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The Influence of Formulation, Exposure Time, and pH on the Herbicidal Action of Dalapon Foliar Sprays Tested on Corn

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Technical and commercial dalapon were tested on corn, with or without one of the surfactants: Vatsol OT, Dynawet, and X-77. Acid dalapon and four of its salts also were tested. The acid and the sodium salt were about equal in effectiveness. The advantage of using various additional surfactants was amply demonstrated.

Dalapon penetrated corn leaves most readily in the nondissociated form, or at low pH in aqueous solutions. However, acute toxicity at very low pH interfered with translocation, which is necessary for effective growth inhibition by the herbicide. Optimum herbicidal results were obtained at about pH 6, near the pH of a solution of commercial dalapon in tap water.

The toxicity to corn of various dalapon formulations is discussed and interpreted in relation to known physicochemical properties of the parent compound, 2,2-dichloropropionic acid.

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The Influence of Formulation, Exposure Time, and pH on the Herbicidal Action of Dalapon Foliar Sprays Tested on Corn[1]

TO BE EFFECTIVE by foliar application, a herbicide must spread on the plant surface, pass through the lipoidal cuticle—either directly or through the stomata—and be absorbed into living cells. Systemic herbicides require translocation within the conducting system of the plant, often for considerable distances. Inefficacy of herbicide applications may be due to failure of penetration, of translocation, or of both. Perhaps poor penetration is what most often prevents successful action. However, the selective action of herbicides is not clearly related to differential penetration in different kinds of plants (Holly, 1956; Weintraub, 1956; Williams, 1956). Dalapon—a chlorinated aliphatic hydrocarbon, 2,2-dichloropropionic acid—possesses the required combination of ionic and polar properties to permit its penetration, transport, and toxic action under appropriate conditions. Its toxicity is low when conditions are unfavorable for penetration, because of improper formulation, high pH, absence of surfactant, or other factors.

Many factors influence the penetration and translocation of herbicides in plants and thus ultimately affect their toxicity. The subject has been discussed by Funderburk and Davis (1960) and by Prasad, Foy, and Crafts (1962). The present article deals with the herbicidal action of dalapon foliar sprays as influenced by chemical formulation, rate of application, added surfactant, exposure time, pH, and various interactions of these factors. Studies on these relationships may ultimately give clues to the mechanisms of foliar penetration.

REVIEW OF LITERATURE

Dalapon Formulation

Early investigation of several derivatives of dalapon failed to reveal any with greater biological activity than the sodium salt. The Dow Chemical Company (1953) reported the acid as equal to the sodium salt in herbicidal effectiveness. Montgomery and Freed (1955) found that these two compounds acted similarly against germinating oats and stated that this biological activity is a function of maximum solubility and concentration of the chemical at a given toxicity level. Day *et al.* (1962) found the triethyleneglycol ester of dalapon slightly more active than the sodium salt.

Munakata *et al.* (1959) tested 46 different esters on seeds of *Echinochloa crusgalli* (L.) Beauv. var. *frumentacea* (Roxb.) W. F. Wight, of *Brassica campestris* L., and of *Oryza sativa* L., in petri dishes. They noted certain interesting selectivities among plant species and suggested that these might be due

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to differences in permeability of seed coats and in penetrating ability of the different esters. Most of the esters—apolar compounds of chloroacetic, trichloroacetic, dichloropropionic, 2,3-dichloroisobutyric, bromoacetic, and iodoacetic acids—inhibited germination more strongly than did the corresponding sodium salts.

Surfactant

Much research supports the claim that various surfactants increase herbicidal effectiveness. Grasses are notably more difficult to wet than are most broad-leaved plants. Ennis, Williamson, and Dorschner (1952) found that corn and johnsongrass, among other grasses, repelled nearly all spray droplets without surfactant, whereas cotton retained them. A suitable wetting agent, however, provided thorough wetting of all plants tested. Currier and Dybing (1959) listed nine factors that may contribute to the effectiveness of surfactants. The Dow Chemical Company (1953) classified some of the surfactants that had been used effectively with dalapon sprays, especially on seedling grasses, in three chemical groups: alkyl aryl sodium sulfonates, lauryl alcohol sodium sulfonates, and alkyl aryl polyether alcohols.

Certain surfactants are more effective than others. Orgell (1957) found that the pH and the ionic charge of the surfactant radical were the principal factors affecting sorption of acid or basic substances by intact cuticle. Ebeling (1939) showed that the contact angle of a spray droplet is relatively independent of its size but varies with the wetting agent and, more significantly, with the substratum. He found that sodium dioctylsulfosuccinate spread more effectively than sodium oleate on viburnum leaves but less effectively on beeswax.

Currier (1954) called attention to three possible relations of a surfactant to herbicidal activity: progressive enhancement with increasing surfactant concentrations, progressive suppression, or no effect. Jansen, Gentner, and Shaw (1961) screened 63 surfactants—anionic, cationic, nonionic, ampholytic, and blended—for their effects on dalapon and three other herbicides. Fifty-three of the compounds increased the activity of dalapon on corn leaves, four suppressed it, and six had little measurable effect. Surfactant effects were not necessarily the same on different plant species, or with all herbicides, or at all initial levels of herbicidal activity. No correlation was found between any one of the effects of a surfactant and its ionogenic classification.

Currier's (1954) observation that Vatsol OT increases dalapon absorption by roots is of interest because roots are readily wetted by water, and in all probability the action must be on root-cell protoplasm primarily. This is in contrast to foliar absorption, where the plasma membrane is only one of the lipid surfaces where surfactants can exert their effect.

In preliminary experiments of Norris and Freed (1962), a C^{14}-labeled surfactant, Pluronic L-62, appeared to be absorbed and translocated in association with 2,4,5-trichlorophenoxyacetic acid, indicating some kind of interaction between surfactant and herbicide.

Exposure Time

Rain falling soon after spray application can wash off the herbicide before maximum penetration occurs (Weaver, Minarik, and Boyd, 1946; Antognini, 1951; Zukel *et al.*, 1956). This has been observed in the field with dalapon and a wide variety of other compounds. Hanson (1956) simulated rain 15 minutes after spraying with dalapon. At first, the herbicidal action seemed only half as complete as in nonsprinkled plots; after 44 days the results were equal. Hanson attributed this behavior to absorption of dalapon through the roots, some time after it was washed off the leaves. From data on leaves washed at different intervals after dipping, Standifer and Ennis (1956) concluded that maximum absorption and translocation of dalapon required 24 hours or longer in young corn. Santelmann and Willard (1954) found that washing five minutes after dalapon treatment did not prevent severe damage to quackgrass leaves, and that longer exposures were still more injurious to the treated leaves and to other plant parts.

Foy (1961) found that radioactive dalapon-2-C^{14} and dalapon-Cl^{36} were still being transported from treated areas of cotton and sorghum leaves two weeks after spraying. Data from plants washed after treatment with radiolabeled dalapon (Foy, 1958) indicated that penetration into the conducting tissues of the plant continued considerably longer than the time the droplets remained visible to the naked eye.

pH

Freed (1956) reported, among other properties of 2,2-dichloropropionic acid, pH (aqueous) 1.38, K_i 2.94×10^{-2}, and pK_i 1.53.

Hamner, Lucas, and Sell (1947) and Lucas *et al.* (1948) showed that pH and buffer composition may be important factors in herbicidal effectiveness.

Apparently several weak acids penetrate cell membranes and are transported in the plant most readily in the nondissociated form, i.e., at the lower pH values (Crafts and Reiber, 1945; Wood, Mitchell, and Irving, 1947; Lucas *et al.*, 1948; Crafts, 1953; Skoss, 1955; Currier and Dybing, 1959). However, Prasad (1961) found some evidence that low pH exerted a greater effect on cell permeability than could be attributed to the degree of nondissociation in the spray. With dalapon, Wilkinson (1955) found that the growth of corn coleoptiles tended to be more inhibited by solutions with lower pH. Hauser and Thompson (1959) reported increasing absorption of dalapon by johnsongrass, *Sorghum halepense* (L.) Pers., from pH 9.0 to 6.5 to 4.5.

Orgell and Weintraub (1957) indicated the importance of different cations for penetration, independent of pH. Under appropriate conditions 2,4-dichlorophenoxyacetic acid (2,4-D) was absorbed as well in an alkaline as in an acid solution. On the other hand, Leopold (1956) stated: "Penetration of 2,4-D into plants is strongly influenced by pH, but only when the plant tissue is submerged in the solution. Spray applications of the acid of course are quite insensitive to pH differences. The pH curve for the entry of acids has been described . . . but other factors are involved in the entry of 2,4-D from sprays . . ."

Szabo and Buchholtz (1961) observed interestingly different effects of various ionic additives on the penetration of 2,4-D through living surfaces (*Sedum* leaves) and nonliving surfaces (collodion membranes).

MATERIALS AND METHODS

Corn, *Zea mays* L., was used as the test plant because it responds to treatments with dalapon—a grass-selective herbicide—over a wide range of concentrations. Moreover, it grows readily and uniformly in the greenhouse, and techniques for testing herbicides on this species have been standardized. However, like most monocotyledons, corn resists wetting by unmodified aqueous solutions.

Arasan-treated seeds of var. Morses Grain Hybrid were planted in 4-inch pots containing steam-sterilized Yolo sandy loam soil. The pots were subirrigated at first, to avoid crusting of the soil surface. Ten days after planting, the corn was thinned to four plants per pot, and ammonium sulfate fertilizer in water was applied at a high but subtoxic rate. Four days later the plants were 25 to 35 cm tall and growing vigorously. At this time, 14 days after seeding, the plants were ranked for uniformity according to replication and treated with the foliar sprays. The four plants in a pot constituted a treatment plot; four or five replications were made of each test. One set of replicates was harvested just before each treatment, and heights of the plants and their fresh green weights were recorded as a basis for measuring subsequent growth of treated plants. This procedure gave coefficients of variability at harvest between 4 and 14 per cent.

Before spraying, the soil surface in all test pots was covered with vermiculite, to prevent the chemicals from reaching the soil. Aqueous solutions of dalapon were sprayed on the foliage at the rate of 40 gallons per acre, using an experimental spraying table similar to that described by Shaw and Swanson (1952). The vermiculite was removed after the sprays dried, before the next irrigation. In the pH experiment, the plants were placed on a turntable and sprayed to runoff with a compressed-air atomizer.

.To study exposure time, the plants were inverted at designated intervals after spraying and washed free of surface dalapon with an ordinary water sprinkler. To avoid the possibility of spray accumulating in the whorls, the plants were left to dry in a horizontal position. From the known solubility of dalapon in water and from washing studies of plants treated with radioactive dalapon (Foy, 1958), it seems safe to assume that washing removed all of the nonabsorbed dalapon—at least when no surfactant was used. Absorbed dalapon is here defined as that which has entered into or passed through the continuous external surface of plant cuticle or has penetrated stomata or other openings. It is possible that imperceptible amounts of dalapon adhered to the leaf surfaces and resisted washing when surfactants were used.

Plant response was recorded by visual observation of symptoms, by photographs, and by measured heights and fresh green weights. All experiments were terminated two weeks after spraying. Figure 1 shows that rather subtle responses to treatment became evident during this period.

Three herbicide solutions were used: technical grade, containing 85 per cent dalapon sodium salt but no wetting agent—solution A; commercial grade, containing 85 per cent dalapon sodium salt plus 4 per cent unidentified anionic wetting agent—solution B; and commercial dalapon plus 0.1 per cent Vatsol OT—solution C. The amount applied per acre was calculated as active dalapon, which is only 85 per cent of either the technical or the commercial solution.

pH readings of the spray mixtures were taken just before each treatment. These readings vary somewhat, because both technical and commercial dalapon contain impurities. However, during several years of experimentation, the formulated materials dissolved in distilled water (which is always about pH 6 in this laboratory) have consistently given pH's well below 7 (see also Dow, 1953).

The salts reported in table 5 (p. 138) were prepared by treating 98 per cent pure acid dalapon with approximately equivalent amounts of sodium, potassium, ammonium, or calcium hydroxide. The amounts of sodium and potassium hydroxides used did not completely neutralize the acid dalapon.

Three surfactants widely used in agricultural sprays were prepared in 5 per cent stock solutions and added to the spray solutions in the necessary proportions. Vatsol OT (American Cyanamid Company) is a relatively pure anionic surfactant, sodium dioctylsulfosuccinate; Dynawet (Dow Chemical Company) is a nonionic mixture of undisclosed composition; X-77 (Colloidal Products Corporation) is nonionic and contains alkyl aryl polyoxyethylene glycols, free fatty acids, and isopropanol.

McIlvaine's standard buffer solutions —0.1 M citric acid and 0.2 M disodium phosphate—were used in preparing the pH series. Concentrated HCl was added to the buffer to obtain solutions below pH 3.0, concentrated NaOH for those above pH 8.0.

EXPERIMENTS AND RESULTS

Rate of Herbicide

In a preliminary test on corn, using commercial dalapon at various concentrations, all of the plants more than doubled in fresh green weight in the two weeks following treatment. However, plants treated with 8 or more pounds of active ingredient per acre were extremely brittle, had few or no normal leaves, and exhibited other characteristic symptoms of dalapon injury. Symptoms were evident to a lesser degree at 4 pounds per acre, barely perceptible at 2 pounds, and imperceptible at 1 pound. Poor wettability obviously limited action at the lower rates. On the basis of this and similar tests, the rates used in later experiments were 2 to 10 pounds per acre, which inhibited growth and injured the plants in varying degrees but did not cause death during the two weeks of observation.

Dalapon Formulation and Exposure Time

A split-plot experiment was conducted for two purposes. (1) Dalapon solutions A, B, and C were compared, to determine the value of the wetting agent included in the commercial formulation of dalapon and to learn whether the herbicidal action of this formulation could be enhanced by additional surfactant. (2) Various exposure times were tested, to explore the rate of entry and translocation of dalapon in corn as indicated by subsequent growth inhibition, and to discover when penetration begins and when it reaches a maximum.

Table 1 shows the advantage of the surfactant in the commercial formulation and the greater inhibition of growth by dalapon with added Vatsol OT. It gives the washing intervals and the effects of the different treatments on plant growth. Figure 1 illustrates the effect of washing at different intervals after treatment with commercial dalapon plus Vatsol OT.

Technical dalapon, solution A, wetted the plants poorly. Sometimes large drops clung to the edges of leaves or collected in the whorls, obviously in poor contact with the leaf surface. The sparsely scattered white residue indicated imperfect coverage and poor penetration, which is more pronounced at low relative humidity and high temperature. Commercial dalapon, solution B, spread over the leaves more uniformly; solution C, with added Vatsol OT, gave still more complete coverage. With both B and C, a faint, powdery residue indicated the extent of spread. Washing removed the visible residues of solutions A and B readily; plants sprayed with solution C were poorly wetted by the wash water and had a uniformly glazed appearance.

Some initial absorption occurred very rapidly: With solutions B and C, enough dalapon entered the plants in five minutes to inhibit growth significantly within the two weeks of observation. Absorption was much slower from solution A. On the basis of growth inhibition, it appears that the plants absorbed approximately as much dalapon in one hour from sprays containing surfactants as in two weeks without surfactant. The herbicidal action of all solutions was most noticeable in plants washed after one hour, but apparently the intake of dalapon continued slowly for much longer periods. Differences in the effects of solutions with and without surfactant were significant when the exposure was one hour or less. Differences in the effects of solutions B and C, containing different amounts of surfactant, were significant at some of the longer exposures.

TABLE 1

MEASUREMENTS OF CORN PLANTS TWO WEEKS AFTER SPRAYING WITH DALAPON,* WITH OR WITHOUT SURFACTANT, FOLLOWED BY WASHING AT SPECIFIED INTERVALS

Exposure time (washing interval)	Final plant heights†				Final plant weights†			
	Technical dalapon	Commercial dalapon	Commercial dalapon + 0.1% Vatsol OT	Mean for washing interval	Technical dalapon	Commercial dalapon	Commercial dalapon + 0.1% Vatsol OT	Mean for washing interval
	cm	*cm*	*cm*	*cm*	*gm*	*gm*	*gm*	*gm*
0 (check)	87.5	84.3	85.0	85.6	58.9	55.4	61.9	58.7
5 minutes	84.8	75.3	79.5	79.8	57.9	54.3	53.5	55.2
1 hour	81.0	67.8	67.5	72.1	57.7	47.6	46.6	50.0
4 hours	76.3	69.0	68.8	71.3	51.0	49.0	51.2	50.7
16 hours	71.3	68.8	59.0	66.3	49.2	49.9	45.3	48.1
64 hours	70.0	53.0	53.0	58.7	46.2	39.8	36.4	40.8
2 weeks (plants not washed)	73.8	56.8	48.3	59.6	47.3	42.6	32.3	40.7
Mean for dalapon formulation	77.8	67.8	65.9	....	52.4	48.4	46.7	....

		Height		*Weight*
LSD between means for any two formulations:	5%	2.4	5%	3.0
	1%	3.2	1%	4.0
LSD between means for any two washing intervals:	5%	4.3	5%	5.6
	1%	5.9	1%	7.7
LSD between means for any two formulations at one washing interval:	5%	8.3	5%	7.9
	1%	11.1	1%	10.5
LSD between means for any two washing intervals for any one or two formulations:	5%	7.8	5%	8.3
	1%	10.4	1%	11.0
Coefficient of variability:		8.3%		11.2%

* Applied at the rate of 10 pounds of active ingredient per acre in 40 gallons of water. The pH reading of the technical dalapon solution was 4.52; of the commercial, 4.09; of the commercial plus 0.1% Vatsol OT, 4.01.

† Each value is the average of 16 plants (4 pots).

Fig. 1. Corn plants two weeks after spraying with commercial dalapon plus 0.1 per cent Vatsol OT, using 10 pounds of active dalapon per acre in 40 gallons of water. Plants were washed at designated intervals after spraying. *a*, Untreated check. Exposures: *b*, 5 minutes; *c*, 1 hour; *d*, 4 hours; *e*, 16 hours; *f*, 64 hours; *g*, 2 weeks (plants not washed).

Kind and Rate of Added Surfactant with Two Dalapon Formulations

Tables 2 and 3 show the effects of three surfactants, each at four concentrations and applied to corn without herbicide, with technical dalapon, and with commercial dalapon.

Vatsol OT in solution without herbicide was more acid than either Dynawet or X-77 (table 2). Vatsol OT added to dalapon lowered the pH very slightly, whereas Dynawet and X-77 raised it, but all sprays as mixed were definitely acid, and none of the surfactants changed the pH significantly. All three surfactants decreased surface tension and visibly improved wetting, and differences in the rates used were evident in the thoroughness of wetting. Dynawet, at five times the rates of the other surfactants, caused much more thorough wetting.

The commercial formulation, solution B, was obviously superior to technical dalapon, solution A. Addition of surfactant to either the technical or the commercial dalapon aided its action under the experimental conditions, but the effect was less pronounced with the commercial formulation. In over-all averages, Dynawet at 0.25 per cent (rate *n*, table 2) was approximately equal in effectiveness to Vatsol OT at the comparable rate of 0.2 per cent (4 *n*). At the rates used (*n*, 2*n*, and 4*n*), Dynawet was significantly more effective than Vatsol OT. In general, X-77 was superior to both. Table 5 (p. 138) compares the three surfactants at the same concentration, 0.1 per cent.

Increased rates of X-77 or of Dynawet gave rather large increases in herbicidal effectiveness, and apparently the maximum was not reached. On the other

TABLE 2

MEASUREMENTS OF CORN PLANTS TWO WEEKS AFTER SPRAYING WITH DALAPON* WITH VARIOUS KINDS AND RATES OF SURFACTANT

Surfactant			Dalapon formulation								
Trade name	Concentration		No herbicide			Technical			Commercial		
			pH	Height	Weight	pH	Height	Weight	pH	Height	Weight
	per cent	*rate*		*cm*	*gm*		*cm*	*gm*		*cm*	*gm*
Vatsol OT.....	0.2	4*n*	3.45	66.6	38.44	3.83	53.6	30.80	3.60	47.6	28.36
	0.1	2*n*	3.65	70.4	39.52	3.94	53.6	32.94	3.65	46.6	29.48
	0.05	*n*	3.93	69.6	39.70	4.01	56.0	31.70	3.68	51.4	30.50
	0	0	....	71.4	40.90	4.09	69.4	35.02	3.69	52.2	31.20
Dynawet......	1.0	4*n*	5.88	68.8	34.86	4.20	36.6	13.12	3.73	35.8	13.92
	0.5	2*n*	5.82	70.2	36.18	4.11	41.8	20.76	3.73	41.4	19.92
	0.25	*n*	5.75	70.2	37.60	4.11	48.4	28.58	3.72	46.8	29.18
	0	0	....	68.8	37.86	4.11	71.4	37.84	3.69	51.0	31.54
X-77...........	0.2	4*n*	5.45	69.4	36.74	4.09	40.8	22.24	3.71	41.4	21.04
	0.1	2*n*	5.75	70.0	38.44	4.06	46.2	27.92	3.69	45.4	25.66
	0.05	*n*	5.65	71.8	42.00	4.08	54.8	32.42	3.68	52.8	34.68
	0	0	....	70.8	41.76	4.07	70.4	36.04	3.69	53.4	34.72

* Applied at the rate of 10 pounds of active ingredient per acre in 40 gallons of water. Each value is the average of 20 plants (5 pots).

hand, increased rates of Vatsol OT caused relatively small growth differences, and the maximum effect was reached between 0.05 and 0.1 per cent concentration. Vatsol OT is somewhat toxic at 0.1 per cent and above. As might be expected, statistical results show significantly different interactions between rates and types of surfactant and between these and the dalapon formulations. Except for minor differences, height and weight measurements show the same trends.

pH and Buffer

The pH of dalapon solutions is considered important because of its control over the polarity of the solution and of the surfaces to be penetrated. A series of experiments was designed to test dalapon in relation to reports that many weak acid sprays penetrate leaves most readily in the nondissociated form, i.e., at low pH in aqueous solution, and also to investigate the effects of acute initial toxicity on total absorption and translocation and on final systemic action. In the first experiment, with commercial dalapon, using 10 pounds of active ingredient per acre in 40 gallons of water, all plants showed some contact injury and all treatments were so inhibitory that no differences were apparent among solutions in the pH range from 1 through 10. In the second test, using commercial dalapon, with only 2 pounds of active ingredient per acre, poor wettability was a factor, and none of the treatments was significantly different from the untreated checks. In the third test, using commercial dalapon plus 0.1 per cent Vatsol OT, at an intermediate rate of 4 pounds of active ingredient in 40 gallons of water, the plants were sprayed to wet rather than on a rate-per-acre basis. Figure 2 shows that all treatments reduced height and fresh green weight of corn significantly, especially at pH 5, 6, and 7, with practically total inhibition at pH 6. In another test, with 2 pounds of active dalapon per acre in 40 gallons of water plus 0.05 per cent Vatsol OT, growth trends were similar.

Two fairly distinct types of symptoms preceded the secondary growth responses. The first was an acute contact injury, with brownish burned spots against the normal bright-green background of foliage; necrosis was rapid, starting less than one minute after exposure at pH 1 and a few hours after exposure at pH 3, 4, or 5. Growth measurements of control plants sprayed with buffer solutions showed that the adversely high hydrogen ion concentration was partly responsible for the injury at pH 1, but that the buffer alone was not significantly injurious above pH 2, where, presumably, the principal effect was due to high dalapon concentration following very rapid penetration.

The second type of injury, characterized by a general grayish-green, slightly wilted appearance, developed one or more days after exposure. The nonlocalized symptoms suggest that internal movement of dalapon was followed by slow desiccation of the cells penetrated. Some necrosis resulted after several days. These two effects represent opposing trends, but the symptoms tended to intergrade at intermediate pH's. Numerical ratings assigned to these responses two days after treatment (table 4) showed good correlation with final growth measurements (fig. 2).

Dalapon Salt Formulation and Surfactant

As the penetration and final effectiveness of herbicides may conceivably be influenced not only by hydrogen ion concentration but also by the nature and concentration of other cations, several formulations of dalapon were compared—alone and with each of the three surfactants. Just before spraying, the dalapon solutions without surfactant gave the following pH readings: acid, 1.48–1.70; sodium salt, 2.20–2.25; potassium salt, 2.72–2.75; ammonium salt,

TABLE 3

STATISTICAL ANALYSIS OF DATA IN TABLE 2

(Coefficient of variability for height measurements was 6.48%; for weight, 4.66%)

TABLE 3A

OVER-ALL EFFECTS OF DIFFERENT DALAPON FORMULATIONS

Dalapon formulation	Final plant measurements*	
	Height	Weight
	cm	*gm*
No dalapon	69.8	38.6
Technical dalapon	53.6	29.1
Commercial dalapon	47.2	27.5
LSD 5%	1.9	1.8
1%	2.8	2.6

* Each value is the average of 240 plants—60 pots: 5 replicates × 3 surfactants × 4 rates of surfactant.

TABLE 3B

OVER-ALL EFFECTS OF DIFFERENT RATES OF SURFACTANT

Rate of surfactant*	Final plant measurements†	
	Height	Weight
	cm	*gm*
4*n*	51.2	26.6
2*n*	54.0	30.1
n	58.0	34.0
0	64.3	36.3
LSD 5%	1.4	2.2
1%	1.9	2.9

* See table 2.
† Each value is the average of 180 plants—45 pots: 5 replicates × 3 dalapon formulations × 3 surfactants.

TABLE 3C

OVER-ALL EFFECTS OF DIFFERENT SURFACTANTS

Surfactant	Final plant measurements*	
	Height	Weight
	cm	*gm*
Vatsol OT	59.0	34.1
Dynawet	54.3	28.5
X-77	57.3	32.8
LSD 5%	1.3	2.0
1%	1.8	2.6

* Each value is the average of 240 plants—60 pots: 5 replicates × 3 dalapon formulations × 4 rates of surfactant.

8.00–8.05; calcium salt, 11.22–11.28. For the surfactant solutions separately, Vatsol OT had pH 3.69; Dynawet, pH 6.42; and X-77, pH 5.68. The distilled water used gave a pH reading of 5.6–6.0.

Solutions containing surfactant spread best, from the point where the drop struck the foliage. Contact injury occurred in scattered flecks over the foliage, corresponding to the wetting pattern, especially with the acid solutions. The familiar whitish residue remained on the leaves after drying of the solutions containing sodium, potassium, or calcium. Filter-paper chromatograms indicated that ammonium was lost by volatilization.

In over-all averages, acid dalapon and the sodium salt were about equal in effectiveness (table 5). Either one inhibited growth more than did any of the other formulations tested, confirming earlier observations by the Dow Chemical Company (1953) and by Freed, McKennon, and Montgomery (1955). The potassium and ammonium salts were somewhat less effective, and the calcium salt was, by far, the least effective.

All three surfactants enhanced the phytotoxicity of dalapon. This effect was more significant with most of the salts than with the acid. Although not all the differences are significant, the over-all order of effectiveness of the three, used at the same rate, was Dynawet > X-77 > Vatsol OT. However, with the sodium salt—the active ingredient of both technical and commercial dalapon and the formulation used in all other experiments reported here—the order of effectiveness was Vatsol OT > Dynawet > X-77. Figure 3 shows the effectiveness of the three surfactants with acid dalapon and two of its salts. None of the surfactants alone inhibited growth significantly. Vatsol OT appears to be incompatible with calcium dalapon or with the excess calcium hydroxide used in preparing the salt.

Without surfactant, all dalapon formulations inhibited growth to some ex-

TABLE 3—*Continued*

TABLE 3D

INTERACTION OF DALAPON FORMULATION AND RATE OF SURFACTANT

Rate of surfactant*	Final plant heights†			Final plant weights†		
	No herbicide	Technical dalapon	Commercial dalapon	No herbicide	Technical dalapon	Commercial dalapon
	cm	*cm*	*cm*	*gm*	*gm*	*gm*
4*n*	68.2	43.7	41.6	36.7	22.1	21.1
2*n*	70.2	47.2	44.5	38.1	27.2	25.0
n	70.5	53.1	50.3	39.8	30.9	31.5
0	70.3	70.4	52.2	40.2	36.3	32.5

	Height	*Weight*
LSD between means for any two rates of surfactant with any one dalapon formulation:	5%.............2.5	5%.............3.8
	1%.............3.3	1%.............5.1
LSD between means for any two dalapon formulations with surfactant at the same or different rates:	5%.............2.9	5%.............3.8
	1%.............4.0	1%.............5.3

* See table 2.
† Each value is the average of 60 plants—15 pots: 5 replicates × 3 surfactants.

TABLE 3E

INTERACTION OF SURFACTANT AND DALAPON FORMULATION

Dalapon formulation	Final plant heights*			Final plant weights*		
	Vatsol OT	Dynawet	X-77	Vatsol OT	Dynawet	X-77
	cm	*cm*	*cm*	*gm*	*gm*	*gm*
No dalapon	69.5	69.5	70.5	39.6	36.6	39.7
Technical dalapon	58.2	49.6	53.1	32.6	25.1	29.7
Commercial dalapon	49.5	43.8	48.3	29.9	23.6	29.0

	Height	*Weight*
LSD between means for any two surfactants with the same or different dalapon formulations:	5%.............2.7	5%.............3.0
	1%.............3.7	1%.............4.2

* Each value is the average of 80 plants—20 pots: 5 replicates × 4 rates of surfactant.

TABLE 3F

INTERACTION OF SURFACTANT AND RATE OF SURFACTANT

Rate of surfactant*	Final plant heights†			Final plant weights†		
	Vatsol OT	Dynawet	X-77	Vatsol OT	Dynawet	X-77
	cm	*cm*	*cm*	*gm*	*gm*	*gm*
4*n*	55.9	47.1	50.5	32.5	20.6	26.7
2*n*	56.9	51.1	53.9	34.0	25.6	30.7
n	59.0	55.1	59.8	34.0	31.8	36.4
0	64.3	63.7	64.9	35.7	35.8	37.5

	Height	*Weight*
LSD between means for any two surfactants at the same or different rates:	5%.............2.6	5%.............3.5
	1%.............3.5	1%.............4.7

* See table 2.
† Each value is the average of 60 plants—15 pots: 5 replicates × 3 dalapon formulations.

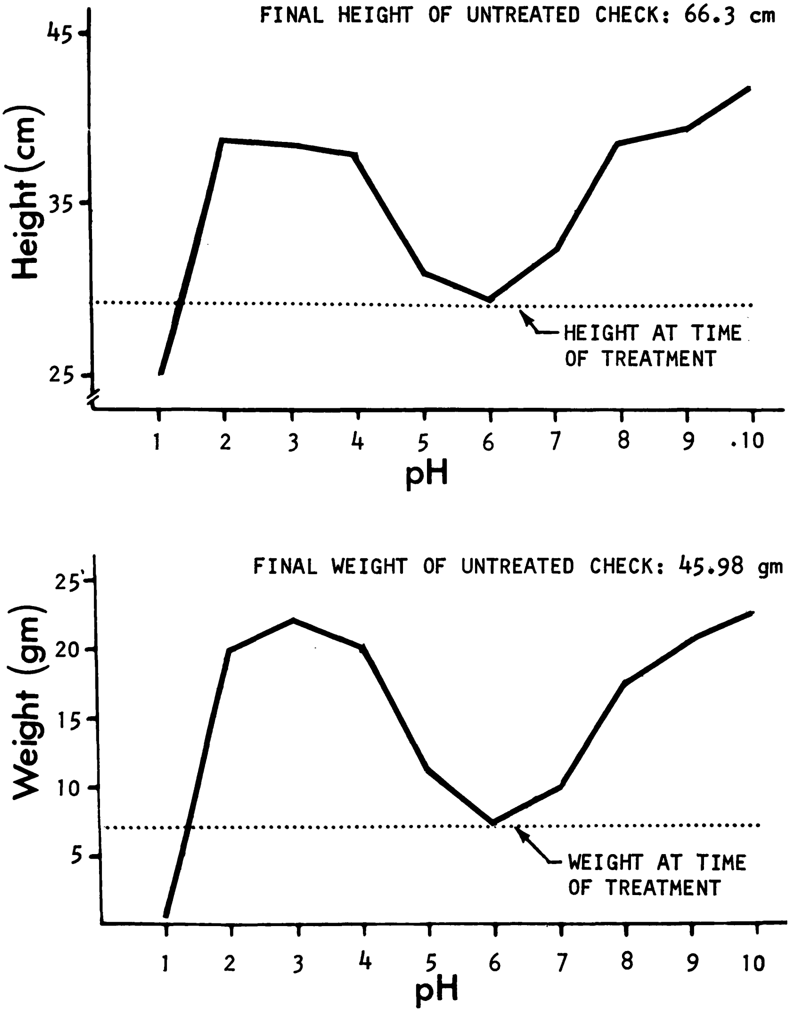

Fig. 2. Measurements of corn plants two weeks after spraying to wet with buffered solutions of commercial dalapon plus 0.1% Vatsol OT, using 4 pounds of active dalapon in 40 gallons of water. Each value is the average of 16 plants (4 pots).

tent, in the following order: acid > Na salt > NH_4 salt > Ca salt > K salt. However, with all three surfactants, the sodium salt was somewhat more effective than acid dalapon. The effects of pH and of the cations were not separable in this experiment, but the more effective treatments were on the acid side.

DISCUSSION OF THEORY

If dalapon is to contact living protoplasm and move symplastically for any distance, it must cross at least two lipoidal barriers—the cuticle, either external or internal, and the outer plasma membrane (ectoplast). This statement assumes continuity of the cuticle, although there are, of course, fissures, insect punctures, and other possible imperfections.

Intact cuticle is known to be a strong barrier to penetration of chemicals, thus preventing cytolysis (Skoss, 1955; van Overbeek, 1956; Orgell, 1957), but all workers seem agreed that herbicides and other substances traverse it. The cuticle is generally considered as a com-

TABLE 4

RATING OF INJURIES TO CORN TWO DAYS AFTER SPRAYING WITH BUFFERED SOLUTIONS OF DALAPON*

pH	Type of injury	
	Acute, localized†	Slower, insidious‡
1	9-10§	10
2	5.0	1.8
3	3.0	1.3
4	1.0	2.0
5	0.5	3.9
6	0	5.1
7	0	4.8
8	0	3.6
9	0	3.3
10	0	2.4
Untreated check	0	0

* Plants sprayed to wet with commercial dalapon plus 0.1% Vatsol OT, using 4 pounds of active ingredient in 40 gallons of water. Each rating is the average of 16 plants (4 pots). 0 = no injury; 10 = all of foliage affected. At pH 1 the types of symptoms were not distinguishable.

† Discrete necrotic areas, foliage otherwise bright, plants erect.

‡ Only occasional necrosis, nonlocalized; foliage generally dull, plants slightly wilted.

§ Growing point not always killed.

plex but relatively inert, semipolar, lipoidal layer. It is wetted readily by oils but not by water and is only slightly permeable to either (Currier, 1954). Roberts, Southwick, and Palmiter (1948) suggested that there may be both polar and apolar routes across the cuticle. Crafts (1956) and Crafts and Foy (1962) considered the possibility that water-soluble herbicides may follow an aqueous path and the more oil-soluble substances a lipid path. However, this hypothesis is not yet supported by adequate research.

Rapid absorption of dalapon, as demonstrated in the exposure-time experiment (table 1), is considered largely stomatal (Foy, 1962*b*), whereas cuticular penetration may account for the slow, sustained uptake over long periods. Both the rapid phase and the slow, continuous absorption of dalapon are most noticeable when a surfactant is used. This effect is due, in part, to the greater retention of dalapon by more efficient wetting and increased spray load. In addition, a surfactant has sealing or humectant properties, so that it slows down droplet drying, provides an aqueous continuum from the leaf surface to the protoplast, and creates a more favorable microclimate for prolonged penetration through the cuticle.

Most surfactants have, in each molecule, both hydrophilic and lipophilic properties, which promote compatibility between otherwise incompatible substances. According to Davson and Danielli (1943), the plasma membrane of a plant usually consists of a bimolecular

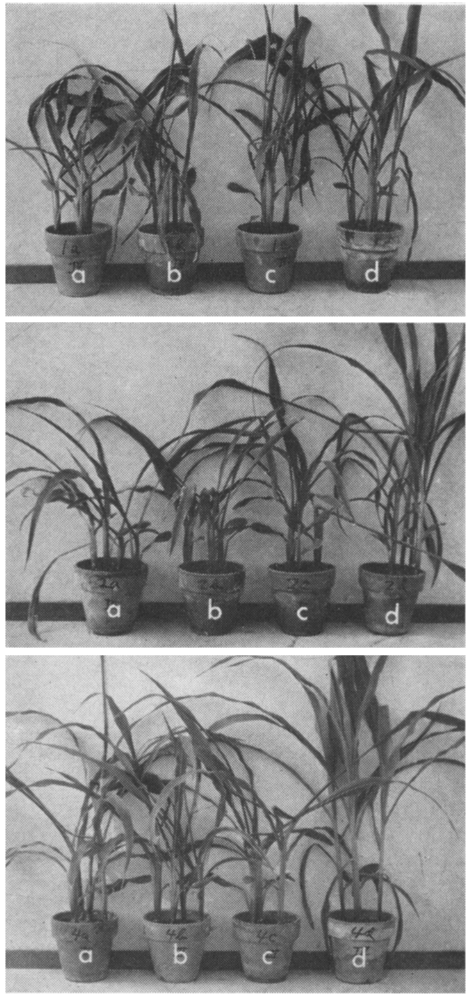

Fig. 3. Corn plants two weeks after spraying at the rate of 10 pounds of active dalapon per acre in 40 gallons of water. *Above,* acid dalapon; *middle,* sodium salt; *below,* ammonium salt. Each dalapon formulation was tested with 0.1 per cent of added surfactant: *a,* Vatsol OT; *b,* Dynawet; *c,* X-77; *d,* no surfactant.

TABLE 5

MEASUREMENTS OF CORN PLANTS TWO WEEKS AFTER SPRAYING WITH VARIOUS FORMULATIONS OF DALAPON* IN COMBINATIONS WITH THREE DIFFERENT SURFACTANTS, EACH AT 0.1%

Dalapon formulation	Final plant heights†					Final plant weights†				
	Vatsol OT	Dynawet	X-77	No surfactant	Mean for dalapon formulation	Vatsol OT	Dynawet	X-77	No surfactant	Mean for dalapon formulation
	cm	*cm*	*cm*	*cm*	*cm*	*gm*	*gm*	*gm*	*gm*	*gm*
Acid, purified	49.2	49.4	50.8	52.6	50.5	34.0	35.5	35.8	39.8	36.3
Na salt	44.6	46.4	49.0	65.6	51.4	28.4	29.3	33.0	44.0	33.7
K salt	51.4	47.0	51.6	77.8	57.0	35.1	33.4	36.6	56.5	40.4
NH_4 salt	55.8	51.4	51.4	73.2	58.0	39.2	35.4	37.5	48.9	40.2
Ca salt	78.6	65.6	64.8	76.6	71.4	50.3	41.3	41.3	50.3	45.8
No dalapon	79.2	80.4	80.6	80.0	80.1	50.7	52.0	55.8	52.1	52.7
Mean for surfactant	59.8	56.7	58.0	71.0	....	39.6	37.8	40.0	48.6	....

		Height	*Weight*
LSD between means for any two dalapon formulations:	5%	2.7	3.0
	1%	3.7	4.1
LSD between means for any two surfactants:	5%	1.9	3.0
	1%	2.5	3.9
LSD between means for any two surfactants tested with the same dalapon formulation:	5%	4.7	7.3
	1%	6.3	9.6
LSD between means for any two dalapon formulations tested with the same or different surfactants:	5%	4.8	6.9
	1%	6.4	9.1
Coefficient of variability:		6.1%	13.8%

* Applied at the rate of 10 pounds of active ingredient per acre in 40 gallons of water.
† Each value is the average of 20 plants (5 pots).

layer of lipids, stabilized on either side by a monomolecular layer of protein. Such a membrane is strongly charged, so that the interior of the cell is not readily accessible to extraneous ions. Lipophilic groups, such as the hydrocarbon chains in Vatsol OT, probably increase the ability of aqueous solutions to penetrate natural membranes. Also, it is believed that, in general, molecules penetrate membranes much more easily than do the corresponding ions, because molecules are neutral, without polar charges.

Membrane Permeability and Herbicidal Action

Dalapon exerts two physiologically distinct types of action—acute toxicity and slower growth inhibition. Presumably the acute toxicity—defined as immediate and localized—is due to its action as an acid and protein precipitant (Redemann and Hamaker, 1954; Olsson, 1957), which causes drastic permeability changes in the plasma membranes and nonselective, localized destruction of cellular constituents.

Acute toxicity may be brought about by a high concentration of herbicide, of toxic wetting agent, or of hydrogen ion, or by other factors, such as temperature, relative humidity, stomatal behavior, etc., which may react indirectly with the first two. The present studies confirm earlier work (Foy, 1961) and indicate that acute toxicity at the point of spray application can reduce or even prevent translocation and subsequent expression of systemic, growth-regulating action. This may be much more important in herbicidal efficacy than is commonly supposed.

Dalapon sprays containing more than 0.1 per cent of Vatsol OT gave relatively poorer herbicidal performance than those with lower rates. Studies with radioactive dalapon (Foy, 1961, 1962*a*, *b*, *c*) showed that this was not due to failure of wetting or to failure of penetration. With the spray volumes used, it is unlikely that the spray load on leaf surfaces was reduced by adding Vatsol OT to the spray. Rather, acute toxicity caused by the high concentrations of Vatsol OT interfered with the translocation of dalapon and thus with secondary growth inhibition.

Whereas acute toxicity may be considered disadvantageous when translocation and systemic action are desired, it is conceivable that a slight amount of local injury to plant cells may be advantageous under certain circumstances, by weakening membranes and so increasing permeability.

The more subtle, delayed response to solutions with lower initial concentrations is manifested in the meristematic regions of a plant, following the transport of dalapon with food materials (discussed by Foy, 1961). In this case, dalapon may accumulate to toxic levels in meristematic cells and act against one or more enzymes or, perhaps, against the membranes of organelles. To accomplish systemic toxicity, the herbicide must move across cell membranes without destruction of the cellular contents and accumulate to toxic concentrations in remote tissues.

Physicochemical Considerations

There are as yet no absolute criteria for determining relationships between the chemical and the biological behavior of a compound such as dalapon. However, both ionic and polar properties are significant.

Ions and molecules behave differently in at least three properties—chemical reactivity, adsorption at surfaces, and penetration of membranes—and some of the selectively toxic agents are active only in the nonionized state. The ease with which some acids are absorbed by plants is inversely proportional to their degree of ionization, except at the point where $pH \leq pK$. Dalapon showed this trend in studies with red-beet-root slices (Foy, 1958), with johnsongrass foliage (Hauser and Thompson, 1959), and with corn coleoptiles (Wilkinson, 1955).

Acid	K	Reference
propionic	1.40×10^{-5}	(Hodgman, 1944)
β – chloropropionic	8.59×10^{-5}	(Hodgman, 1944)
α – chloropropionic	1.47×10^{-3}	(Hodgman, 1944)
2,2-dichloropropionic	2.94×10^{-2}	(Freed, 1956)
2,2,3-trichloropropionic	9.94×10^{-2}	(Freed, 1956)
acetic	1.75×10^{-5}	(Hodgman, 1944)
chloroacetic	1.40×10^{-3}	(Hodgman, 1944)
dichloroacetic	5.00×10^{-2}	(Hodgman, 1944)
trichloroacetic	2.00×10^{-1}	(Abernethy, 1949)

It penetrated lipoidal membranes more readily with decreasing pH of the solutions.

The present studies (fig. 2) indicate that the nondissociated, or neutral dalapon molecules in aqueous solutions at low pH penetrate corn leaves more readily than do the dissociated ions in alkaline solutions of dalapon. Systemic herbicidal action was most effective at pH 5 to pH 7. The acute local toxicity of solutions at pH 1 to 4 greatly reduced the systemic response by injuring plant tissues and preventing downward translocation of the herbicide.

Replacement of H with halogen in aliphatic carboxylic acids yields acids that ionize to a greater extent than if unsubstituted (Abernethy, 1949). This is because the strongly electronegative halogen ions tend to attract electrons, and the electron bond between the H and the O of the COOH is shifted toward the O and away from the H. In any series, this effect is greater when an acid is more highly substituted or when the halogen on the chain is nearer to the COOH. The ionization constants (K, above) for two series of organic acids illustrate these relationships.

Acetic and propionic acids, weakest acid members of the two series, are usually considered rather nontoxic, but in the nondissociated state either may be highly toxic to plant cells (van Overbeek and Blondeau, 1954). Thus, their highest activity occurs in oil, an apolar solvent; in aqueous solutions they are active only at low pH. Because of the presence and position of its two chlorine atoms, dalapon is fairly acid but somewhat intermediate in the series of propionic acids. TCA and 2,2,3-trichloropropionic acid, at the acid extremes of their two series, are marked protein precipitants. Acute toxicity to foliage is one probable reason for differences between the herbicidal action of TCA and that of dalapon. However, dalapon also may cause acute toxicity when the rate and degree of penetration are above the optimum, under conditions such as very low pH, excess surfactant, or open stomata.

The distinction between polar and nonpolar (apolar) compounds is often stressed in literature on the action of herbicides. Nonpolar compounds are generally regarded as oil-like, hence more lipophilic; polar compounds as more water-like, or hydrophilic. Daniels (1953) refers to a relationship between the ionic character of a compound and its relative polarity: Polar compounds exhibit chiefly electrostatic attraction, which results in the formation of heteropolar bonds (ionic linkages). Nonpolar (homopolar or electron-pair) bonds involve an "exchange-energy binding", understandable on the basis of quantum mechanics. However, the two types of bonds are not mutually exclusive, and both are operative in most linkages between atoms. Also there are gradations between. Therefore, although dalapon may be regarded as relatively ionic, hydrophilic, and polar, it becomes permissible to speak also of its more penetrative, lipophilic tendencies when it is in the nondissociated state.

Chemical manipulation, also, such as the addition of a suitable surfactant to a polar, aqueous solution of dalapon, may make it more compatible with plant waxes and possibly even with plasma membranes. Another possible factor is that surfactants (amphipatic molecules) may accumulate or become oriented at the plasma membrane and exert a kind of narcotic action. However, considering the broad array of possible solution additives, there is at present no clear-cut relation between surface activity and dalapon toxicity. The present studies and the work of Orgell and Weintraub (1957) indicate that little-understood but specific cation-competition effects may exist also.

Robbins, Crafts, and Raynor (1952) stated: "From consideration of the toxicity of hydrocarbons . . ., it is apparent that increase in polarity enhances the inherent reactivity of a molecule whereas increase in its oil-like properties promotes penetration." As the toxicity of herbicidal solutions and their penetration seem to be opposite processes, those authors concluded that "there must be an optimum point in the balance between them, and this in reality represents a compromise between toxicity resulting from polarity of the molecule and compatibility with the cuticle resulting from oil-like properties." This line of reasoning may be helpful in interpreting the penetrating ability of systemic growth regulators such as dalapon. Surfactants are probably important stabilizers at the solution-plant surface interfaces, in effect achieving a more nearly optimum balance between polar and oil-like properties within the same herbicide molecule. One important consideration (Foy, 1961) is that the final spray mixture should cause little or no acute injury to the absorbing and translocating cells.

SUMMARY

In greenhouse and laboratory investigations, a small amount of dalapon was absorbed by corn leaves almost instantly, when a suitable surfactant was included in the spray. If no acute toxic action resulted, absorption and translocation continued for several days, although spray droplets appeared to dry within minutes. The wetting agent in the commercial dalapon formulation greatly enhanced penetration, and the advantage of using various additional surfactants was amply demonstrated: On the basis of growth inhibition, it appeared that corn absorbed as much dalapon in one hour from sprays containing surfactant as in two weeks from a solution without surfactant. In general, increasing rates of nontoxic surfactants continued to increase herbicidal activity, but this was not true of the toxic wetting agent Vatsol OT.

The acid and the sodium salt of dalapon were about equal in effectiveness. Both inhibited growth more than did the potassium, ammonium, or calcium salt. Some interesting interactions between formulations and surfactants were disclosed. For example, Vatsol OT, an excellent surfactant with the sodium salt of dalapon, was completely ineffective with the calcium salt.

Dalapon penetrated corn leaves most readily in the nondissociated form, or at low pH in aqueous solutions. However, when growth inhibition—which depends on effective translocation—was used as the criterion, acute toxicity at very low pH created an opposing trend, so that the most effective treatments were those at intermediate rather than at low pH. Optimum herbicidal results were obtained at about pH 6, near the pH of a solution of commercial dalapon sodium salt in tap water.

The toxicity to corn of various dalapon formulations is discussed and interpreted in relation to known physicochemical properties of the parent compound, 2,2-dichloropropionic acid.

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