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ENTRAPMENT OF HERBICIDES IN STARCH FOR SPRAY APPLICATIONS

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Sprayable controlled-release formulations were made with the herbicides trifluralin, 2,4-D ester, alachlor and butylate. Aqueous dispersions of gelatinized cornstarches or flours containing herbicides were sprayed and dried to water-resistant films that entrapped the herbicide. Formulations containing 3% Miragel®, 3% cooked pearl, or 7% pregelatinized corn flour and one tenth these levels of active ingredient (a.i.) provided as emulsifiable concentrates had stable viscosities in the 75–260 cP range over 24 hours. The best entrapment was obtained by cooking 3% starches or flours at least 30 min at 100°C and dispersing the emulsifiable concentrates into the cooled whole pastes. Dried formulations based upon 3% Miragel® entrapped 88% trifluralin, 96% 2,4-D ester, 75% alachlor, and 9% butylate. Butylate retention increased to 42% with 6% Miragel® that had been pyrolyzed 1 h at 200°C. Release of trifluralin from Miragel® in the presence of α-amylase solution increased with decreasing particle size and increasing level of active ingredient.

INTRODUCTION

Herbicide application for field use often favors spray mixes over granular forms because of versatility and ease of application, and inherent thoroughness of target coverage [1,2]. In typical large-volume spray mixes, herbicides are applied at concentrations near 1% in water at 15–20 gal/a [3]. However, spray mixes are prone to wind drift into non-target areas. Following application, rapid losses of herbicide often occur through volatilization, photodegradation, and leaching.

Wind drift is normally controlled by adding high molecular weight adjuvants such as sodium carboxymethylcellulose at levels of 0.15–1.0% to increase viscosity and drop size [4]. Loss of herbicide from the target site can be considerable unless additional means are used to protect the herbicide from the environment.

We have shown that cornstarch is capable of encapsulating herbicides at 15–20% levels of active ingredient by several processes that lead to granules [5–10] in which the herbicide is entrapped as tiny cells within a solid matrix. Advantages of such formulations include decreased dermal toxicity [11], reduced leaching [12], and longer residual activity [13–16] of active ingredient.

In view of this encapsulating ability of starch and the large market for herbicides in spray

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mixes, it was of interest to develop starch-based systems for use in spray applications. Ideally the sprays should dry to films that entrap active ingredients for subsequent controlled release and that offer some resistance to redispersion in water. Such systems should be easy to formulate and use on a practical basis. They should show reasonable viscosity stability and be resistant to rapid degradation by microorganisms.

Based upon results with granular starch-based formulations, the ratio of starch to active ingredient should be appreciably greater than 1 to 1 in a spray mix in order to achieve efficient entrapment. Starch might serve as an anti-drift adjuvant because it increases viscosity and droplet size. Although adjuvants such as carboxymethylcellulose could entrap active ingredients [17] at higher ratios of adjuvant to herbicide, the mixture would be too viscous for conventional spray equipment. Since these adjuvants normally control drift at ratios of adjuvant to active ingredient of less than 1 to 1, little entrapment is expected. A suitable starch of lower viscosity might not only control drift but offer entrapment for controlled release after spraying and drying.

MATERIALS AND METHODS

Experiments were conducted under a well-vented hood, and plastic gloves were worn to prevent skin contact with herbicides.

Chemicals

Starches and flour contained 10–12% moisture and were obtained from the following sources: Miragel 463®, A.E. Staley Mfg. Co., Decatur, IL; pregelatinized corn flour 12687, Illinois Cereal Mills Corp., Paris, IL; pearl cornstarch, Globe® 3005, CPC International, Englewood Cliffs, NJ.

Herbicides were supplied as emulsifiable concentrates (ECs) and included trifluralin as Treflan® (41.2%), Elanco Products Co., Indianapolis, IN; alachlor as Lasso® (45.1%), Monsanto Co., St. Louis, MO; EPTC as Eradicane® 6.7E (82.6%) and butylate as Sutan® 6.7E (85%) both from Stauffer Chem. Co., Westport, CT; a low volatile ester of 2,4-D as Weedone® LV4 (60.8%), Union Carbide Agr. Prod. Co., Inc., Research Triangle Park, NC.

Termamyl® 60 L and 120 S enzyme (Novo Laboratories, Wilton, CT) had activities of 60 and 120 KNU/g, where one kilo Novo α-amylase unit (1 KNU) is defined as the amount of enzyme that breaks down 5.26 g of soluble starch per hour at 37°C and pH 5.6 in the presence of 0.0043 *M* calcium ion [18,19].

Procedures

Dispersions were prepared at 3% levels by mixing pregelatinized starch or flour (25 g) near pH 7 in water (805 ml) in a Waring blender (Model B, Waring Corp., New York, NY) or by suspending starches in water, adjusting the pH to 7 with 1 *N* sodium hydroxide, and cooking at 100°C for one hour followed by cooling to room temperature. Dispersions were stirred in the blender and herbicides were added at ratios of herbicide to starch or flour calculated to give 10% active ingredient (a.i.) in the final dried product. Starch or flour percentages in the mix were varied by altering the ratios of these solids to water. Starches were modified through pyrolysis (one hour at 200°C) or by enzyme treatment [20] with Termanyl® 60 L. The water solubility of the pregelatinized corn flour was determined by dispersing the product (8.0 g) in water (96 ml) in a blender. After one hour, the dispersion was centrifuged. The supernatant was decanted and evaporated overnight on a 9-cm petri dish to determine the weight of the soluble portion, and the remainder was removed and similarly evaporated to determine the insoluble portion. Viscosities were determined with a Brookfield LVF viscometer at 6 rpm. The pH values were obtained with an Orion digital pH meter.

Dispersions containing starch, water, and

herbicide (40 ml) were sprayed at ambient temperature onto 50×50 cm plastic sheets by means of an air-driven glass sprayer with a 1.5 mm orifice. The sprayed sheet was dried under a forced-air hood overnight, then scraped with a razor blade to obtain the product. The dried material was sieved to collect a 10–20 mesh (800–2,000 μm) fraction. Herbicide on the surface was removed by washing with hexane.

Total herbicide was determined by mixing the sieved material (25 mg) with concentrated (10 *N*) hydrochloric acid (0.5 ml) until the material dissolved (5–10 min), then extracting the mixture with five portions of hexane (5 ml) to a total of 25 ml. Acid-sensitive herbicides such as alachlor were determined by mixing the sieved material (100 mg) with water (2 ml) and Termanyl® 60 L enzyme (20 μl). After shaking at room temperature for 3 h, the mixture was extracted with portions of hexane and diluted to 100 ml. Herbicides were determined by GLC [21] by using suitable internal standards. Trifluralin and alachlor were used as co-internal standards in a program between 150–180°C. Alachlor was used as internal standard for the ester of 2,4-D in a program between 175 and 215°C. EPTC and butylate were used as co-internal standards in an isothermal program at 110°C. Trifluralin was determined independently at 374 nm in hexane with a Beckman DU-50 spectrophotometer.

TABLE 1

Trifluralin entrapment in particles of dried Treflan®-Miragel® dispersions[a]

Miragel® in dispersion, %	Viscosity, cP		Entrapped a.i., %
	Initial	18 h	
1	40	30	2.8
2	50	50	6.7
3	75	260	8.8
3[b]	75	200	9.3
3[c]	75	75	4.6

[a]Trifluralin incorporated to give 10% a.i. in dried product.
[b]Paste cooked 1 h at 100°C.
[c]Termamyl® 60 L enzyme (0.1 ml) added to uncooked paste prior to spraying.

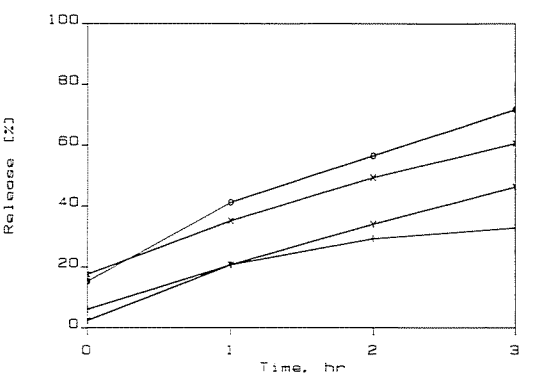

Fig. 1. Release of trifluralin from particles of dried 3% Miragel® dispersions at 24°C in the presence of 0.01% Termamyl 120 α-amylase at pH 6.0 in 0.01 *M* phosphate buffer; 5% a.i. (10–20 mesh) +, 10% a.i. (10–20 mesh) ×, 5% a.i. (20–40 mesh) Y, 10% a.i. (20–40 mesh) O.

RESULTS AND DISCUSSION

Most of the exploratory studies were conducted with trifluralin [19] because of its ease of measurement. Miragel® was initially used because it is a pregelatinized starch of unusual structure [22] derived from pearl starch by a special process [23]. This starch has been shown to be effective for encapsulation under mild, neutral conditions [24, 25].

The ability of Miragel® dispersions to entrap trifluralin after spraying, drying, and washing with hexane is shown in Table 1. Dried 1–3% dispersions of Miragel® showed increasing entrapment. The 3% dispersion, which was near the maximum at which stable pastes could be obtained, entrapped 8.8% a.i. (88%). When this level of Miragel® was cooked 1 h at 100°C prior to trifluralin dispersion, entrapment was 9.3% a.i. When the 3% Miragel®–trifluralin dispersion was treated overnight with 0.1 ml of Termanyl enzyme, entrapment was only 4.6% a.i.

The release of trifluralin from dried 3% Miragel® dispersions in the presence of 0.01% Termamyl 120 amylase [18] is shown in Fig. 1. Release is more rapid with smaller particles

(20–40 mesh) and higher (10%) a.i. Values fall into a range intermediate between those obtained under comparable conditions with particles of the xanthide and calcium procedures. The dried particles resisted disintegration in the enzyme solution.

A special pregelatinized flour was used because of its ability to form stable pastes of relatively high solids at room temperature. This flour was dispersed in water at levels up to 10% (uncorrected for moisture). Viscosities varied from 50 cP at 3% to 450–500 cP at 10%. About one-fifth of the solids were soluble and the remainder were insoluble under these conditions. The ability of this flour to entrap trifluralin after drying is shown in Table 2. Entrapment improved as the level of flour in the initial dispersion increased from 3% to 7%. When the pregelatinized flour was cooked 1 h at 100°C, the pastes became thicker and sprayable only at lower flour levels. The entrapping properties of the cooked flour became superior to those of the uncooked flour.

The entrapping abilities of pearl cornstarch for Treflan® are shown in Table 3. An early study [26] indicated that cooked pearl starch was unsuitable because of incomplete dispersion. A repeat of this experiment showed that pastes formed at the 5% level retrograded rapidly and became too thick to spray. When the starch was cooked at 3% concentration, the viscosity was lower and more stable. After the cooled paste had been mixed with Treflan® in the Waring blender, entrapping properties of the spray-dried product were comparable to Miragel®–trifluralin.

The ability of uncooked Miragel® to entrap various herbicides in spray mixes after drying is shown in Table 4. Entrapment was best for trifluralin and the LV ester of 2,4-D, fair with alachlor and poor with butylate. When Miragel® was pyrolyzed 1 h at 200°C, sprayable 6%

TABLE 2

Trifluralin entrapment in particles of dried Treflan®-flour dispersions[a]

Flour in dispersion, %	Viscosity, cP		Entrapped a.i., %
	Initial	18 h	
3	50	50	5.5
5	75	60	8.6
7	75	170	8.1
3[b]	60	50	8.3
5[b]	125	350	9.5
7[b]	380	4,650	9.4

[a]Trifluralin incorporated to give 10% a.i. in dried product.
[b]Paste cooked 1 h at 100°C.

TABLE 3

Trifluralin entrapment in particles of dried Treflan®-cooked pearl starch dispersions[a]

Starch in dispersion, %	Viscosity, cP		Entrapped a.i., %
	Initial	18 h	
5[b]	1,675	16,400	8.2
5[c]	2,325	22,500	6.5
3[b]	250	370	7.3
3[c]	230	300	7.5
3[d]	125	150	8.8

[a]Trifluralin incorporated to give 10% a.i. in dried product.
[b]Cooked 30 min at 100°C with propeller dispersion of trifluralin.
[c]Cooked 1 h at 100°C with propeller dispersion of trifluralin.
[d]Cooked 1 h at 100°C with blender dispersion of trifluralin.

TABLE 4

Entrapment of herbicides in particles of dried Miragel® dispersions[a]

Herbicide	Miragel® in dispersion, %	Viscosity, cP		Entrapped a.i., %
		Initial	18 h	
Trifluralin	3	75	260	8.8
LV 2,4-D ester	3	75	150	9.6
Alachlor	3	75	130	7.5
Butylate	3	75	200	0.9
Butylate	6[b]	125	175	4.2

[a]Herbicide incorporated to give 10% a.i. in dried product.
[b]Pyrolyzed 1 h at 200°C.

dispersions of stable viscosity allowed entrapment at 4.2% a.i. (42%).

SUMMARY

Aqueous starch or flour (3–7%) dispersions having stable viscosities (75–260 cP) and containing the herbicides trifluralin, 2,4-D ester, alachlor, and butylate formulated at 10% a.i. relative to the entrapping material were sprayed and dried to particles that entrapped the herbicides (7.5–9.6% a.i.). Particles entrapping trifluralin in starch resisted disintegration in the presence of α-amylase enzyme solution and showed release of a.i. intermediate between comparable particles of the xanthate and calcium procedures.

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