basic regions. The pH 2 and 3 data produced values for k_A, and the pH 10, 11, and 12 data produced values for k_B. The averages of these values are given in Table V. Applying the Arrhenius rate constant theory to the values obtained for k_A and k_B yields an activation energy of 9.4 kcal/mol for the acid hydrolysis and 18 kcal/mol for the base hydrolysis of PPDA. Although these activation energies indicate that the acid hydrolysis would be faster than the base hydrolysis, the Arrhenius A factor for the base hydrolysis is 5×10^6 times greater than the A factor for the acid hydrolysis and thus overshadows the difference in the activation energies.

Registry No. PPDA, 7450-69-3; PPA, 45951-59-5; PDAA, 10043-91-1; NH_3, 7664-41-7; phenol, 108-95-2; urease, 9002-13-5.

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Starch Matrix for Controlled Release of Urea Fertilizer

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Methods are described for blending urea and a nitrogen stabilizer with starch and converting the blend to particles for potential application as a controlled-release nitrogen source for agriculture. Depending upon the technique used, 5-g samples of the particles released 15–40% and 15–60% of the formulated urea when exposed to 30 and 50 mL of water for 1 h, respectively. Nitrapyrin was slowly volatilized from moist particles, but evaporation from dry particles was negligible.

Some fertilizers, especially urea, are so water soluble that they are readily leached from the crop root zone or cause plant damage due to excessive concentrations. Approaches to obviate these disadvantages have included the development of synthetic fertilizers such as urea–formaldehyde and the use of protective coatings of sulfur (Dalal and Prasad, 1975), bitumens (Elbe et al., 1979), or coal tar (Reddy and Prasad, 1975).

While controlled-release systems are showing considerable success, there are instances where coatings may crack during shipment and also where the release of nutrients is too slow for certain applications. This paper describes two methods for blending urea with starch to yield granular products having potential for application where fast rates of release are desirable. One method utilizes the recently reported technique for encapsulating a wide variety of pesticides (Shasha et al., 1984). An aqueous, alkaline dispersion of starch or flour and urea is rendered particulate by blending with boric acid and then with dry starch. The second method involves extruding a gelatinized dispersion of starch, urea, and water followed by either pelletizing or grinding to the desired particle size. Either method allows the inclusion of other chemicals such as nitrogen stabilizers or sulfur, often used to improve the efficiency of nitrogen fertilization.

EXPERIMENTAL SECTION

Commercially available corn starch, 10.5% moisture (CPC International, Englewood Cliffs, NJ), and pregelatinized corn flour, 4% moisture (Illinois Cereal Mills, Inc.,

Paris, IL) were used. Nitrapyrin [N-serve, 93% active 2-chloro-6-(trichloromethyl)pyridine, technical grade] was obtained from Dow Chemical Co., Midland, MI. All other chemicals, including urea, were reagent grade.

Extrusion Method (Table I). Urea and, optionally, KOH were first dissolved in water (45 mL of $H_2O/55$ g of total formulation solids) and then blended with air-dried starch for 45 min at 95–100 °C in a Brabender mixer (type R.E.E.-6, manufactured by C. W. Brabender Instruments, Inc.). The mixture was then extruded with an extrusion head attached to a Brabender Plasti-Corder Type PL-V300 at a barrel temperature of 105 °C. The screw of the extruder was 1.9-cm diameter; it had a length:diameter ratio of 12 and a compression ratio of 2:1. The die had four holes of 1.5-mm diameter each. After drying at ambient conditions, the extrudate strands were reduced to particles passing 8 mesh by grinding with a Waring Blendor. Two products listed in Table I (no. 82 and 83) were extruded through a 1 mm diameter die and cut to 2–3 mm lengths with scissors prior to complete drying to simulate pelletizing.

Starch and Flour Borate Method (Table I). In a Waring Blendor at 25–30 °C, pregelatinized corn flour was dispersed in a solution of urea, water (50 mL of $H_2O/50$ g of urea), and concentrated ammonium hydroxide (4 mL/100 g of final dry product). Then boric acid (2 g/100 g of final product) was mixed with the gelatinized flour–urea mixture to form a rubbery product. Air-dried corn starch (18 g/100 g of final product) was then added slowly with stirring, which caused the rubbery mass to break down into particles passing 8 mesh. On a dry basis these formulations contained 2% boric acid, 18% ungelatinized starch, and 80% urea and gelatinized flour. The percentage starch or flour reported in Table I for this method

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Table I. Effect of Formulation Method and Composition on Water Dissolution of Starch-Urea Fertilizer

sample no.	composition on dry basis		after soaking 5 g in 30 mL of H₂O for 1 h			after soaking 5 g in 50 mL of H₂O for 1 h			urea leached[c] with H₂O, %		
	starch or flour, %	urea, %	H_2O filtered off, %	urea[a] extracted, %	ratio[b]	H_2O filtered off, %	urea extracted, %	ratio[b]	10 mL	20 mL	30 mL
	0	100							78	95	100
Extruded Starch and Urea											
63	80	20	29	28	0.97	62	42	0.68	14	29	42
64	70	30	31	28	0.90	60	36	0.60	23	36	32
65	60	40	34	26	0.76	62	34	0.55	21	36	42
66	50	50	73	27	0.37	75	36	0.48	24	31	34
83[d]	50	50	56	39	0.70	76	41	0.54	22	30	30
67	40	60	62	32	0.52	82	44	0.54	31	39	55
Extruded Starch, Urea, and KOH											
71[e]	49	49	79	26	0.33	86	26	0.30	32	42	43
80[f]	48.5	48.5	65	35	0.54	83	31	0.37	27	38	41
82[f,d]	48.5	48.5	44	18	0.41	66	15	0.23	25	31	34
81[f]	39.3	57.7	71	32	0.45	81	28	0.34	28	32	36
Precipitated Borate–NH₄OH Pregelatinized Corn Flour											
7A	76.6	21.4	42	28	0.67	64	48	0.75	20	51	67
7B	68.9	29.1	39	33	0.85	64	49	0.77	31	71	84
7C	59.5	38.5	41	38	0.93	70	60	0.86	36	67	85
7D	46.9	51.1	50	35	0.70	70	50	0.71	41	69	84
7E	40.3	57.7	40	33	0.83	62	48	0.77	44	73	87
Precipitated Borate–NH₄OH Corn Starch											
18A	58	40	50	40	0.80	69	42	0.61	36	56	74
18B	48	50	40	34	0.85	66	50	0.76	40	58	78
18C	38	60	18	15	0.83	50	38	0.76	36	58	78

[a] Percent of formulated urea found in filtrate. [b] Percent urea found in filtrate divided by calculated percent if all the formulated urea was uniformly dissolved in all the added water. [c] All leaching studies conducted on samples containing 1 g of urea mixed with 10 g of sand. [d] Product cut with scissors. [e] Product contained 2% KOH. [f] Contained 3% KOH.

Table II. Formulation and Release Rate of Nitrapyrin-Containing Samples[a]

sample no.	formulation, % starch or flour–urea–nitrapyrin	nitrapyrin recovered, %[b]	nitrapyrin retained after wet–dry cycle, %,[b] for days				nitrapyrin retained after 4 days of dry aging, %[c]
			1	2	3	4	
Extruded Starch Products							
4-1	39.3–59.8–0.9	76	58	47	33	44	63
5-4	49.3–50.0–0.76	62	68	45	62	57	73
Extruded Starch Products with 3% KOH							
6-5	37.6–58.5–0.91	67	63	48	59	49	61
Pregelatinized Flour–Borate Products							
12A	77.70–20.0–0.30	86	76	69	69	66	90
12B	67.55–30.0–0.45	86	79	79	77	65	84
12C	57.40–40.0–0.60	84	77	74	70	61	83
12D	47.25–50.0–0.75	74	60	62	60	49	80
12E	37.10–60.0–0.90	78	69	62	55	48	78
Starch–Borate Products							
19A	57.40/40.0/0.60	75	61	59	49	41	81
19B	47.25/50.0/0.75	90	75	66	60	52	89
19C	37.10/60.0/0.90	77	77	67	56	46	92

[a] Nitrapyrin was not uniformly dispersed in samples, which accounts for discrepancies in some of the data. [b] Percent of formulated nitrapyrin found in the final dry product. [c] Percent of formulated nitrapyrin found after standing dry in an open dish for 4 days.

includes both the gelatinized flour and ungelatinized starch. Ungelatinized corn starch was easily substituted for the gelatinized flour (no. 18A–C, Table I) in formulations containing 40–60% urea because this level of urea solution was sufficient to gelatinize the starch at 25–30 °C.

Nitrapyrin Formulations (Table II). The above-described borate procedure was repeated but, in addition, a chloroform solution of nitrapyrin (0.3–0.9 g/5 mL of chloroform) was dispersed into the starch- or flour–urea–ammonia mixture prior to adding the boric acid and dry starch (caution: chloroform is a carcinogen). For the extrusion method, a heated extruder could not be used because of the volatility of nitrapyrin. To avoid excess moisture in the extrudate, the minimum amount of water needed to dissolve the urea and KOH (17–19 mL/54 g of final dry product) was used. The mixture was heated rapidly (3–5 min) until a clear gel resulted (60–80 °C) and immediately air cooling was started. When the mixture temperature was 35–40 °C (50-min total mixing time), crystalline nitrapyrin was added and mixed for 5 min prior to extruding into 1 mm diameter strands. All of these samples were cut with scissors into 2–3-mm lengths.

Analyses. Urea analyses were conducted by a colorimetric method using p-(dimethylamino)benzaldehyde (DMAB) reagent as described by Potts (1963). Nitrapyrin content was determined by suspending samples (1.00 g) in 2 N HCl (10 mL) in a 250-mL Erlenmeyer flask equipped with a drain cock. Isooctane (10 mL) was added

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to form a top layer, and the sample was digested by heating on a steam bath for 5 min. The flask and contents were cooled in an ice bath and shaken to extract nitrapyrin into the isooctane. The aqueous phase was drained off and extracted 3 more times with 5-mL portions of isooctane. The extracts were combined, centrifuged, and diluted to 100 mL with chloroform. Nitrapyrin content was determined with a Beckman DB spectrophotometer operated at 271 nM.

Dissolution Rate of Urea during Soaking and Continuous Leaching with Water (Table I). Separate 5-g samples of starch–urea formulations were allowed to stand at 25–30 °C in 30 and 50 mL of water for 1 h. The water solution was then separated from the residue by vacuum filtration and analyzed for urea. As a second check on these analyses, the weight of residue found from evaporating to dryness each of these solutions was equal to the analyzed weight of urea when corrections were made for other solubles such as KOH and borate.

Leaching experiments with water were conducted by mixing samples containing 1.00 g of urea with 10 g of sand. These mixtures were placed in small fritted glass funnels and eluted separately with 10, 20, and 30 mL of water added dropwise from a buret over 5–10 min. Adhering water was removed by suction and the filtrate was analyzed for urea.

Rate of Nitrapyrin Release from Wet and Dry Samples (Table II). For each of the products prepared, four samples (1.00 g each) containing 1.5% nitrapyrin based on urea were mixed with water (2 mL) and allowed to stand 24 h in an open dish. One sample was analyzed for nitrapyrin content, and the remaining three samples were treated with another 2 mL of water and allowed to dry. This procedure was repeated 3 more times to simulate the loss of nitrapyrin that might occur after four separate rainfalls. Losses of nitrapyrin from dry samples in open dishes over the same 4-day period were also determined.

As controls, dry samples of the starch–urea mixture (10 g) were mixed with solutions of nitrapyrin (60–90 mg) in chloroform (5 mL) (caution: chloroform is a carcinogen), and the chloroform was evaporated to give 1.5% nitrapyrin–urea formulations. These surface-treated samples were allowed to stand in open dishes and then were analyzed for nitrapyrin at 30-min intervals for 2 h as well as after 18 h.

RESULTS AND DISCUSSION

High levels of aqueous urea ($\geq$40% urea; $\leq$60% starch) quickly gelatinize starch at low temperatures, which greatly simplified the preparation of starch–urea composites. For composites with lower levels of urea, either strong alkali or heat was used to gelatinize starch. Alternatively, formulations with lower urea levels can be prepared by using pregelatinized corn flour instead of starch. Once the urea is uniformly dispersed within the starch or flour, the product must be converted into a dry granular material suitable for agronomic application. In one approach this was achieved by complexing the starch with boric acid in the presence of ammonia. The resulting rubbery mass was easily broken into small particles by blending with additional dry starch, which simply coated the broken gel particles and prevented reaggregation. When water-insoluble pesticides are formulated into such a system we find by scanning electron microscopy that the pesticide is trapped in many tiny cells within the particles (Trimnell et al., 1982). Urea is much more compatible with starch; we assume it is more uniformly dispersed within the particles. Boron is a recommended nutrient (1–4 lb/acre) for many crops; therefore, the boron (0.35%) in these

products should not be toxic to plants for most levels of fertilizer applications.

As an alternate approach for combining starch and urea, we chose to use much better mixing equipment, higher temperature, and in some cases strong alkali to improve starch gelatinization and extrusion processing to both remove moisture and aid in forming particles. We are not equipped to pelletize the extrudate, so we resorted to grinding and, for some samples, the extrudate was cut with scissors.

Water-Dissolution and Leaching Rates. Products containing 20–60% urea made by both extrusion and borate complexing are listed in Table I together with their dissolutions and leaching rates. When 5-g samples of these products were soaked 1 h in 30 mL water, generally $^1/_4$–$^1/_3$ of the formulated urea was extracted from the particles; with 50 mL of water, $^1/_3$–$^1/_2$ of the urea was extracted. Exceptions to these rates were those samples extruded with KOH present, which show no increase in extraction rate with the larger volume of water. Only products 82 and 83 (Table I) were cut with scissors (1-mm diameter, 2–3 mm long) rather than being ground. The one without alkali present (no. 83) revealed no major difference in dissolution rate from the ground samples. The one made with alkali (no. 82) retained much more urea during soaking in water.

One reason the products in Table I retain urea is their high water retention, ranging from about 1–5 g of H_2O/g of product. However, this is not the only reason for urea retention; a value of 1 should be found for the ratio of urea concentration in the filtrate to the calculated urea concentration if all of the urea had dissolved in the 30 or 50 mL of water used for extraction ($\approx$% urea extracted/% water filtered off). This ratio (Table I) approached 1 for extruded products made with low levels of urea and is relatively high (0.61–0.93) for all of the borate products. However, the ratio is much lower (0.22–0.54) for extruded products made with high levels of urea, especially for those that contain KOH. A low value for the ratio predicts that increasing the amounts of water used for soaking would not cause a proportional increase in the amount of urea extracted. In fact, none of the samples made with KOH had more urea extracted as the amount of water used for soaking was increased from 30 to 50 mL. Product no. 6–5 (Table II) lost 15% of the formulated urea while soaking 1 h with 50 and 100 mL of H_2O. Extensive water extraction of samples made with KOH and analyses of the extracts revealed that only trace amounts of the urea were lost due to chemical action of the KOH.

During these soaking tests, products made by the borate method with 50% or less urea retained their original granular structure, and the water extract was clear. The borate products with 60% urea and all of the extruded samples made without alkali retained their particle structure during soaking; but the extract was cloudly, indicating some disruption of the starch matrix. Those extruded with alkali became quite gummy, often fusing together, and the water extract was usually very cloudy.

Leaching data (Table I) correlated reasonably well with the soaking studies in that less urea was leached from the extruded samples compared with the borate products, especially as the amount of leaching water was increased. Also, there was little difference in percentages of urea leached as the level of urea in the products was increased from 20% to 50%. As indicated by a control in which pure urea was added to sand, some urea is retained by moisture adhering to the sand when only 10 mL of water was used; but this retained water did not appear to retain significant amounts of urea when 20 and 30 mL of water were used.

Table III. Losses of Adsorbed Nitrapyrin from Starch-Urea Matrix at Ambient Conditions[a]

starch, %	urea, %	nitra-pyrin add-ed, %	cumulative nitrapyrin lost, %					
			initial	30 min	60 min	90 min	120 min	18 h
57.40	40	0.60	35	39	43	62	70	97
47.25	50	0.75	25	41	56	63	67	97
37.10	60	0.90	26	34	39	52	62	97

[a] Starch–urea matrix prepared by the borate method.

Surprisingly, there was no major difference during leaching studies between those samples with KOH and the other extruded products.

Formulation and Release Rate of Nitrapyrin (Table II). Nitrapyrin was evaluated with these starch–urea systems because it helps stabilize nitrogen for more efficient plant use and because it evaporates quickly when applied to soil. We incorporated 1.5% nitrapyrin (based on urea) into all the formulations listed in Table II.

Some data reported in Table II list more nitrapyrin after aging than initially, and some products show erratic release rates. These inconsistencies are attributed to the lack of uniform dispersion of nitrapyrin within the matrix. Hence, we could not determine accurate release rates over the 4-day wet and dry aging, because different samples were needed for each analysis. However, the data were sufficiently consistent to allow some general conclusions on recovery and release characteristics of the nitrapyrin.

Slightly more nitrapyrin was lost (24–38%) during formulating and drying by the extrusion method than was lost (10–26%) by the borate method. We believe that techniques could be devised for improving the retention of nitrapyrin. Once the products were dry, there was little if any further loss of nitrapyrin when the products stood in an open dish for 4 days. Nitrapyrin release was accelerated with moisture, with about half of the formulated amount evaporating after four 24-h cycles of wetting and ambient drying. These simulated tests suggest that nitrapyrin would be readily available to stabilize released urea during several rain leachings.

In contrast, data in Table III reveal much faster rates of nitrapyrin evaporation when it is coated or absorbed onto the surface of particles and exposed to moisture-drying cycles. Essentially all of the nitrapyrin evaporated within 18 h from the dry products, even without exposure to the moisture-drying cycles.

This study has shown that the dissolution rate of urea can be reduced by formulating with starch and other materials. Only through field testing can the viability of these systems as controlled-release fertilizer be determined because of the differing soil moisture levels and the effects of microorganisms on starch. Field testing of some formulations described in this paper has been initiated at other locations.

Any useful economic considerations of these systems would also require results of field testing. During the past few years, starch has sold for about 10¢/lb, which approximates the material cost per pound of sulfur coating including sulfur, sealant, and conditioner. Apparently, about 20.5% coating weight is sufficient for the sulfur method whereas 40% or more starch might be required.

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Effects of Low-Dose γ-Irradiation on Grapefruit Products

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Products obtained from Florida grapefruit irradiated with low-dosage γ-rays as a possible treatment for infestation by larvae of the Caribbean fruit fly were evaluated to determine effects on flavor and composition. Seven tests were run in which twenty-two lots of fruit were exposed to 7.5, 15, 30, 60, or 90 krd of γ-irradiation covering the 1981–1982 and early 1982–1983 harvesting season. There were few significant adverse flavor effects on products from irradiated fruit with the exception of the first test run on early-season fruit. In some cases, particularly at the lower doses of radiation, there was a significant improvement of flavor in grapefruit sections. There were no marked differences in vitamin C, sugar, or acid levels in juice nor on essential peel oil composition of volatile constituents from irradiated fruit when compared with those from untreated fruit.

Grapefruit, *Citrus paradisi* Macf., grown in Florida are susceptible to infestation with larvae of the Caribbean fruit

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fly, *Anastreeha suspensa* (Loew). Currently, ethylene dibromide (EDB) fumigation and cold treatment are the only accepted postharvest treatments for preventing the spread of this fly to citrus-growing areas where these fruit are shipped. These treatments are particularly important for meeting the quarantine set by the Japanese on the 100