Ureaform Fertilizer–Herbicide Combinations

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Ureaform fertilizer–herbicide combinations have been prepared in which the herbicide is occluded uniformly throughout the fertilizer particles. Herbicides used were phenoxy acids and Herban [norea or 3-(3a,4,5,6,7,7a-hexahydro-4,7-methanoindan-5-yl)-1,1-dimethylurea]. Laboratory, greenhouse, and field tests have demonstrated that these herbicides retain their normal activity in these combinations, are leach-resistant, provide sustained activity for at least 3 months, and show reduced phytotoxicity. Other pesticides could be used with similar advantages. Such products should offer cost savings by reducing pesticide loss or crop damage and by avoiding frequent applications. The benefits of the gradual release of nitrogen from the ureaform fertilizer would also be realized.

Blends of pesticides and fertilizers have been formulated and marketed for some years. The advantage of such materials is the application of both pesticide and fertilizer in a single operation. In this paper we describe development of the additional pesticide advantages of: prolonged activity, resistance to leaching, and reduced phytotoxicity, as well as protection from outside agencies such as light, air, and soil microorganisms.

These advantages have been realized by suspending the pesticide in a urea–formaldehyde prepolymer and carrying out the acid condensation to prepare a ureaform fertilizer; the pesticide is uniformly occluded throughout the solid particles. Pesticides used were phenoxy acids, for control of the broadleaf weeds, and Herban [norea or 3-(3a,4,5,6,7,7a-hexahydro-4,7-methanoindan-5-yl)-1,1-dimethylurea], which is a pre- and postemergence herbicide for most annual weeds and grasses. In addition to controlling the rate of release of the pesticide, the ureaform acts as a controlled release fertilizer in its normal manner (Clark *et al.*, 1956).

The literature does not disclose ureaform–pesticide materials in which the ureaform component meets the generally accepted specifications (AAFCO, 1966, 1967). Foamed pesticide combinations made with a urea–formaldehyde type of fertilizer have been described (Renner, 1966). The low water-insoluble nitrogen content disclosed and the presence of surfactants suggest that these fragile foamed products would offer poor protection for pesticides. Pesticides have also been combined with other urea–formaldehyde products which were adhesive or resin types, rather than ureaform fertilizers (Geary, 1965; Alexander *et al.*, 1964; Graenacher and Matter, 1949; Benigus, 1953; Brookes, 1962). Ureaform fertilizers have also been made in which trace elements and chelating agents were distributed uniformly through the material (O'Donnell, 1959, 1966).

MATERIALS

Ureaform Prepolymer. The method described by O'Donnell (1958, 1959) was used. Urea (Du Pont fertilizer grade) (8 mol) was dissolved in 44% aqueous formaldehyde (5.7 mol of formaldehyde) adjusted to pH 8.6. The mixture was heated for 1 hr at 50°C and cooled to 25°C.

Phenoxy Acid Mixture. Equal parts by weight of 2,4-dichlorophenoxy acetic acid, (2,4-D) (Hercules Inc.) and 2,4,5-trichlorophenoxy propionic acid (silvex) (Hercules Inc. were mixed and finely ground.

Ureaform–Herban (0.64%). Ureaform prepolymer (300 g) and finely ground Herban 80% wettable powder (Hercules Inc.) (1.45 g equivalent to 1.16 g of technical Herban) were thoroughly mixed and cooled to 20°C. With good agitation, 10% sulfuric acid (15 g) was rapidly added to the mixture. Agitation was continued until the mixture became thick. Reaction was allowed to continue until the temperature of the semisolid mass reached 65–70°C. The solid mass was then broken up to hasten cooling, transferred to a closed container, and aqueous ammonium hydroxide (29% ammonia, 15 g) was added to neutralize the polymerization acid. After at least 2 hr, the product was dried at 50°C and ground to pass a No. 8 U.S. sieve. This procedure yielded 180 g of product containing 0.64% technical Herban. Solubility analyses [Association of Official Agricultural Chemists (AOAC), 1965] were as follows: WIN (percent water-insoluble nitrogen), 30.2; HWIN (percent hot water-insoluble nitrogen), 16.0; AI (Activity Index), 47; %N, 38.8.

Ureaform–Herban (1.9%). This was prepared as above, except that 4.4 g of Herban 80% wettable powder was used: WIN, 27.5; HWIN, 14.2; AI, 48; %N, 38.6.

Ureaform–Herban (0.34%). This was prepared as above, except that 0.76 g of Herban 80% wettable powder was used: WIN, 27.1; HWIN, 14.3; AI, 47; %N, 39.1.

Ureaform–Phenoxy (0.9%). This was prepared from ureaform prepolymer (300 g) and phenoxy acid mixture (1.68 g), using the same procedure described for the ureaform–Herban materials: WIN, 24.8; HWIN, 13.8; AI, 48; %N, 38.2.

Ureaform. Nitroform (Hercules Inc.) was used: WIN, 26.6; HWIN, 14.5; AI, 46; %N, 38.3.

Ureaform Coated with Phenoxy (0.9%). Ureaform was screened to give −12 +40 U.S. sieve size particles. Five grams of these particles was placed in a closed container with 0.045 g of finely ground phenoxy acid mixture and gently mixed until the phenoxy acids were uniformly coated on the ureaform granules.

METHODS

Activity Index. The AOAC procedure (1965) was used. Samples for both cold and hot water solubility tests were crushed to pass a U.S. No. 40 sieve (35 mesh).

Nitrification Rates. The procedure of Clark *et al.* (1956), as described by Hays *et al.* (1965), was used.

Laboratory Leach Test. Ureaform–herbicide granules were screened to give −12 +40 U.S. sieve size particles. Five grams of these particles was placed to give a 5-in. col-

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umn in an upright glass tube fitted with a bottom screen and liquid outlet. A 200-ml portion of distilled water was allowed to percolate slowly (2 hr) at 25°C through the granules, keeping them immersed in water at all times. The aqueous leachate was then analyzed for phenoxy acid content by an ultraviolet spectrophotometer. The residual ureaform–herbicide granules were removed, dried, and weighed to determine what portion of the original granules had dissolved in water.

Activity of Leached Products. Ureaform–Herban (1.9%) and Herban 80% wettable powder were applied on soil in pots at Herban rates of 2 and 4 lb per acre. Each pot was treated with 3 in. of surface water; the first 0.5 in. of water which drained through the pot was retained for bioassay (Table II). Mustard and rye seeds were then sowed in these pots and in control pots containing no Herban. After 7 weeks in the greenhouse, the extent of plant injury was determined (Table I).

RESULTS AND DISCUSSION

On exposure to water and soil microorganisms for 3 months, about 60% of the nitrogen in commercial ureaform fertilizers is gradually converted to the available nitrate form (Hays *et al.*, 1965). When pesticides are protected by occlusion within such fertilizer granules, they would be expected to be released at much the same rate. This has been found to be the case for two ureaform–herbicide combinations used, a phenoxy acid product designed for control of broadleaf weeds and a Herban product for control of most annual weeds and grasses. Laboratory, greenhouse, and field tests showed that these pesticide combinations were leach resistant, retained their initial activity, gave sustained activity for at least 3 months, and showed reduced phytotoxicity.

Leach Resistance. The leach resistance of these products was shown in laboratory tests in which, under very severe aqueous leach conditions, a maximum of 60% of a phenoxy acid mixture was dissolved from a ureaform combination made with 0.9% of a mixture of phenoxy acids. A similar leach test using ureaform granules coated with the same amount of phenoxy acids showed that 85% of the phenoxy acids were leached; approximately the same amounts of total water-soluble material (25 and 22%, respectively) were dissolved from each composition.

To demonstrate leach-resistant properties further, a ureaform–Herban (1.9%) product was subjected to greenhouse bioassay studies with Herban 80% wettable powder as a control (Table I). After leaching with 3 in. of surface water, the ureaform–Herban composition still gave complete kill. The Herban 80% wettable powder at the lower concentration was largely leached as shown by 20–30% kill of the weed plants; at the higher concentration the wettable powder retained 90% kill.

The first 0.5 in. of water leaching through the experimental pots in each case was tested, as indicated in Table II. Here we find low kill corresponding to low leaching for the ureaform–Herban and higher kill for the more readily leached wettable powder.

Field experiments in Georgia have also demonstrated the leach resistance of a ureaform–Herban (0.34%) product. This material and Herban 80% wettable powder were applied at the rate of 3 lb of Herban per acre to plots in which several varieties of camellias were grown. During a 14-day period after the treatment, 13 in. of rain fell on the test plots. Twenty days after the treatment the ureaform–Herban plots showed 90% weed control, while there was 0% weed control in the plots treated with the Herban 80% wettable powder.

Table I. Bioassay Studies on Leachability

Form applied to the Soil	Rate of application of Herban (lb active ingredient/acre)	% kill of plants growing in leached soil	
		Mustard	Rye
Ureaform–Herban (1.9%)	2	100	100
Herban 80% wettable powder	2	20	30
Ureaform–Herban (1.9%)	4	100	100
Herban 80% wettable powder	4	90	90

Table II. Bioassay Studies of the Water Leachate from Soil

Source of leachate	Original rate of application of Herban (lb active ingredient/acre)	% kill of plants after application of 0.5 in. of leachate	
		Mustard	Rye
From ureaform–Herban (1.9%)	2	5	5
From herban 80% wettable powder	2	100	40
From ureaform–Herban (1.9%)	4	20	20
From herban 80% wettable powder	4	100	60

Table III. Herbicidal Activity

Plot treatment	% weed covering on grass plots after 2.5 months growth	
	Floratine St. Augustine	137 Bermuda grass
None (check plots)	96	59
Ureaform (20 lb/1000 ft²)	100	68
Ureaform–Herban (0.34%) (20 lb/1000 ft² equivalent to 3 lb Herban per acre)	0	0
Ureaform–phenoxy (0.9%) (10 lb/1000 ft² equivalent to 4 lb phenoxy acid mixture per acre)	20	13

Initial Activity. The initial activity of the ureaform–herbicide products was demonstrated in greenhouse studies. Mustard and millet seeds were planted in soil in pots. Herban was applied at the rates of 1, 2, or 4 lb per acre as the ureaform–Herban product and as the 80% wettable powder. In all cases, the ureaform–Herban products containing either 0.64 or 1.97% Herban matched the almost complete kill shown by Herban applied as the 80% wettable powder.

Sustained Activity. The sustained herbicidal activity of the ureaform–herbicide products, due to gradual release from the ureaform, was demonstrated at several field test locations. At Fort Lauderdale, Fla., freshly cut plugs of Floratine St. Augustine and 137 Bermuda grass were placed in clean soil containing a large variety of weed seeds, especially green amaranth, spiny amaranth, water sedge, purslane, crabgrass, and several species of spurge. Ureaform–Herban (0.34%) and ureaform–phenoxy were applied and compared with controls of straight ureaform and no treatment (Table III).

Ureaform–Herban gave complete control compared with 13–20% for ureaform–phenoxy; some of the weeds present, such as crabgrass, are unaffected by phenoxies. In all the plots there was no apparent injury or slowing of growth of either the Floratine St. Augustine or 137 Bermuda grass. At another location in Fort Lauderdale, the sustained herbicidal activity of this ureaform–phenoxy (0.9%) product was confirmed. Plugs of St. Augustine and Bermuda grass were planted in clean soil containing weed seeds, mainly oldenlandia, nutgrass, goosegrass, crabgrass, water sedge, purslane, and several species of spurge. Those weeds sensitive to phenoxies were still controlled 1 month after treatment.

Another sustained activity field demonstration was conducted on cotton test plots in Georgia. After a 9-week period, during which 11.7 in. of rain fell, plots treated with ureaform–Herban (0.34%) at the rate of 4 lb of Herban per acre still showed 60% weed control. Adjacent plots treated with 2 lb of Herban as the wettable powder showed no weed control after the same period and crabgrass was growing 10 in. high. A set of trials showing the prolonged effectiveness of the ureaform–Herban (0.34%) product was also conducted at Auburn University, Auburn, Ala. When applied at the rate of 4 lb of Herban per acre, this material gave 90% broadleaf weed control after a 9-week period. Control plots treated with Herban 80% wettable powder at the higher rate of 6 lb per acre showed only 50% effectiveness after the same period. The sustained activity of the ureaform–Herban material was also demonstrated in a nursery at Hollywood, Fla. Weed control was still 85% after 3 months in containers of Double Red Hibiscus which were treated with ureaform–Herban (0.34%) at the rate of 6 lb of Herban per acre and watered daily. After the same period, containers treated with Herban 80% wettable powder, at the rate of 3 lb of Herban per acre, showed no better control than those treated with no herbicide.

Reduced Phytotoxicity. Reduced phytotoxicity of a herbicide incorporated within ureaform particles was also shown in the above nursery tests run at Hollywood, Fla. Herban 80% wettable powder applied at the rate of 3 lb of Herban per acre killed Double Red Hibiscus, while Herban applied at double the rate (6 lb per acre) in the form of the ureaform–Herban (0.34%) combination gave no injury.

In the previously described field tests run at Fort Lauderdale, Fla., a ureaform–phenoxy (0.9%) combination was applied to Bermuda grass and St. Augustine grass at the very high rate of 16 lb of phenoxy acid mixture per acre. At such a rate, a phenoxy acid mixture would be expected to damage the turf quality of Bermuda grass significantly and cause serious deterioration of St. Augustine grass. Because of the reduced phytotoxicity of the phenoxy acids protected in the ureaform combination, it was observed that the quality of the Bermuda grass turf was not affected while the growth of the St. Augustine grass was only slightly suppressed.

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