

Decomposition of Di-Syston (*O,O*-Diethyl *S*-[2-(ethylthio)ethyl] Phosphorodithioate) on Fertilizers by Infrared, Gas-Liquid Chromatography, and Thin-Layer Chromatography

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Commercial fertilizers and fertilizer ingredients were impregnated with Di-Syston and stored for 1 year at room temperature and at 40° C. for 6 weeks. Studies were conducted to determine the rate and extent of decomposition of Di-Syston and to identify the decomposition products by analyzing samples periodically during storage. Treatment with deactivators decreased the rates of decomposition, while extensive breakdown was

exhibited on three of the 11 untreated materials. On the fertilizer ingredients superphosphate and ammonium nitrate, all but a trace of Di-Syston was oxidized to the oxygen analog sulfone and oxygen analog sulfoxide. Hydrolysis accounted for significant breakdown in several fertilizers as well. Conversely, Di-Syston was relatively stable on triple superphosphate and most of the other materials.

Di-Syston (registered trade-mark of Farbenfabriken Bayer AG, Chemagro Corp. licensee) (Thiodemeton or Disulfoton) is a systematic insecticide and its formulations are used for control of sucking insects and mites on plants. The most commonly used formulations are spray concentrates and impregnated granules. A more recent application is the direct impregnation of fertilizer to protect the plant through the early growth period.

Early analytical work showed that recovery of Di-Syston from some commercial fertilizers was poor even immediately after impregnation, while on others it was good (Chemagro Corp., 1964a, b, c). Therefore, a study was conducted on seven fertilizers and four fertilizer ingredients impregnated with Di-Syston, for 1 year at room temperature and for 6 weeks at 40° C., with and without deactivator, to determine the probable cause and rate of decomposition. The deactivator used for some of these materials consisted of a protective coating of Celite, diethylene glycol, or both, applied before impregnation in an attempt to minimize contact between the Di-Syston and the fertilizer. Table I also includes the ingredients used in the preparation of the fertilizers.

A variety of compositions and fertilizer ingredients was chosen to isolate and identify the characteristic most probably responsible for the decomposition ob-

served. The identification of breakdown products could conceivably indicate a mechanism for the decomposition and, perhaps, suggest a means to avoid or limit it.

EXPERIMENTAL

Impregnation. One kilogram of commercial fertilizer or fertilizer ingredient was treated with approximately 10.5 grams of technical Di-Syston dissolved in 400 ml. of methylene chloride in a 1-liter round-bottomed S.T. flask. After mixing well, the flask was attached to a rotary evaporator and rotated under vacuum at room temperature until no solvent remained. The resulting dry mix was bottled and sealed in 30-gram portions for storage stability studies.

Apparatus and Reagents. Thin-layer chromatography (TLC) plates were 0.5-mm. thick silica gel G prepared and stored according to Gordon and Eastoe (1964). 2,6-Dibromo-*N*-chloro-*p*-quinoneimine (DCQ) was used as the chromogenic reagent for spraying the plates after development.

A Perkin-Elmer Model 800 gas-liquid chromatograph (GLC) was used, equipped with a flame-ionization detector and stainless steel column, ¼ inch × 4 feet, packed with 3% silicone rubber SE-30 on acid- and base-washed Ekono-Pak W 60/80 mesh, treated with dimethyl chlorosilane.

Infrared data were obtained with a Perkin-Elmer Model 521 recording spectrophotometer fitted with a 0.5-mm. NaCl cell.

Extractions were carried out in a standard Soxhlet extraction apparatus using 25 × 82 mm. thimbles. A rotary vacuum evaporator capable of holding ground

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Table I. Impregnation of Fertilizer

Designation	Material Added	Designation	Material Added
6-8-6 (granule) ^a	Di-Syston	6-24-0 (granule) ^e	Di-Syston
6-8-6D	26% concentrate ^d	18-46-0 (granule) ^f	Di-Syston
8-24-8 (granule) ^b	Di-Syston	8-32-16 (granule) ^g	Di-Syston
8-24-8D	26% concentrate ^d	Superphosphate	Di-Syston
20-10-10 (blend) ^c	Di-Syston	8-32-0 (granule) ^h	Di-Syston
20-10-10D	26% concentrate ^d	Ammonium nitrate (AN ₁)	Di-Syston
Ammonium sulfate	Di-Syston	Ammonium nitrate (AN ₂)	2% Celite followed by Di-Syston
Triple superphosphate	Di-Syston	Ammonium nitrate (AN ₃)	1% diethylene glycol in CH ₂ Cl ₂ followed by 26% concentrate

^a Superphosphate treated with sulfuric acid, neutralized with nitrogen solution (25% ammonia, 69% ammonium nitrate, and 6% water) and anhydrous ammonia, blended with dolomite and potassium chloride, then dried to granules.

^b Mixture of triple superphosphate, normal superphosphate, phosphoric acid, sulfuric acid, nitrogen solution, and anhydrous ammonia, blended and passed through a hot air-drying kiln to produce homogeneous pellets; potassium chloride added.

^c A blend of 10-10-0, urea, 18-46-0, and potassium chloride.

^d 26% concentrate = Di-Syston 26%, diethylene glycol 2%, Celite 72%.

^e Calcium phosphate rock treated with sulfuric acid, final slurry neutralized with ammonia, then processed through drying drum to form pellets. pH controlled in range of 4.5 to 6.5.

^f Both phosphoric acid and ammonia sprayed on small particles of ammonium phosphate and continuously circulated through a dryer with particles built up to sufficient size, then separated.

^g Dry potash sprayed with mixture in 18-46-0 above ^f and granulated in same way.

^h Same as 8-24-8 but without potassium chloride.

joint flasks was used for removing solvent from the extract at reduced pressure and temperature.

Reagent grade chemicals and solvents were used. Standard 1% solutions in chloroform of *O,O*-diethyl *S*-[2-(ethylthio)ethyl] phosphorodithioate (Di-Syston) I, *O,O*-diethyl *S*-[2-(ethylsulfinyl)ethyl] phosphorodithioate (sulfoxide) II, *O,O*-diethyl *S*-[2-(ethylsulfinyl)ethyl] phosphorothioate (oxygen analog sulfoxide) III, *O,O*-diethyl *S*-[2-(ethylsulfonyl)ethyl] phosphorodithioate (sulfone) IV, and *O,O*-diethyl *S*-[2-(ethylsulfonyl)ethyl] phosphorothioate (oxygen analog sulfone) V, were prepared and refrigerated when not in use.

PROCEDURE

Gas-Liquid Chromatographic Method. A 25-gram sample was extracted in a Soxhlet extraction apparatus with 75 ml. of chloroform for 16 hours. The chloroform was partially evaporated using a rotary vacuum evaporator in a 45° to 50° C. water bath. The solution was made up to volume in a 25-ml. volumetric flask. The following conditions were set on the Perkin-Elmer Model 800 GLC: injector port 200° C., attenuation 1K or 2K, nitrogen and hydrogen pressures 16 p.s.i., air pressure 35 p.s.i. The injection volumes were 2 μl. for both sample and standard.

The oven temperature was programmed from 150° to 250° C. at a rate of 8° per minute. The standards were chromatographed individually and collectively. Each peak in the sample was identified by matching its retention time with the corresponding one in the standard.

Standard III was converted to the corresponding sulfone (V) by adding about 8 mg. of potassium permanganate to 1 ml. of a 1% solution of III in acetone. The solution was shaken for 1 minute, centrifuged, and chromatographed as above. Injection immediately after centrifuging was necessary to avoid hydrolysis.

Water was determined on fertilizers by drying at

130° C. for 5 hours. The pH measurements were made on well-stirred 10% suspensions in distilled water.

Thin-Layer Chromatographic Method. Di-Syston and its oxidation products were identified by spotting 50 μl. of the chloroform solution and a known amount of standard solutions of the oxidation products of Di-Syston on a silica gel G plate. The plate was developed in chloroform-methanol 39 to 1, sprayed with DCQ reagent, heated in a 110° C. oven for 5 minutes, and exposed to dilute (yellow) bromine fumes.

Infrared Method. The chloroform solution previously used for GLC analysis was evaporated to dryness using a rotary vacuum evaporator in a 45° to 50° C. water bath. 1,2-Dimethoxyethane (50 ml.) was pipeted into the flask which had been cooled to room temperature. The absorbances of the sample and a standard were compared at 15.2 microns (658 cm.⁻¹) using a suitable infrared spectrophotometer. The absorbance of the extract of the fertilizer without Di-Syston, treated in the same manner as the sample, was determined as a correction.

Results. Preliminary extraction studies on the fertilizers were performed with chloroform, carbon disulfide, ethyl ether, and dimethoxyethane. Carbon disulfide and ethyl ether gave good recoveries but were eliminated because of their high flammability. Dimethoxyethane yielded very turbid solutions. Chloroform, which exhibited none of the above disadvantages, was used for all extractions.

Analysis for active ingredient by the infrared procedure gave recoveries ranging from 94 to 100%. The data on samples stored for 1 year at room temperature, and for 6 weeks at 40° C., are given in Tables II and III, respectively. Figure 1 summarizes the oxidation pathways of Di-Syston on fertilizers. Di-Syston was first oxidized to II on all fertilizers. II was further oxidized to III and/or to IV on 8-32-0, superphosphate, and untreated ammonium nitrate (Figures 2 and 3).

Table II. Di-Syston Remaining on Fertilizer Samples Stored at Room Temperature (Per cent relative)

Fertilizer	Water	pH	Months				
			2	3	5	8	12
6-8-6	8%	5.2	97	96	94	88	83
6-8-6D			99	95	97	86	87
8-24-8	9%	4.1	89	86	85	79	71
8-24-8D			91	89	86	84	77
20-10-10	23%	6.2	84	73	72	76	68
20-10-10D			95	73	84	80	73
Ammonium sulfate			100	99	97	99	92
Triple superphosphate			88	88	87	87	90
6-24-0			100	98	97	99	95
18-46-0			100	86	79	77	67
8-32-16			92	96	86	82	90
Superphosphate			48	0	0
8-32-0			81	80	69	59	45
AN ₁	6%	3.5	92	85	66	0	...
AN ₂			79	79	70	34	2
AN ₃			86	80	84	65	50

Oxidation progressed beyond this stage with the formation of V (Figure 3) on ammonium nitrate free of diethylene glycol deactivator (AN₂).

Table II shows that Di-Syston was least stable on superphosphate; complete decomposition also occurred on AN₁ and AN₂, but not until much later. Considerably better stability was evident on 8-24-8, 8-24-8D, 20-10-10, 20-10-10D, 18-46-0, 8-32-0, and AN₃. The most stable formulations were 6-8-6, 6-8-6D, ammonium sulfate, triple superphosphate, 6-24-0, and 8-32-16. The deactivators varied in effectiveness, preventing about half of the decomposition on ammonium nitrate (AN₃) and 5 to 6% on the other materials treated. There was a significant increase in the stabilization of ammonium nitrate treated with both deactivators over the same treatment with celite alone.

Some infrared results are higher after storage than

before (Tables II and III). This is due in large measure to the difficulty of maintaining a thorough dispersal of the dust in the stock sample. Mixing of fertilizers during addition of solution and use of closely sized fertilizer increased uniformity (Creamer and Lamont, 1961).

DISCUSSION

At the conclusion of the experiments an attempt was made to relate rate of hydrolysis to water content and/or pH. However, a sufficient quantity of only four materials was available for obtaining these data (Table II). There appears to be no relationship between the water contents or pH's and the over-all stabilities of the fertilizers shown in Table II. This does not mean that moisture was without any effect, however, as evidenced by the TLC of Figure 4. The origins for 8-24-8 and

Table III. Di-Syston Remaining on Fertilizer Samples Stored at 40°C. (Per cent relative)

Fertilizer	Days			Weeks			
	1	4	5	1	2	4	6
6-8-6	84	80	88	83	100	96	83
6-8-6D	100	89	100	89	92	90	95
8-24-8	99	95	96	96	88	97	99
8-24-8D	100	100	100	100	94	96	93
20-10-10		89		84	81	86	94
20-10-10D		88		95	85	91	90
Ammonium sulfate	99	100		98	97	100	93
Triple superphosphate	94	87		89	92	88	86
6-24-0	100	100		97	97	94	100
18-46-0	100	90		100	84	93	86
8-32-16	88	91		84	84	87	90
Superphosphate	97	82		88	77	78	9
8-32-0	91	98		81	85	62	83
AN ₁	92	71	72	70	76	60	39
AN ₂	95	71	72	70	73	68	32
AN ₃	92	82	83		81	74	68

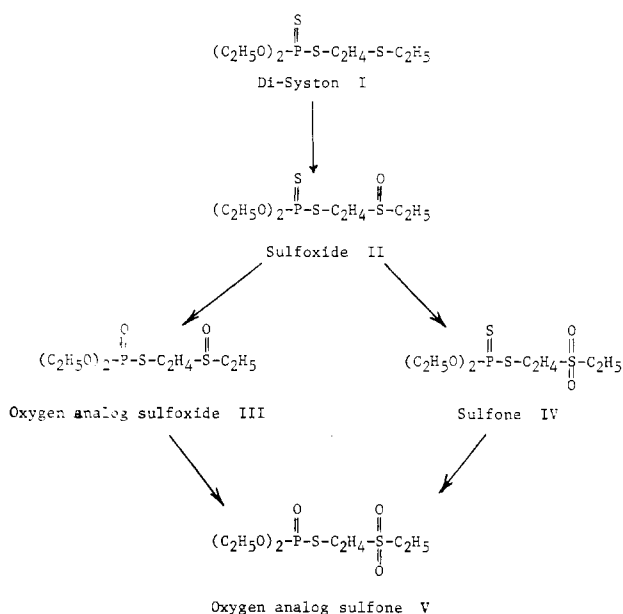


Figure 1. Oxidation pathways of Di-Syston on fertilizer materials

20-10-10 showed additional red spots which are probably acidic hydrolysis products and account for about one third of the loss of Di-Syston.

The results of the GLC work tended to confirm the TLC findings. III gave a very poor response by GLC but this was greatly improved by oxidation with potassium permanganate to the sulfone (V). This treatment was performed on 1 ml. of the extracts of AN₂ and 8-32-0 stored for 1 year at room temperature. GLC on the extract of AN₂ before oxidation (broken line, Figure 5) shows III and V (*R_t* 8.0 minutes). An increased response in the V peak after treatment with potassium permanganate shows that III was oxidized to V.

With regard to 8-32-0, the GLC scan (Figure 5) shows three oxidation products, II, III, and IV (broken line *R_t* 1.6, 5.5, and 8.5 minutes, respectively). Treating the extract with potassium permanganate oxidized II and III to their respective sulfones (IV and V) (solid line, *R_t* 8.5 and 8.0 minutes, respectively).

Storage stability studies at elevated temperature indicate that a sharp decrease in the Di-Syston value occurred within 6 weeks on superphosphate and am-

Figure 2. Thin-layer chromatograms of 1% Di-Syston on superphosphate and 8-32-0, stored at room temperature

Chloroform-methanol 39 to 1, DCQ

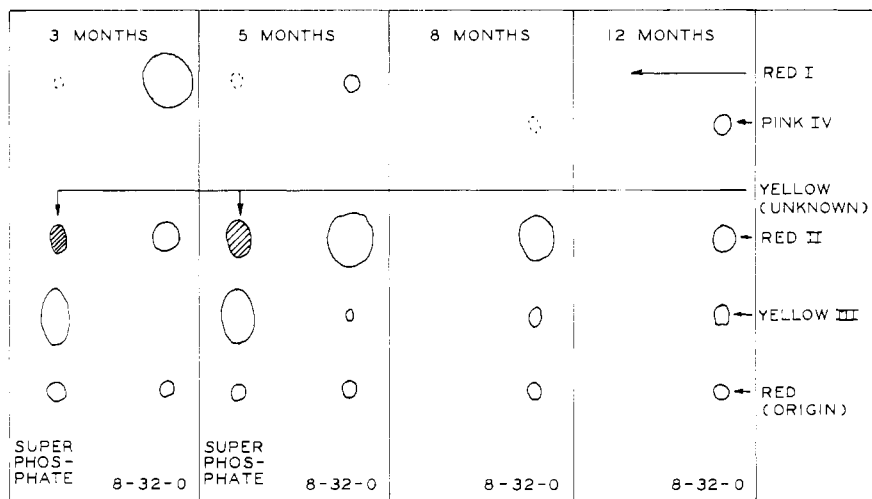
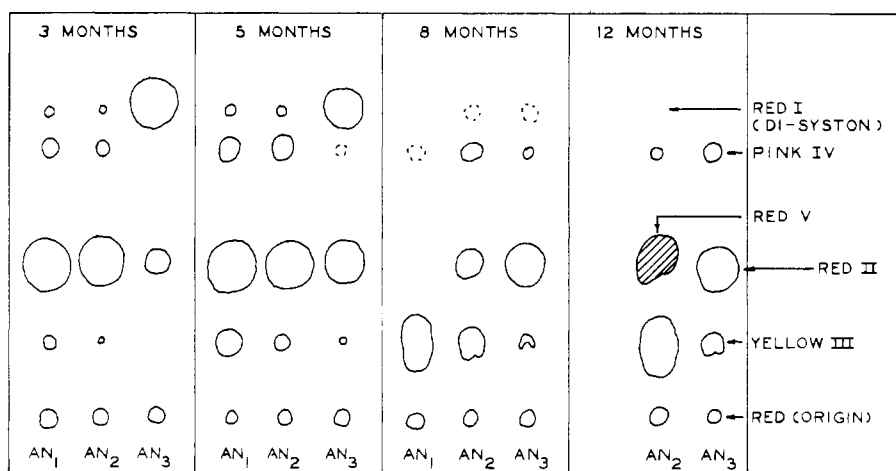


Figure 3. Thin-layer chromatograms of 1% Di-Syston on treated and untreated ammonium nitrates stored at room temperature

Chloroform-methanol 39 to 1, DCQ



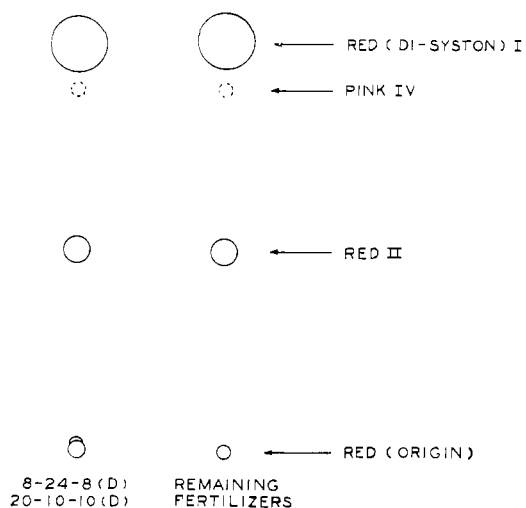


Figure 4. Thin-layer chromatogram of 1% Di-Syston on fertilizers stored for one year at room temperature

Chloroform-methanol 39 to 1, DCQ

monium nitrate, contrary to the more than 65% recovered from the other fertilizers shown in Table III. It is not difficult to envision the oxidation of Di-Syston by ammonium nitrate in the presence of a trace of acid. Predictably, more oxidation, hydrolysis, and formation of new unknown spots occurred at 40° C. than at room temperature. The unknown spots were usually colored orange, pink, or purple, were transitory in nature, and occurred at R_f 's between I and II.

Decomposition of Di-Syston on fertilizers may be attributed wholly or partially to surface activity (catalytic oxidation). Also, during the conversion of phosphate rock to normal superphosphate sufficient sulfuric acid may accumulate interstitially for oxidation to occur. Preferential adsorption of toxicant by certain portions

of a mixed fertilizer has been shown to accelerate decomposition of the toxicant (Creamer and Lamont, 1961). If discrete particles of normal superphosphate or ammonium nitrate occur in the fertilizer mix, there is no question but that the Di-Syston would be less stable on these particles than on other particles in the mix.

Pore structure of fertilizers such as superphosphate can be a critical element in determining the rate of reaction of absorbed materials. Caro and Freeman (1961) contended that the volume of fine pores is the important criterion with respect to the reactivity of phosphate rock and that coarse pores have little or no effect on reactivity. They further showed that micropores and fine macropores are prominent in phosphate rock but extremely small in extent in triple superphosphate. The fact that normal superphosphate promotes rapid decomposition of Di-Syston may indicate that its pore characteristics are more similar to those of natural phosphate rocks than to triple superphosphate.

In agreement with our observations, Creamer and Lamont (1959) found that superphosphate formed the least stable mixtures with insecticides (chlorinated hydrocarbons in that study)—for example, Endrin lost three chlorine atoms per molecule. In contrast to our results, they observed that ammonium nitrate had little or no effect on the stability of the insecticides, but this is not surprising in view of the fact that they were working with Endrin and similar compounds which are not as readily oxidized as Di-Syston. Fleck and Haller (1945) have observed that no fertilizers except dolomitic limestone showed catalytic activity when placed in contact with DDT. Instability of insecticides in fertilizer mixtures has also been related to minor characteristics of the fertilizers, such as iron content and surface acidity (Bellin *et al.*, 1956). More basic materials can cause appreciable decomposition of alkali-

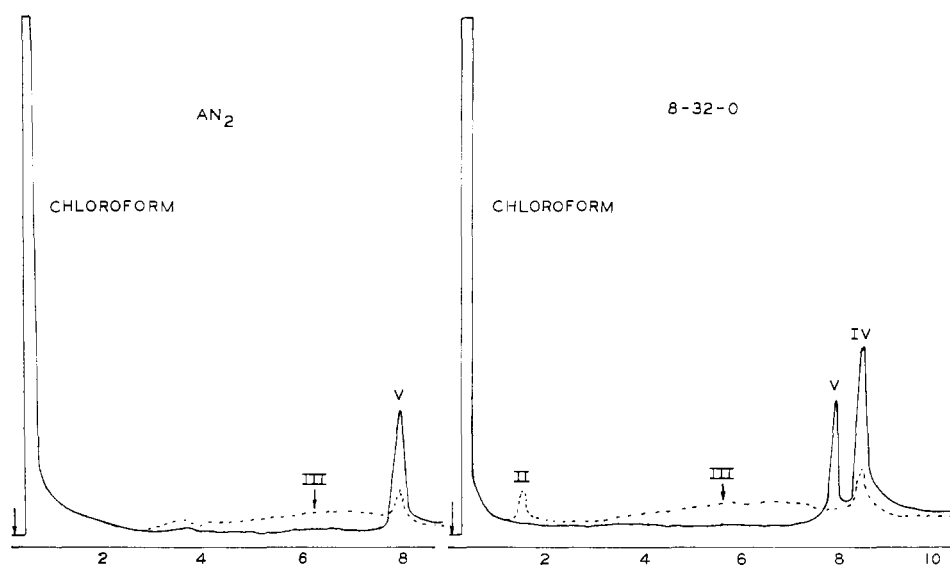


Figure 5. Temperature-programmed chromatogram of 1% Di-Syston on AN₂ and 8-32-0, stored one year at room temperature

sensitive insecticides (Chandra and Bollen, 1960; Chemagro Corp., 1965).

CONCLUSIONS

The low values in Table II are in general attributable to hydrolysis of Di-Syston. Oxidation reactions leading to III, IV, and V are believed responsible for the greater loss on fertilizers containing normal superphosphate or ammonium nitrate.

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