Pesticide Encapsulation Using a Starch–Borate Complex as Wall Material*

D. TRIMNELL, B. S. SHASHA, R. E. WING, and F. H. OTEY, *Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois 61604*

Synopsis

A new technique has been developed for encapsulating pesticides for controlled release. The method consists in mixing starch, pesticide, and water; adding alkali to gelatinize the starch; and treating the mixture with boric acid. The solid product is a starch–borate adduct, entrapping the pesticide within small cells. Initially, the adduct is a rubbery gel which, when treated with alcohol or ground with additional pearl starch, yields particles suitable for drying to the 10–35-mesh range. When the starch is used to break up the gel, the technique is useful for retaining water-soluble compounds. Water-insoluble pesticides, emulsifiable concentrates, and wettable powders are encapsulated and recovered in high yields. Acid-labile pesticides such as diazinon are stable in the borate gel. The process was scaled up successfully by use of a double planetary mixer.

INTRODUCTION

Although the United States attempts to control weeds, insects, nematodes, and fungi with about 2 billion pounds of pesticides per year, these pests are still responsible for farm production losses of an estimated 35 billion dollars a year. This loss is equivalent to 30% of the total value of farm products sales.[1] Part of the problem involves a lack of full availability of the pesticide to the target; losses occur through evaporation, leaching, and degradation and through waste on nontargeted areas. There is an obvious need for more efficient pesticide formulations and usage.

One way of achieving improved efficiency is through controlled-release formulations capable of reducing rates of application, allowing fewer applications, limiting control to targeted areas, reducing evaporative and degradative losses, and providing a slow release of pesticide concurrent with the presence of moisture and soil microorganisms. In addition, controlled release provides for a safer environment, reduces phytotoxicity to desirable plants, makes pesticides safer to handle, and extends residual life of pesticides without carryover into the subsequent growing season.

We have successfully developed controlled-release pesticide formulations through encapsulation as tiny pesticide cells within a starch matrix. Moisture can penetrate and soil microorganisms can attack this matrix to initiate release.[2–9]

---

* This paper reports the results of research only. Mention of a pesticide in this paper does not constitute a recommendation for use by the U.S. Department of Agriculture nor does it imply registration under FIFRA as amended. The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

Journal of Applied Polymer Science, Vol. 27, 3919–3928 (1982)
Published by John Wiley & Sons, Inc.

CCC 0021-8995/82/103919-10$02.00

Initially, in 1976, we reported the encapsulation of pesticides within a starch xanthide matrix.[2] The process involved dispersing the active agent in starch xanthate, crosslinking the xanthate with oxidants or metallic salts, dewatering the resulting product, and then grinding and drying this material. The dried substance usually retained more than 75% of the active agent. These products showed improved efficiency over encapsulated material in several greenhouse and field studies.[10–17]

Further research showed that pesticides could be encapsulated within a starch–calcium adduct by dispersing them in a paste of alkali starch followed by addition of a calcium chloride solution.[6] Encapsulation by this technique gave 60–95% retention of active agent within the matrix. The calcium adduct method had an important processing advantage over the xanthide method in that flammable and toxic carbon disulfide was not required.

Each of these techniques offer specifiç advantages and are providing economically feasible starch-based encapsulated pesticides that perform well in greenhouse and field tests. We have now found that, by substituting boric acid for the calcium chloride, the concept of encapsulating with starch can be extended to offer further advantages. Both the calcium adduct and xanthide methods of encapsulation are carried out at a relatively low solids concentration of 12–14% starch in water. These methods are designed to allow separation of processing water by filtration that removes most water-soluble pesticides and additives. Also, these low concentrations require large mixing tanks relative to the amount of final product. By use of boric acid to complex the starch, much higher solids concentrations are possible. At these higher concentrations, all of the processing water is retained prior to drying. As the processing water evaporates, water-soluble materials are deposited within the dry particles. This effect is especially important for pesticide mixtures formulated with water-soluble additives such as crop protectants. Furthermore, recovery of the pesticide is nearly quantitative.

EXPERIMENTAL

Materials

Commercial pearl corn starch of 12% moisture, from CPC International, Englewood Cliffs, NJ, was used in all experiments. Chemicals such as sodium hydroxide and boric acid were reagent grade. A stock of 6.6% sodium hydroxide solution was made and used throughout. The pesticides were commercially available as technical solids and liquids, emulsifiable concentrates (EC), and wettable powders (WP). Those designated by a "+" contain the crop protectant R-25788 (*N,N*-diallyldichloroacetamide) from Stauffer Chemical Co. Numbers such as 6.7 and 7 following commercial names represent pounds of active ingredient (ai) per gallon of pesticide.

General Laboratory Procedure

A suspension of starch (45 g) and pesticide (10 g ai, as EC, WP, etc.) in water (70 mL) was agitated in a Waring Blender as sodium hydroxide solution (50 mL) was added to gelatinize the starch. Where low-melting solids such as trifluralin were used, the paste was agitated at high speed until the temperature reached about 50°C and the solid melted and became well dispersed. When the pesticide was well blended into the starch gel, powdered boric acid (5 g) was added and mixed at least 10 min until a uniform rubbery mass was obtained. Starch (6 g) was added and the high-speed mixing continued until particles were obtained. The particles were then forced through an 8-mesh sieve and air-dried overnight.

Scale-Up Procedure

Starch (900 g) in water (1400 mL) was mixed with EPTC + EC (358 g, 300 g ai) at 20–90 rpm in a 2-gal double planetary mixer (Charles Ross and Son Co., Hauppauge, NY). The starch was gelatinized with sodium hydroxide solution (1000 mL) and boric acid (100 g) was added while continuously mixing. After 5 min, a rubbery mass resulted. Additional starch (120 g) was added in 20 g increments. Mixing was discontinued when the mass broke down to small nonadherent particles. The product was ground in the Bauer Mill (The Bauer Bros., Springfield, OH) using additional starch (55 g). It was pressed through an 8-mesh sieve and air-dried overnight.

Analyses

The commercial samples and most of the encapsulated materials were analyzed for ai content by elemental analyses for nitrogen (Kjeldahl method), sulfur, or chlorine (oxygen flask method). Metham (vapam) was determined[18] by ultraviolet spectroscopy (max 281 n*M*), and urea was determined[19] by visible spectroscopy (max 440 n*M*), using a Beckman DB recording spectrophotometer.

To determine the amount of ai encapsulated, the amount of unencapsulated or adsorbed ai was subtracted from the total amount of ai recovered as determined by the above analytical procedures. To find the amount of unencapsulated ai, the dried particles (10 g) were washed with acetone (5 × 20 mL). If the pesticide was nonvolatile, the acetone was evaporated and the residue was weighed. For volatile pesticides,[20] quantitative gas–liquid chromatography (GLC) was performed on the acetone extract. The column consisted of 6 ft × 0.25 in. o.d. glass tubing packed with Chromasorb WHP, 80/100 mesh coated with 3% OV-1 silicone rubber. Column temperatures were 135–180°C, and all determinations were done isothermally. Analysis for *N*,*N*-diallyldichloroacetamide, an additive protecting field crops from butylate damage, was achieved by quantitative GLC.

RESULTS AND DISCUSSION

The reactions involved in this process are uncertain due to the complex nature of borate chemistry.[21] Gelation may involve both crosslinking and extensive hydrogen bonding with the electron deficient boron that allows extensive water retention. Borate bridges may form near the branch points of starch chains[22] where there could be a suitable steric orientation of hydroxyl groups. Under alkaline conditions, the special requirements of *cis*-oriented hydroxyl groups may no longer apply,[23] and each boric acid molecule may react with two or more independent hydroxyl groups to give crosslinked alkoxyborate salts.

Synthesis Variables

In order for starch-based encapsulation processes to be useful, it was necessary to obtain nonadherent particles that could be dried to the 10–35-mesh range and retain pesticides after drying. Such products of the starch xanthide and starch–calcium adduct processes were obtained by filtering and grinding prior to drying; other means of obtaining such particles had to be devised for the borate procedure because the gel could not be filtered.

The starch–borate gel that formed had a rubbery, nonfilterable quality over a wide range of initial starch concentrations (10–30%). The efficacies of several methods designed to recover the product as particles are reported in Table I. When the rubbery mass was broken manually into small pieces and allowed to dry, the product was so hard and coarse that only 7–28% of the product could be broken further to pass 10–35 mesh without severely disrupting the encapsulating cell walls. In another approach, the manually broken gel was easily dehydrated with alcohol to yield nonadherent particles that were in the 10–35 mesh range. However, this method extracted too much pesticide. At 10–12% starch concentrations, only 33% of the pesticide was recovered. Increasing the starch concentration to 25–30% improved pesticide recovery to 48%; decreasing the pesticide loading from 25.1 to 10.0 g further increased recovery to 83%.

Finally, we found that the gel could be broken readily into small particles, with good pesticide recovery, by blending in granular starch. When the gel contained 120 g H_2O, 45 g starch, and 17 g pesticide, the amount of recovered product in the acceptable range of 10–35 mesh increased from 22% to about 90% as the amount of granular starch was increased from 6 g to 30 g. The granular starch in this study was 18 g, which gave good product recovery and pesticide retention over a range of 10–25.1 g of pesticide. In subsequent studies, however, we found that by adding only 6 g of granular starch acceptable levels of particles within

TABLE I
Optimization of Encapsulation and Recovery of EPTC[a] in the Starch–Borate Adduct

		Particles in the 10–35 mesh range			
EPTC (g)	Method of recovery	% in range	yield (%)	% ai[b] in adduct	% ai recovered
25.1	Manual	17	13.1	24.9	78
17.0	Manual	7	5.2	21.5	89
10.0	Manual	28	18.4	14.1	91
25.1[c]	400 mL EtOH	94	58.3	13.8	33
25.1	200 mL EtOH	97	66.0	17.8	48
10.0	200 mL EtOH	96	60.9	13.1	83
17.0	6 g starch	22	16.3	19.9	89
17.0	12 g starch	61	50.5	17.6	87
10.0	18 g starch	87	72.2	12.4	97
17.0	18 g starch	88	78.1	19.3	97
25.1	18 g starch	96	92.9	22.3	85
17.0	24 g starch	90	84.2	17.0	89
17.0	30 g starch	88	88.5	16.5	91

[a] Adduct made with 45 g starch, 70 mL H_2O, 50 mL (3.3 g dry basis) sodium hydroxide solution, and 5 g boric acid.

[b] Active ingredient determined by elemental analysis.

[c] Same as (a) except that 250 mL H_2O, 75 mL NaOH solution, and 5 g boric acid were used.

the 10–35 mesh range could be obtained with a high % ai if the product was forced through an 8-mesh sieve prior to drying.

The minimum level of boric acid needed was not clearly established. Molar ratios of boric acid to sodium hydroxide were evaluated over a wide range (1:3; 1:2; 1:1; and 2:1), and at each level acceptable recoveries and particle sizes were obtained. We arbitrarily used the 1:1 ratio because it appeared to give slightly better handling characteristics during mixing and isolation of the final granules.

EPTC was used since it is highly volatile,[20] and the percent EPTC recovered (Table I) represents the total amount of the pesticide that was fully encapsulated. Any adsorbed or nonencapsulated EPTC evaporated from the particles during air drying.

By use of the general laboratory procedure, several pesticides were encapsulated to illustrate the scope of the starch–borate procedure (Table II). Enough starch (6 g) was used to impart good workability of the particles while keeping the highest % ai. For good encapsulation, high-melting solids had to be pulverized to pass 60 mesh. Most recoveries and encapsulations were in the 90–100% range. Certain volatile, alkali-labile pesticides such as DBCP and salt-forming pesticides such as dinoseb were not effectively encapsulated in this procedure.

Scale-Up Process

Larger scale encapsulations of EPTC and butylate EC's by use of the borate procedure were compared with results of similar scale encapsulations involving the xanthate ($FeCl_3/H_2SO_4$ crosslinking) and calcium adduct procedures (Table III). High recoveries of pesticides were maintained in the borate procedure on this scale, and recoveries exceeded those of the xanthate and calcium procedures because no filtration was involved. It was essential to mix the pesticide with the starch slurry before gelatinization because the pesticide did not disperse well in the double planetary mixer after the starch had gelatinized.

Retention of Water-Soluble Additive

Crop protectant retention in the various starch encapsulation procedures is shown in Table IV. Butylate, formulated as butylate + 6.7 EC containing a 24:1 butylate:crop protectant R-25788 ratio, was encapsulated to 20.9% ai butylate in the xanthide procedure (H_2O_2/H_2SO_4 coupling), to 20.8% ai butylate in the calcium adduct procedure, and to 22.7% in the borate complex procedure. Dried encapsulated samples were pulverized in the presence of acetone for analysis by GLC. A K value of 0.88 was determined from a solution of 0.2% ai butylate and 0.2% ai R-25788 (*N,N*-diallyldichloroacetamide) crop protectant (safener) by the formula

$$K = \frac{\mathrm{PH}_p}{\mathrm{PH}_s} \times \frac{W_s}{W_p},$$

where PH_p, PH_s, W_p, and W_s are peak heights and weights of pesticide and crop protectant (safener), respectively. The experimental W_s/W_p for Sutan + used in these encapsulated was 1/25.8. GLC analysis based upon this starting value

TABLE II
Encapsulation of Pesticides by the Starch–Borate Procedure[a]

Chemical name, C.A.	Accepted name	Formulation	% ai recovered	% encapsulated
Dimethyl 2,3,5,6-tetrachloro-1,4-benzenedicarboxylate	Chlorthaldimethyl	75 WP	99	94
2,4,5,6-Tetrachloro-1,3-benzenedicarbonitrile	Chlorothalonil	75 WP	100	100
N-(1,1-dimethylethyl)-*N*′-ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine	Terbutryne	80 WP	98	91
O-ethyl-*S*-phenyl ethylphosphonodithioate	Fonofos	Liquid, 95–99% tech	81	94
O,*O*-diethyl-*O*-6-methyl-2-(1-methylethyl)-4-pyrimidinyl phosphorothioate	Diazinon	Liquid, 8 EC	96	94
1,2-Dibromo-3-chloropropane	DBCP	Liquid, 95–99% tech	32	100
S-ethyl bis(2-methylpropyl)-carbamothioate	Butylate	Liquid, 98% tech	91	98
	Butylate+	Liquid, 6.7 EC	100	100
S-ethyl dipropylcarbamothioate	EPTC	Liquid, 98% tech	86	99
	EPTC+	Liquid, 6.7 EC	91	99
S-propyl dipropylcarbamothioate	Vernolate	Liquid, 7 EC	94	99
S-propyl butylethylcarbamothioate	Pebulate	Liquid, 6 EC	96	99
S-ethyl cyclohexyl-ethyl carbamothioate	Cycloate	Liquid, 6 EC	95	99
S-ethyl hexahydro-1-*H*-azepine-1-carbothioate	Molinate	Liquid, 98% tech	84	100
S-(2,3,3-trichloro-2-propenyl)-bis(1-methyl-ethyl) carbamothioate	Triallate	Solid, 92% tech	95	98
2,4-Dichlorophenoxy-acetic acid, propylene glycol butyl ether ester	2,4-D	Liquid, 73% EC	94	96
2,6-Dinitro-*N*,*N*-dipropyl-4-(trifluoromethyl) benzenamine	Trifluralin	Solid, 95% tech	91	98
	Treflan	Liquid, 44.5% EC	98	91
N-butyl-*N*-ethyl-2,6-dinitro-4-(trifluoromethyl) benzenamine	Benfluralin	Solid, 95% tech	100	96
N-ethyl-*N*-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl) benzenamine	Ethalfluralin	Solid, 97% tech	100	96
Sodium methylcarbamodithioate	Metham–sodium Vapam	Liquid, 32.7% aq	100[b]	
Urea	Carbamide	Solid, water sol	100[c]	

[a] General laboratory procedure used for pesticide encapsulations.

[b] Measured at 281 n*M*[18] after release into water.

[c] Measured at 440 n*M*[19] as *p*-dimethylaminobenzaldehyde adduct after release of urea into water.

TABLE III
Encapsulation of EPTC and Butylate EC's by Use of a Double Planetary Mixer

Pesticide formulation[a]	Starch (g)	Total water (mL)	ai[b] used (g)	Dry starch added (g)	Encapsulation method	Product recovered		
						Yield (g)	% ai[c]	% ai[d] recovered
EPTC+ (6.7 EC)	1350	9,740	500	0	Xanthate (Fe^{+3}/H_2SO_4)	2142	22.0	94
	1350	10,340	500	0	Calcium	1940	19.9	76
	900	2,400	300	175	Borate	1536	19.2	98
Butylate+ (6.7 EC)	1350	11,740	500	0	Xanthate (Fe^{+3}/H_2SO_4)	1886	17.0	72
	1350	10,340	500	0	Calcium	1978	20.0	79
	900	2,400	200	170	Borate	1462	13.3	97
EPTC (7.0 EC)	1350	12,750	500	0	Xanthate (Fe^{+3}/H_2SO_4)	1896	20.3	76
	1350	10,340	500	0	Calcium	1922	18.3	68
	1350	3,600	500	350	Borate	2418	16.4	78

[a] + indicates addition of the crop protectant R-25788 (*N*,*N*-diallyldichloroacetamide).

[b] Active ingredient.

[c] Active ingredient in the 10–35-mesh fraction.

[d] Total recovery.

TABLE IV
Influence of Starch Encapsulation Procedure upon the Loss of Crop Protectant R-25788 (*N,N*-diallyldichloroacetamide) from Butylate+[a]

Procedure	% ai	Crop protectant loss
Xanthide	20.9	23.4
Calcium	20.8	23.0
Borate	22.7	8.8

[a] Butylate+ emulsifiable concentrate containing 6.7 lb/gal butylate and 4% crop protectant R-25788.

showed that losses in the xanthide and calcium adduct procedures were above 23% and in the borate procedure about 9%. Some crop protectant losses may have occurred through instability and polymerization of the crop protectant and during the isolation of the xanthide and calcium adduct by filtration.

Effect of Encapsulation on Pesticide Decomposition

Since diazinon is known to decompose rapidly under certain field conditions, it was used as a control to determine the effect of starch–borate encapsulation on retarding the rate of pesticide decomposition under accelerated aging con-

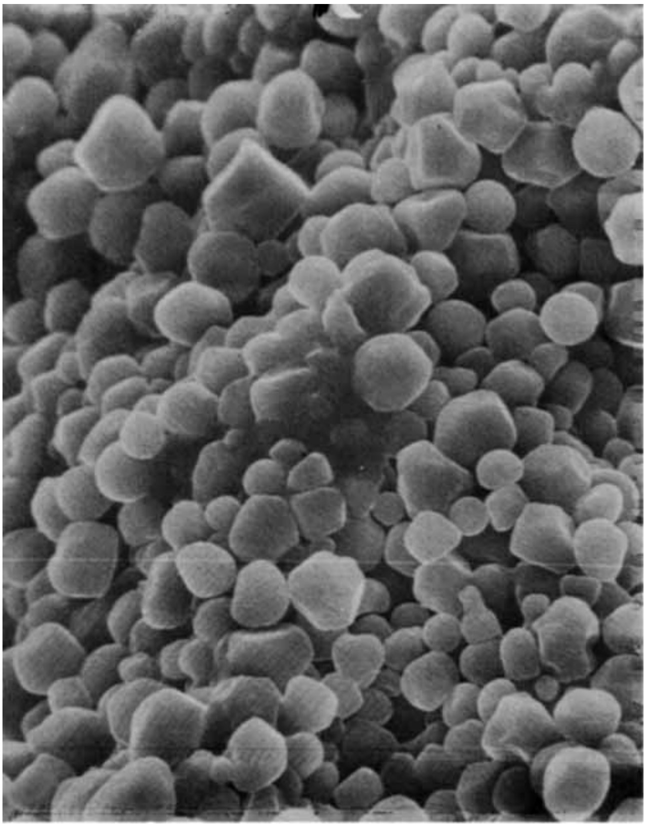

Fig. 1. Pearl corn starch surface coating on starch–borate-encapsulated EPTC.

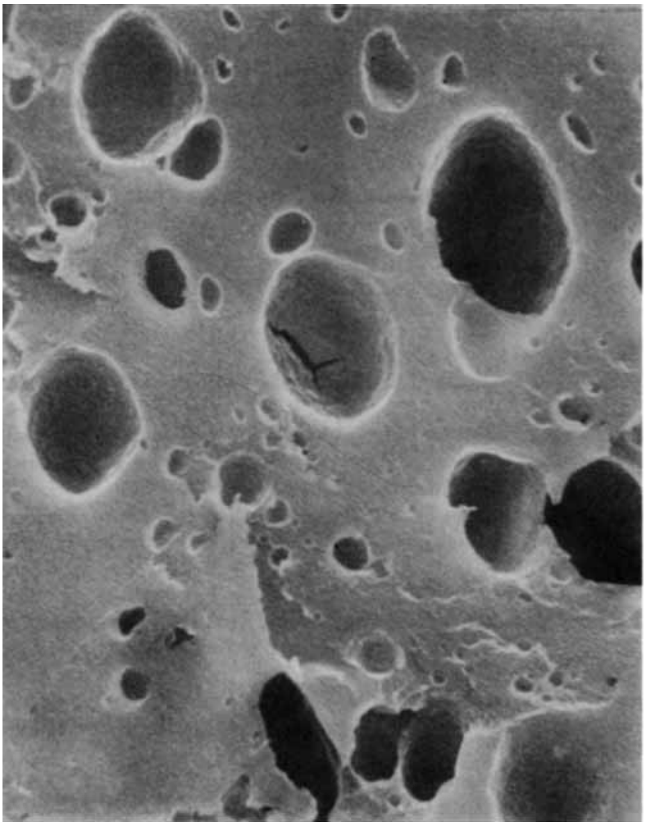

Fig. 2. Internal matrix structure of starch–borate-encapsulated EPTC.

ditions. Diazinon encapsulated by the general laboratory procedure containing 12.6% ai (2 g) was kept at 70°C in a sealed tube and sampled weekly for diazinon content, using GLC analysis with trifluralin as internal standard. Only 8% ai was lost after 4 weeks of aging. This loss was comparable to that for diazinon encapsulated by the starch–calcium adduct procedure and superior to that for calcium oxide-stabilized diazinon[4] encapsulated by the xanthide procedure.

Particle Structures

Figure 1 is a scanning electron micrograph of a starch–borate particle showing granules of dry starch that were added to break the rubbery gel into particles. This starch coating is believed to retard pesticide release and also to provide a means for decreasing particle adhesion.

Slices of the particles (Fig. 2) reveal small cells that contain the pesticide. These cells are similar to those seen in the xanthide and calcium adduct particles. Cracks within the cells may be due to shrinkage of the matrices during drying. Rate of release information comparing the xanthide, calcium adduct, and borate encapsulation procedures will be published shortly.

SUMMARY

An alternate procedure for encapsulating pesticides was developed involving the use of a starch–borate gel. The scope of the encapsulation was comparable to that obtained by the starch xanthide and starch–calcium adduct methods. The procedure was useful for water-soluble compounds, emulsifiable concentrates, wettable powders, retention of crop protectants, and preservation of acid-labile pesticides such as diazinon.

References

1. Anonymous, *Chemical Week*, April 1, 1981, p. 62.
2. B. S. Shasha, W. M. Doane, and C. R. Russell, *J. Polym. Sci., Polym. Lett. Ed.*, **14,** 417 (1976).
3. B. S. Shasha, "Starch and Other Polyols as Encapsulating Matrices for Pesticides," in *Controlled Release Technologies: Methods, Theory, and Applications*, A. F. Kydonieus, Ed., Chemical Rubber Corporation Press, Boca Raton, FL, 1980, Vol. II, pp. 207–223.
4. D. Trimnell, B. S. Shasha, and W. M. Doane, *J. Agric. Food Chem.*, **29,** 145 (1981).
5. D. Trimnell, B. S. Shasha, and W. M. Doane, *J. Agric. Food Chem.*, **29,** 637 (1981).
6. B. S. Shasha, D. Trimnell, and F. H. Otey, *J. Polym. Sci., Polym. Chem. Ed.*, **19,** 1891 (1981).
7. B. S. Shasha, "Encapsulation of Bioactive Material within Starch Matrices," 8th International Symposium on Controlled Release of Bioactive Materials, Fort Lauderdale, Fla., July 29, 1981, pp. 149–151.
8. G. E. Hamerstrand, "Starch Encapsulated Pesticides: A Preliminary Cost Estimate," 8th International Symposium on Controlled Release of Bioactive Materials, Fort Lauderdale, Fla., July 29, 1981, pp. 288–299.
9. B. S. Shasha, D. Trimnell, and F. H. Otey, *J. Agric. Food Chem.*, **29,** 1099 (1981).
10. J. Feldmesser, B. S. Shasha, and W. M. Doane, *Proc. Int. Controlled Release Pestic. Symp.*, University of Akron Community Technical College, Engineering Science Division, Akron, OH, 1976, 6.18–6.29.
11. J. Feldmesser and B. S. Shasha, "Evaluation of Controlled Release DBCP—Starch Xanthide Granules in Laboratory and Greenhouse Soil Tests," Proceedings of the 1977 International Controlled Release Pesticide Symposium, Corvallis, OR., August 22–24, 1977, pp. 205–213.
12. B. N. Devisetty and J. R. Hanson, "Evaluation of Controlled Release Formulations of Dinitramine and Trifluralin," Proceedings of the 1978 North Central Weed Conference, St. Paul, MN.
13. M. E. Foley and L. M. Wax, *Weed Sci.*, **28,** 626 (1980).
14. M. M. Schreiber and M. D. White, *Weed Sci.*, **28,** 685 (1980).
15. C. B. Coffman and W. A. Gentner, *Weed Sci.*, **28,** 21 (1980).
16. M. M. Schreiber and M. D. White, "Effect of Formulation Technology on the Release of Starch Encapsulated EPTC," Proceedings of the 1980 British Crop Protection Conference—Weeds, p. 225.
17. J. R. Baur, *J. Environ. Qual.*, **9,** 379 (1980).
18. F. Takami, K. Tokuyama, S. Wakahara, and T. Maeda, *Chem. Pharm. Bull.*, **21,** 329 (1973).
19. T. J. Potts, *J. Assoc. Off. Agric. Chem.*, **46,** 303 (1963).
20. *Herbicide Handbook of the WSSA*, WSSA Herbicide Handbook Committee, Champaign, IL, 4th ed., 1979, p. 197.
21. Kirk-Othmer, *Encyclopedia of Chemical Technology*, Wiley, New York, 3rd ed., Vol. 4, p. 77.
22. J. Holló and J. Szejtli, *Fette Seifen Anstrichm.*, **59,** 94 (1957).
23. H. Steinberg, *Organoboron Chem.*, Interscience, New York, 1964, Vol. 1, Chaps. 14, 15.

Received March 1, 1982
Accepted April 26, 1982