

Starch-Borate Complexes for EPTC Encapsulation

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Synopsis

A modification of the starch-borate technique for encapsulating the herbicide *S*-ethyl dipropylthiocarbamate (EPTC) was explored. It consists of mixing the herbicide into a neutral paste of pregelatinized starch or flour followed by addition of ammonia or an amine. The paste is treated with boric acid or a borate salt to form a gel, which is coated with additional starch or flour to facilitate breaking down the gel to particles in the 10–35-mesh range suitable for drying. An important advantage of this new technique is the moderate operating pH range (9.0–11.0) and final pH range (7.2–8.5) of aqueous suspensions of the dried product, which may allow encapsulation of acid and alkali labile substances. Addition of a surfactant in the encapsulation mixture improves the recovery of the volatile EPTC. Also, about 15% less water is required than in the original technique. In the presence of water, these particles show greater swelling than particles encapsulated by the starch xanthate or starch calcium adduct techniques. However, swelling is decreased by increasing the borate content. EPTC encapsulated by this new technique shows no loss of active ingredient when dry and exposed to the atmosphere, but shows loss when placed in water. The rate of release of active ingredient through several wetting and drying cycles compares favorably with that of products made by other starch-based encapsulation methods.

INTRODUCTION

Encapsulation of pesticides to control their release has the potential to solve problems associated with their use. Initially we encapsulated pesticides by dispersing the pesticide within starch xanthate to give a granular material that entrapped the active agent.^{1–3} The technique was effective in dealing with such diverse problems as overcoming volatility losses of 1,2-dibromo-3-chloropropane (DBCP) used in the control of root-knot nematodes of tomatoes,⁴ providing adequate release of *S*-ethyl dipropylthiocarbamate (EPTC) and butylate for both initial and residual activity in weed control,⁵ increasing the persistence of trifluralin in weed control,⁶ improving the safety in handling of highly toxic insecticides such as parathion,⁷ and controlling flies that breed in chicken droppings.⁸

A second starch-based encapsulation process involves dispersing the pesticide in alkali starch followed by coagulation with calcium chloride.⁹ This method overcomes the need for carbon disulfide, which is a flammable and toxic liquid required for making xanthates.

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A third process involves dispersing the pesticide within a highly concentrated paste of alkali starch followed by gelation with boric acid.¹⁰ The gel is broken into small particles suitable for drying after coating with pearl starch or silica. Advantages include avoidance of the filtration step needed with the xanthate and calcium procedures and applicability to both water soluble and water-insoluble compounds.¹¹

In all of these starch-based products, a spongelike structure is formed that locks in the pesticide when dry but releases active ingredient upon wetting.^{3,12}

Since some pesticides are alkali-sensitive, the main objective of this study was to modify the borate procedure to allow encapsulation at a lower pH range. The earlier methods required a pH of 13–14 to gelatinize the starch. By using pregelatinized starch or flour and surfactants, we were able to replace sodium hydroxide with milder bases, such as ammonia or amines, and to operate under pH 12.

EXPERIMENTAL

The following commercially available starches and flours were used: Pearl corn starch (CPC International, Englewood Cliffs, N.J.), pregelatinized wheat starch (MSWS-1000, Midwest Solvents Co., Inc., Atchison, Kansas), and pregelatinized corn flour (Illinois Cereal Mills, Inc., Paris, Illinois). Pregelatinized corn starch was made as follows: Pearl corn starch (200 g) in water (1 L) was mixed in a double planetary mixer¹⁰ (50 rpm) and cooked by steam jacketing at 95°C for 30 min. The jacket was cooled and the dispersed starch was precipitated by adding 95% ethyl alcohol (5 L). The precipitated material was filtered and washed twice with liter portions of absolute ethanol, then filtered again. The product was air dried overnight.

Chemicals including sodium hydroxide, ammonia (ammonium hydroxide, 29% NH₃), hydrazine hydrate (85%), triethylamine, boric acid, sodium perborate, sodium metaborate, sodium tetraborate, and ammonium pentaborate were reagent grades. The herbicide EPTC (Stauffer Chemical Co., Mountain View, Calif.) was used both as the emulsifiable concentrate (EC) at 6.7 lb/gal and as the technical grade. Tween 80 [polyoxyethylene (20) sorbitan monooleate], practical grade (J. T. Baker Chemical Co., Phillipsburg, N. J.), and "Joy" (Procter and Gamble Co., Cincinnati, Ohio) were liquid surfactants. Technical grade hydrated amorphous silica, Flo-Gard AG-150 (PPG Industries, Inc., Natrium, W. V.), was used for coating.

General Laboratory Procedure. Pregelatinized starch or flour (50 g) was mixed with water (99 mL), Tween 80 (1 g), and ammonia (2 mL, 0.03 mol). EPTC (EC) (20 g) was mixed in two increments (10 g each) using a Waring Blendor. The mixture was converted to a rubbery gel by stirring with boric acid (2 g, 0.03 mol). The rubbery gel was converted to particles by stirring in a Waring Blendor with a 1:1 mixture of pearl corn starch and pregelatinized corn flour (20 g). The starch-flour-coated particles were sieved to pass 8 mesh and air dried (20–25°C) overnight. Recovery of EPTC was determined by weight and sulfur analysis of the dried particles. The dried particles were sieved to collect fractions coarser than 10 mesh, 10–35 mesh, and finer than 35 mesh.

Scale-up Procedure. Pregelatinized corn flour (500 g) in water (950 mL)

containing "Joy" (50 g) and ammonia (40 mL) was mixed in the double planetary mixer. EPTC (EC) (200 g) was mixed in two 100-g portions until the dispersion was uniform. This dispersion was mixed 10 min at high speed (90 rpm) until the initially oily material had an adherent "buttery" consistency. Boric acid (20 g) was mixed for 5 min to form a rubbery mass. The product was mixed with a 1:1 mixture of pearl corn starch and pregelatinized corn flour (100 g) and then ground in the Bauer mill¹⁰ with another 100 g of the same mixture. The product was passed through an 8-mesh sieve and air dried overnight. The final material contained 18.4% active ingredient, and recovery was quantitative.

Swelling Ratio. Dried 10–35 mesh particles (5 g) were placed in a 50-mL graduate cylinder and the dry volume was recorded. Water (50 mL) was added, and the particles were mixed with the water by inversion and allowed to settle. Wet volumes of the particles were recorded at hourly intervals, and the ratio of wet volume to dry volume was determined after 2 h.

pH Measurements. The pH's of 10% particle-in-water suspensions were recorded after 1 h using a Beckman Electromate pH meter.

Wet Tests. Samples of encapsulated EPTC in the 10–35-mesh range (1 g) were mixed with water (2 mL) and allowed to evaporate under the hood overnight. Loss of active ingredient was deduced from quantitative determination of EPTC. Samples were rewetted with 2 mL of water and evaporated again in second- and third-day cycles, and cumulative losses of EPTC were obtained.⁹ All of the EPTC released during water evaporation in these wet-dry cycles evaporated from the surface of the particles.

Xanthate Procedure. Pearl corn starch or pregelatinized corn flour (45 g), carbon disulfide (5 mL), and water (250 mL) were mixed with a solution of sodium hydroxide (5 g) in water (75 mL) and allowed to remain at room temperature for 1 h. 20 g of EPTC (EC) was mixed using a Waring Blendor. The mixture was cooled with ice (100 g), and a solution of sulfuric acid (6.5 g) and 30% hydrogen peroxide (6.5 mL) in ice water (100 mL) was added slowly while stirring continuously. The coagulated dispersion was filtered through cheesecloth with suction, using a rubber dam. The filter cake was broken up manually and re-filtered in the same manner. The resulting product was broken up in a Waring Blendor, sieved to pass 8 mesh, and air dried overnight. Recovery of EPTC was 89–90% as determined by weight and nitrogen analysis. The dried particles were sieved to collect fractions coarser than 10 mesh, 10–35 mesh, and finer than 35 mesh.

Calcium Procedure. Pearl corn starch or pregelatinized corn flour (45 g) in water (250 mL) was mixed with a solution of sodium hydroxide (5 g) in water (75 mL). EPTC (EC) (20 g) was added to this alkali starch and dispersed in a Waring Blendor. The dispersion was mixed with a solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (10 g) in water (20 mL) to bring about coagulation. After several minutes, the mass was filtered through cheesecloth with suction using a rubber dam. The resulting cake was broken up in the Waring Blendor to particles that passed 8 mesh and then was air dried overnight. Recovery of EPTC was determined to be 64–69% by weight and nitrogen analysis. The dried particles were sieved to collect fractions coarser than 10 mesh, 10–35 mesh, and finer than 35 mesh.

Borate Procedure. Pearl corn starch or pregelatinized corn flour (45 g) was suspended in water (70 mL) and mixed in a Waring Blendor with a solution of sodium hydroxide (3.3 g) in water (50 mL). EPTC (EC) (20 g) was mixed in two

TABLE I
Properties of Encapsulated EPTC

Method	% EPTC in product	% EPTC incorporated	Dried particles ^a		pH ranges		Swelling ratio	w.t.f				
			>10 ^b	10-35	<35 ^c	Initial ^d		Final ^e	1	2	3	
Xanthate												
CS ^g	21.8	89	—	97	3	13	—	—	5	14	18	
PCF ^h	22.7	90	1	89	10	—	—	8	21	34		
Calcium												
CS ^g	17.4	69	—	97	3	13	—	10	21	22		
PCF ^h	15.8	64	—	91	9	—	—	2	7	12		
Eorate												
CS ^g	18.2	84	27	72	1	13	—	7	10	13		
PCF ^h	16.2	90	—	93	7	—	—	2	12	12		
Eorate ammonia												
PCF ^h	17.0	95	2	95	2	11	—	4	11	20		

^a Percent of total weight in indicated mesh ranges.

^b Coarser than 10 mesh.

^c Finer than 35 mesh.

^d pH of initial starch paste.

^e pH of final products of methods when particles are suspended in water.

^f Cumulative percent EPTC loss after successive wet tests (w.t.) in 1, 2, and 3 days.

^g Pearl corn starch.

^h Pregelatinized corn flour.

10-g increments until a uniform paste was obtained. Powdered boric acid (5 g) was added to form a rubbery mass. The gel was coated with additional pearl corn starch (20 g) and stirred in a Waring Blendor to convert the gel to small particles. The particles were sieved to pass 8 mesh and air dried overnight. Recovery of EPTC was 84–90% by weight and nitrogen analysis. The dried particles were sieved to collect fractions coarser than 10 mesh, 10–35 mesh, and finer than 35 mesh.

RESULTS AND DISCUSSION

For comparative purposes, EPTC was encapsulated by the previously reported xanthate, calcium adduct, and borate complex procedures. Properties of these products are summarized in Table I. Recoveries of active ingredient were higher using the xanthate or the borate procedures than with the calcium procedure.

Over 90% of the particles could be obtained directly in the 10–35 mesh range using the xanthate and calcium procedures; this range was achievable in the borate procedure by regulating the amount and type of surface coating. The material being encapsulated is exposed to a wide pH range in the xanthate procedure, and the final product is mildly acidic. The range of pH exposure is much narrower in the calcium procedure, but it is strongly alkaline both during encapsulation and in the final product. In the borate procedure there is a broader, moderately alkaline range during formation and a less alkaline final product. In the borate-ammonia procedure, the final product is nearly neutral (pH 8).

Various capsules possess differing tendencies to imbibe water with time depending upon the method of encapsulation. These tendencies were measured and expressed as swelling ratios—the ratios of the wet volumes of particles in 1:10 suspension with water to the dry volumes of these particles. Wet volumes were measured after 2 h, since maximum imbibition was usually observed in this interval. Swelling ratios were lowest in the xanthate and highest in the borate procedures.

Products of all procedures showed gradual EPTC release in wet tests over 3 days. Products of the xanthate procedure remained particulate after drying. Those of the calcium and borate procedures coalesced to adherent sheets.

Under the most favorable conditions studied, up to 100% of the pesticide is retained in the final product. Variables influencing the retention of EPTC in procedures involving boric acid and ammonia are shown in Table II. EPTC approaches quantitative retention when the ammonia is added to the initial mixture as in the general laboratory procedure. If the addition of ammonia and boric acid is reversed, or the ammonia and boric acid are premixed, recovery decreases to 71–72%. Therefore, to obtain good retention, it appears necessary to make the pasted mixture alkaline prior to treatment with boric acid. Replacing the 1:1 pearl corn starch:pregelatinized corn flour coating with pearl corn starch alone maintains the retention but decreases particle size of the final product. When silica is used, less coating is necessary to produce particles of the 10–35 mesh range, but there is some loss of EPTC, due to the abrasive action of the silica. The retention of EPTC is improved by adding surfactant to the formulation mixture. Without surfactant, the retention is only 62%, but as the amount of surfactant increases up to the amount used in the general laboratory procedure, retention increases until it is nearly quantitative. Increased amounts

TABLE II
Effects of Reaction Variables upon EPTC Recovery and Particle Distributions in Encapsulation
Using the Starch-Borate Ammonia Complex

Procedure	% EPTC in product	% EPTC incorporated	Dried particles ^a		
			>10 ^b	10-35	<35 ^c
General laboratory	17.0	95	2	95	2
Add ammonia after pesticide and before adding boric acid	17.4	98	1	96	3
Double the amount of ammonia	16.5	92	—	97	3
Double the amount of ammonia and use 20 g of CS ^d as the final coating	17.3	95	—	89	11
Use 5 g of silica as a final coating	18.8	86	—	93	6
Reverse addition of ammonia and boric acid	13.3	71	—	96	3
Premix ammonia and boric acid	13.1	72	—	97	2
Eliminate Tween 80	11.7	62	1	97	1
Use 0.1 g of Tween 80	13.5	72	1	97	2
Use 0.5 g of Tween 80	16.2	88	1	97	2
Eliminate Tween 80 and use 120 mL of water	15.8	88	52	48	1
Replace PCF ^e with PWS ^f	14.9	78	43	55	1
Replace PCF ^e with PCS ^g	14.8	81	6	93	1
Use 0.2 g of boric acid	15.1	81	1	97	2
Replace ammonia with 0.26 g of NaOH and use 0.2 g of boric acid	15.9	87	2	97	1
Replace ammonia with 3.6 g (0.062 mol) of hydrazine hydrate	17.0	94		98	
Replace ammonia with 6.3 g (0.062 mol) of triethylamine	17.2	99		92	

^a Percent of total weight in indicated mesh ranges.

^b Coarser than 10 mesh.

^c Finer than 35 mesh.

^d Pearl corn starch.

^e Pregelatinized corn flour.

^f Pregelatinized wheat starch.

^g Pregelatinized corn starch.

of water in the formulation can replace surfactant, but it greatly increases the number of particles coarser than 10 mesh. Replacement of pregelatinized corn flour with pregelatinized wheat starch or pregelatinized corn starch decreases the retention. The amount of boric acid used can be varied within wide limits. A decrease of boric acid from 2.0 g of the general laboratory procedure to 0.2 g still gives good particle formation and retention. The ammonia can be replaced with a small amount of sodium hydroxide (0.26 g) or with other bases such as hydrazine or triethylamine without affecting the retention of EPTC. However, we made no attempt to determine if these organic additives may have reacted with the EPTC.

TABLE III
Influence of Borate Type upon the Properties of Products Formed in the Encapsulation of EPTC Using the Starch-Borate Ammonia Complex^a

Borate	Amount (g)	% EPTC incorporated	10-35 mesh (%)	pH	Swelling ratio
Boric acid	2.0	100	92	8.3	3.2
Sodium perborate	4.9	92	89	9.4	3.3
Sodium metaborate	4.4	98	91	9.2	3.6
	8.9	100	88	9.5	2.8
Sodium tetraborate	3.1	92	95	8.9	4.2
	12.3	100	87	8.9	2.6
Ammonium pentaborate	1.7	86	91	8.5	3.5
	17.5	100	87	8.5	2.4

^a General laboratory procedure using double the amount of ammonia and "Joy" (5 mL) instead of Tween 80.

Various borates may effectively replace boric acid in the general laboratory procedure, as shown in Table III. The pH is lowest for boric acid and ammonium pentaborate (8.3-8.5) and highest for sodium perborate and sodium metaborate (9.4-9.5). Swelling ratios with sodium metaborate, sodium tetraborate, and ammonium pentaborate decreased as the amounts of these salts were increased.

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