried capsules prior to accelerated aging, and increases of diazinon concentration in the capsules, gave moderate improvement in stability.

The effects of xanthate DS and method of coupling upon diazinon stability are shown in Table II. Stability is greatest at the lowest xanthate DS (0.10) in all coupling methods, presumably because of the lower amounts of acid required for neutralization and occluded in the final product. When sulfuric acid is used, the capsules from DS 0.10 and 0.17 are stable for a short period, and then there is rapid and total decomposition. Stability is improved by using the acetic acid–sodium nitrite system. However, this system was somewhat inferior to the other methods in that the formation of nitrogen oxides during coupling caused irregular fissures in the final products. The most stable products were obtained with acetic acid–ferric chloride as the coupling agent using DS 0.10 and 0.17.

Various carbonates and urea were added as aqueous solutions or slurries to the moist capsules after filtration. The capsules were dried and tested for stability (Table III). All of these substances generally gave moderate stability improvements, presumably because they neutralize acidic decomposition products both from the encapsulating xanthide and from the diazinon. Table III also shows the effects of various additives physically separated from the

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Table IV. Effect of Calcium Oxide and Oils upon the
Stability of SX-Encapsulated Diazinon at 70 °C

calcium oxide added (w/w), %	oil added (w/w), %	diazinon lost, %		
		7 days	14 days	21 days
none[a]	none	50-90	100	100
10		12	54	84
20		10	17	17
30		15	21	21
40		12	24	25
none[b]	none	100	100	100
20	10, vegetable	19	35	64
20	10, mineral	14	22	36

[a] SX DS 0.17; H_2O_2-H_2SO_4 coupling; 10 mL of
diazinon/100 g of SX. [b] SX DS 0.17; H_2O_2-H_2SO_4 coupling; 15 mL of diazinon/300 g of SX.

capsules in porous packets. Silica gel and alumina moderately improved the stability and calcium oxide greatly improved the stability of the diazinon, presumably because they take up volatile acidic decomposition products of the capsules.

A series of additives tested in order to see if certain types of reported stabilizers were effective in stabilizing SX-encapsulated diazinon included Vikoflex 9010 (an epoxidized oil), cyclohexene oxide, *p*-quinone, aluminumtris (acetylacetonate), Carbowax 400 [a poly(ethylene glycol)], and ethylene glycol. None of these significantly improved diazinon stability.

Since calcium oxide caused the most notable improvement in stability, the effect of this additive was studied in more detail. Table IV shows the effects of increasing amounts of calcium oxide admixed with the capsules upon the diazinon stability. It may be seen that the maximum stabilization is obtained in this control series at 20% (w/w) calcium oxide. When vegetable or mineral oils are used to improve adhesion of the calcium oxide to the capsules, there is some sacrifice of stability.

Figure 1 illustrates the decomposition pattern of diazinon encapsulated by the H_2O_2-H_2SO_4 method in air-dried capsules alone (a) and kept with 20% calcium oxide (b). Similarly, decomposition curves of diazinon 14G alone (c) and mixed with 20% calcium oxide (d) are illustrated. It may be seen that the calcium oxide increases the half-life of encapsulated diazinon from ~7 days to over 40 days and diazinon 14G becomes almost completely stabilized. Diazinon encapsulated by the other xanthate coupling methods was also greatly stabilized. Encapsulated diazinon is similarly stabilized when kept with a packet of calcium oxide at 70 °C.

CONCLUSIONS

Stability of diazinon in SX-encapsulated formulations is improved by adding water, increasing the diazinon loading, and adding various alkaline substances that will take up acidity. Stability is greatest at low xanthate DS presumably because there is less acid occluded and generated upon decomposition of the capsules. Several substances reported to improve diazinon stability were of little value with the SX-encapsulated formulation. However, calcium oxide was found to be particularly useful in stabilizing diazinon in all SX preparations and also in a commercial granular formulation based upon ground corn
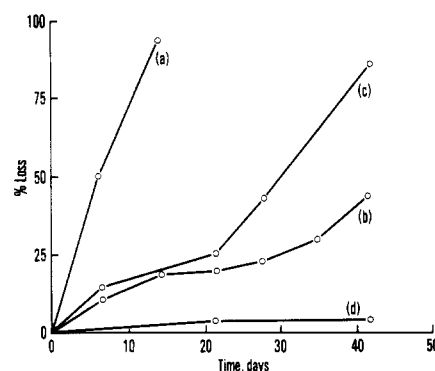

Figure 1. Effect of calcium oxide upon diazinon formulations at 70 °C. (a) H_2O_2-H_2SO_4; DS 0.17; 10 mL of diazinon/100 g of SX. (b) Capsules of (a) mixed with 20% CaO. (c) Diazinon 14G. (d) Diazinon 14G mixed with 20% CaO.

cob. Encapsulated diazinon suitable for prolonged storage in bags prior to field use might include ~20% calcium oxide dusted onto the capsules by using a small amount of mineral oil as an adhesive. The presence of calcium oxide may also provide an alkaline environment for the encapsulated diazinon that could retard decomposition by soil acids.

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