Polymer Coating on Urea Prills To Reduce Dissolution Rate

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The effect of encapsulating urea prills with polymeric materials on reducing the release rate of urea in water was studied. Various types of polymers, including polystyrene, polycarbonate, a copolymer of vinyl chloride and vinyl acetate, poly(vinyl acetate), and low-density polyethylene (LDPE) were tested. Except for LDPE-coated urea, very high dissolution was observed (95%), even at a high coating percentage (15%). This was mainly due to the presence of large pinholes and to the nonuniformity of the coating film. LDPE-coated urea had much lower dissolution. For a coating percentage of 6, the dissolution was 25–30%.

Urea is considered one of the world's leading nitrogen fertilizers due to its high nitrogen content (46%), low cost, and commercial availability. It has, however, the major limitation of easy dissolution in water and rapid hydrolysis. This causes high nitrogen losses through ammonium volatilization.

The need to control nitrogen losses initiated a wide range of research activities that fall under four development categories: 1, slightly soluble materials such as urea formaldehyde (ureaform); 2, materials for deep placement such as urea supergranules (USG); 3, urease and nitrification inhibitors; 4, fertilizers coated with semipermeable or impermeable membranes. This paper deals with the last approach, particularly with polymer-coated urea.

Coated fertilizers are physically prepared from granules of conventional fertilizers coated with materials that reduce their dissolution rate. Commercially available coated fertilizers can be divided into two categories: sulfur-coated urea (SCU) and polymer-coated urea. SCU has been under development by the Tennessee Valley Authority (TVA) since 1961 (Young, 1974). Sulfur was selected as a coating material on the basis of economy and efficiency. TVA started with coating small batches of urea in small rotating drums to continuous coating in a pilot plant with a capacity of 1 ton/h. (Shirley and Meline, 1975).

A process for manufacturing SCU in a spouted bed was developed by Meisen and Mathur (1978), who tested this technique because of its success in coating pharmaceutical tablets (Mathur and Epstein, 1974).

The first commercial polymer-coated fertilizers were developed by the Arthur Daniels Midland Co. (ADM). The main component of the coating is a copolymer of dicyclopentadiene with a glycol ester (Powell, 1968). Nutrients are released through osmotic exchange with moisture from the soil. The Sierra Chemical Co. currently produces this coated fertilizer under the trade name Osmocote. Two other polymer-coated fertilizers are produced commerically: Sierrablen and Agriform. Most of these products are based on ammonium nitrate mixed fertilizers and on single nutrients, according to customers' requests.

Hecht et al. (1973) developed a coating material formed of a water-insoluble synthetic resin and particles foreign to the resin. The amounts of foreign particles in the resin layer range from 1% to 50% by weight of the resin, depending on the desired dissolution rate. When rapid release of the fertilizer is desired, large quantities of the foreign particles (about 50%) are included; smaller quantities (about 2%) are used when release rates are to be slow. Types and amounts of foreign particles include salts (1–5%), oxides (3–12%), metals (3–20%), and organic substances (5–20%). The resin is a copolymer of vinyl

chloride and acrylic esters such as methyl acrylate.

Otto (1977) developed a cement-coated fertilizer. The cement used may be of the portland, masonry, or gypsum type. This fertilizer can be encapsulated in a semipermeable elastomer layer. Traces of micronutrients such as calcium, zinc, cobalt, and magnesium can be mixed with the cement before the polymer film is added. Otto argued that using cement and elastomer together is less expensive than using polymer alone.

This paper examines the effect of different coating materials and process variables on reducing urea dissolution rate. A fluidized-bed technique is used for encapsulation.

EXPERIMENTAL PROCEDURE

Materials. The urea from the Petrochemical Industries Co. had a nitrogen content of 46.6% and a particle size range of 0.5–2 mm. Vinyl chloride copolymer, poly(vinyl alcohol), and poly(vinyl acetate) were from BDH Chemical Ltd.; polystyrene, polycarbonate, and low-density polyethylene were from CDP Chemie. Laboratory-grade carbon tetrachloride, acetone, methanol, and toluene were purchased from May and Baker Ltd. and BDH Chemical Ltd.

Apparatus and Method. A schematic diagram of the modified fluidized-bed equipment is shown in Figure 1. In a typical experiment, the product container is filled with about 1 kg of urea and is inserted into the apparatus and sealed pneumatically. The turbine is run for 5–10 minutes to preheat and fluidize the urea particles. The spraying process begins by starting the dosing pump and the atomizing air. After the film coating solution is sprayed, about 200 mL of pure solvent is sprayed to clean the tubes and nozzle assembly. The final step is drying. The air temperature is raised to 80 °C, and the atomizing air is shut off. Drying time (usually 5–10 min) depends on the required moisture content.

The coated product is evaluated by such control tests as total coating, nitrogen content, dissolution, crushing strength, and moisture content.

Total Coating. The actual coating percentage is determined as follows: 20 g of coated urea is crushed and blended with water to accelerate the dissolution of the urea. The solution is then filtered, and the remaining insoluble solid material is dried in the oven until its weight becomes constant. The coating percentage is calculated from eq 1. This value is compared with the expected percentage of coating, which is equal to the weight of the polymer in the coating solution divided by the final weight of the product.

$$\% \text{ coating} = \frac{\text{wt of solid (g)}}{20} \times 100 \qquad (1)$$

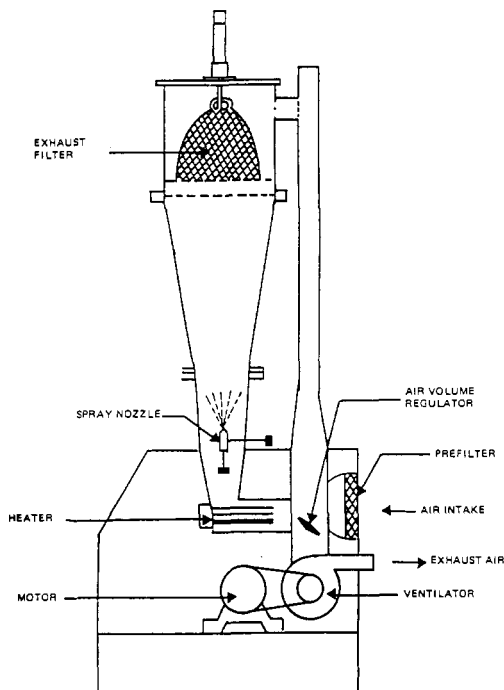**Nitrogen Content.** The nitrogen content of coated urea is determined by the standard Kjeldahl method. The

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Figure 1. Schematic diagram of the fluidized-bed apparatus.

Figure 2. Effect of coating percentage (vinyl chloride copolymer) on urea dissolution at 22 °C.

sample is treated with sulfuric acid to yield ammonium sulfate. The nitrogen content can be calculated by the hydrolysis of ammonium sulfate. The nitrogen content is calculated more accurately from the total coating percentage by eq 2.

$$\% \ N = \frac{46.6(100 - \% \ coating)}{100} \qquad (2)$$

Dissolution. The conventional method for determining the dissolution (Blouin et al., 1971) for coated urea is a static test in which 50 g of the product is placed in a bottle and 100 mL of distilled water is added. The temperature was controlled by using a water bath. All experiments were carried out at 22 °C except for the comparison between LDPE-coated urea and SCU, which was conducted at 37 °C. The refractive index of the solution is measured at 30 °C as a function of time (daily for 7 days). The grams of urea dissolved in water (X) can be read directly from a standard curve (a correlation between refractive index and concentration). The dissolution rate is calculated by eq 3.

$$\text{dissolution} \ (\%) = \frac{X}{50 - \% \ coating/2} \times 100 \qquad (3)$$

Crushing Strength. The crushing strength test is carried out according to standard methods. The crushing strength, i.e., force per unit area of sample required to induce fracturing, is determined for 10 prills of equal size, one at a time. The average value will be the crushing strength for that particular prill size. The lower the crushing strength, the easier the fracture of coated urea and, therefore, the easier the release of nitrogen.

Moisture Content. The moisture content test is conducted according to the standard procedure using the Karl Fischer apparatus. The Fischer reagent and methanol with a water content of 0.02% are used as reagents. The moisture content is calculated from eq 4, where V = volume of consumed Karl Fischer reagent (mL), t = weight of water equivalent to 1 mL of Karl Fischer reagent (g), and a = weight of urea sample (g).
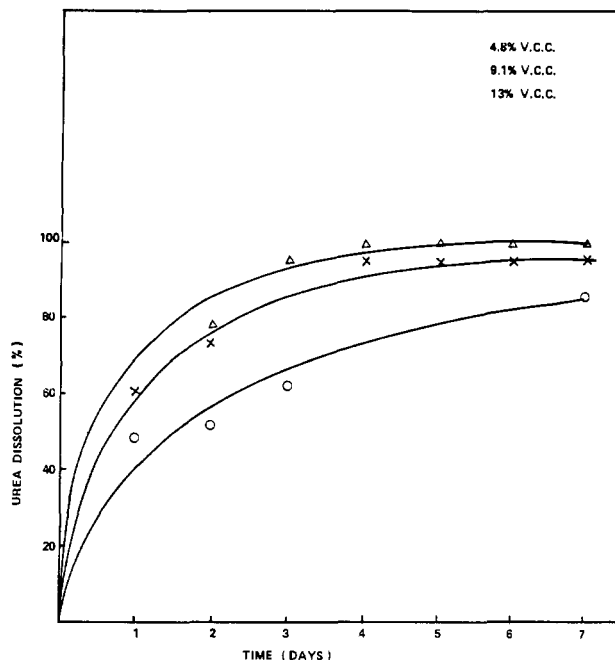
$$\% \ H_2O = \frac{Vt}{a} \times 100 \qquad (4)$$

RESULTS AND DISCUSSION

The quality of the coating depends on a number of process variables. Therefore, preliminary experiments were conducted to examine these variables and to find the optimum coating conditions. The main process variables include (1) weight of urea, (2) atomizing air pressure, (3) fluidizing air flow rate, (4) process temperature, (5) total coating percentage, (6) type of coating material, (7) viscosity of coating solution, and (8) flow rate of coating solution.

The amount of urea to be coated is limited by the capacity of the ventilator. If the weight of the urea particles exceeds 1.5 kg, they cannot be fluidized. Furthermore, a minimum of 600 g of urea is required to cover the spray nozzle. The weight of the urea had no appreciable effect on the 7-day dissolution (94.3–95.3%) as long as it was in the range of 600–1000 g. In these experiments, vinyl chloride copolymer was used as a coating material and all other process variables were kept constant.

Similarly, ranges of 1–2.5 bar for the atomizing air pressure and 100–200 m³/h for fluidizing air flow rate were found to be optimum. Values higher than the upper limit cause particle attrition, which gives rise to a high powder content and an increase in the dissolution rate. Values below the lower limit will prevent fluidization and proper atomization of the coating solution. As a result, urea particles agglomerate and prevent uniform coating. Again, when we operated within these pressure and flow rate ranges, no major change in the dissolution was observed.

The process temperature varies with the type of coating material and the solvent used. As a rule of thumb, the polymer solution temperature at the spray nozzle should be within the boiling point range of the solvent. Instant drying of the coated particles cannot be achieved if low processing temperatures are used. Also, agglomeration of particles can result from a low process temperature.

Of these variables, the last four are the most important. Poly(vinyl alcohol) and poly(vinyl acetate) cannot be used in the fluidized bed because they form thin fibers that block the spray nozzle. Other tested polymers, however, can be used. The effect of coating percentage on the dissolution for vinyl chloride copolymer (VCC), poly-
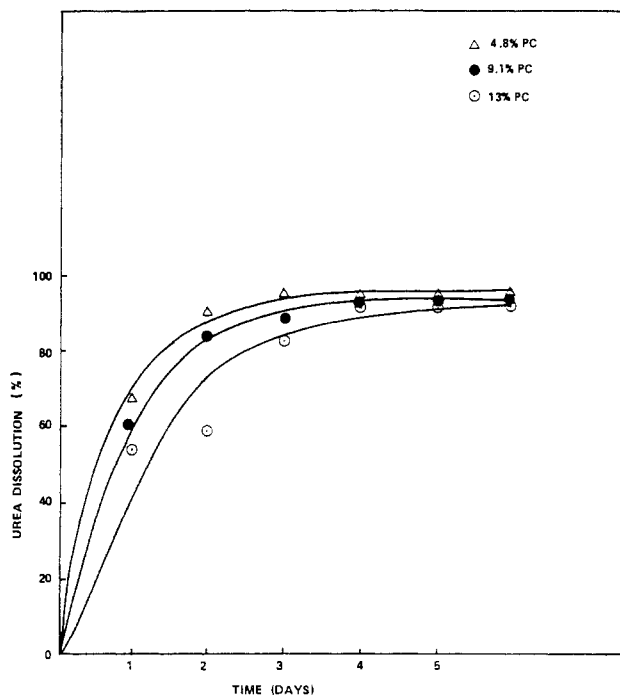
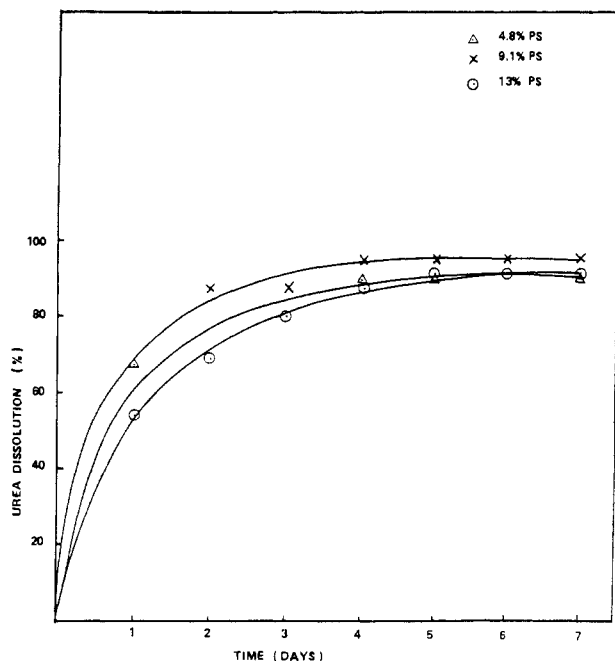**Figure 3.** Effect of coating percentage (polycarbonate) on urea dissolution at 22 °C.

Figure 4. Effect of coating percentage (polystyrene) on urea dissolution at 22 °C.

Figure 5. Effect of coating percentage (low-density polyethylene) on urea dissolution at 22 °C.
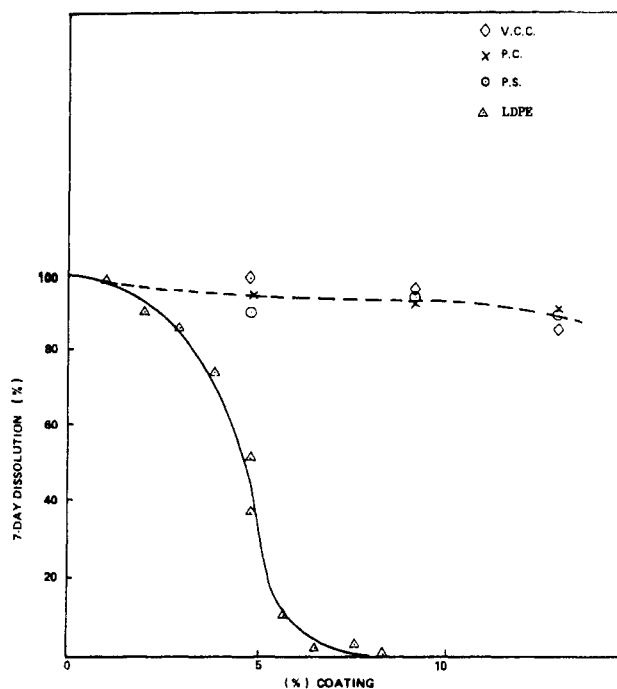
Figure 6. 7-Day dissolution as a function of coating percentage for various polymers at 22 °C.

carbonate (PC), polystyrene (PS), and low-density polyethylene (LDPE) coated urea is demonstrated in Figures 2-5, respectively. It is clearly shown that as the total coating increases, the dissolution decreases. This effect is smaller with the first three polymers than with LDPE. Dissolution after 7 days dropped from 99% to only 85% when the total coating of VCC was increased from 4.8% to 13%. For shorter times (2 days), the drop is approximately twice as much. PC-coated urea and PS-coated urea showed drops in dissolution with increasing coating percentage only at shorter times (less than 3 days). After 7 days of incubation at 22 °C, the difference was practically negligible. For LDPE-coated urea, however, the effect of total coating is considerably larger. Urea release after 7 days dropped from 86% to 11% as a result of increasing
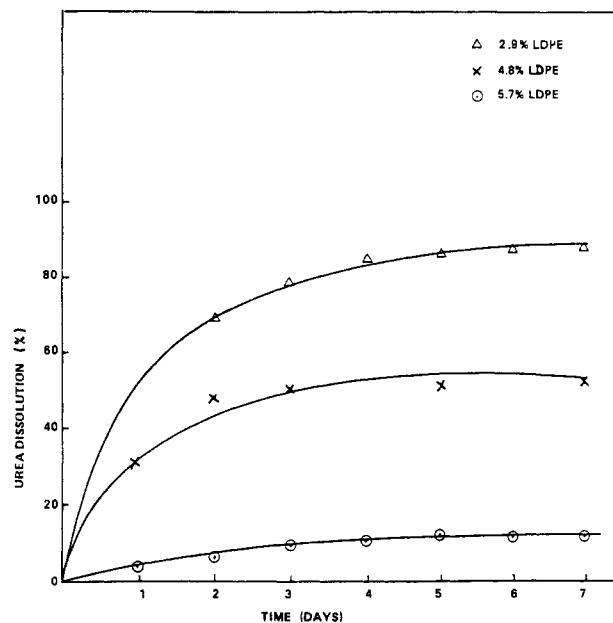
the total coating from 2.9% to only 5.7% (Figure 5).

A clear distinction between LDPE-coated urea and VCC-, PC-, and PS-coated urea is demonstrated in Figure 6. With a total coating of 5%, LDPE-coated urea had a 7-day dissolution of about 30%. With the other polymers, however, the dissolution was almost 3 times higher for the same coating percentage.

The difference between LDPE and the other polymers is caused by the degree of uniformity and perfection of the coating film. Defects in the coating film can be identified by scanning electron microscopy (Figure 7). Pinholes may be clearly seen in (a)-(c). These relatively large pinholes (10-20 μm) are the principal path for the release of urea with the observed high dissolution. The exterior surface of LDPE-coated urea (d), however, is quite uniform and free from detectable (at 800X magnification) pinhole capillary pores, although the coating percentage is lower. The
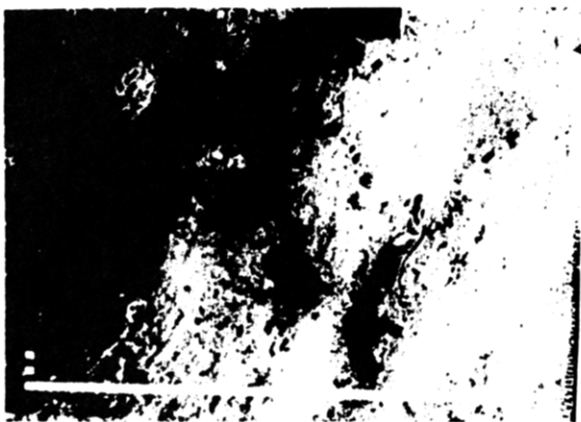
(a) Polycarbonate

(b) Vinyl chloride copolymer
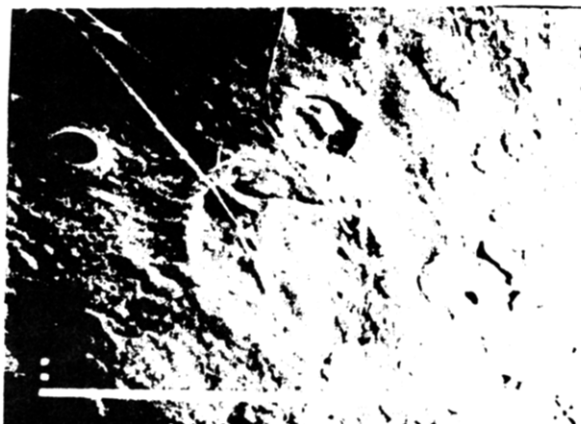
(c) Polystyrene

(d) LDPE

Figure 7. Scanning electron microscope observations of the exterior of polymer coatings: (a) polycarbonate (9.1%); (b) vinyl chloride copolymer (9.1%); (c) polystyrene (9%); (d) low-density polyethylene (5.6%).

main reason for the uniformity of the LDPE film is a characteristic property of LDPE solutions. LDPE is in solution form when it is hot but forms a gel in which the resin component is uniformly distributed when cooled. It should be mentioned that pinholes are present in LDPE film but their number and size are quite small.

The effect of polymer solution viscosity on dissolution is presented in Figure 8. The viscosity of each solution was measured at 80 °C, the temperature at which spraying occurs. It is clear that the dissolution decreases with the increasing viscosity of the LDPE solution (Figure 8). The dissolution dropped almost 1 order of magnitude by lowering the viscosity from 8.3 to 4.4 cp. This is probably because of rapid solvent evaporation for the less viscous solution at the prill surface. Thus, uniform distribution of the resin component in the solution to cover the whole surface is hindered. This is verified by SEM observations (Figure 9). It is clear that the low-viscosity solution (b) produces a coating film that is much less uniform and less dispersed, giving rise to higher dissolution.

The flow rate of the polymer solution during spraying is also an important process variable. A general trend of increasing dissolution with increasing flow rate was observed. This effect can be explained by the relationship between flow rate and residence or coating time. Longer times are allowed for the distribution of polymer solution on the surface of urea prills with low flow rates. Thus, the
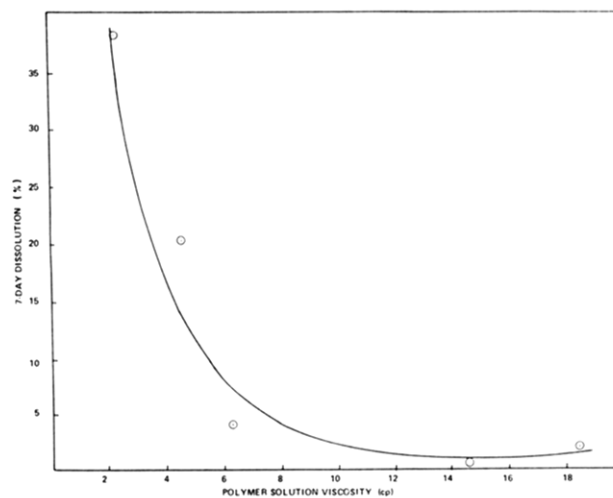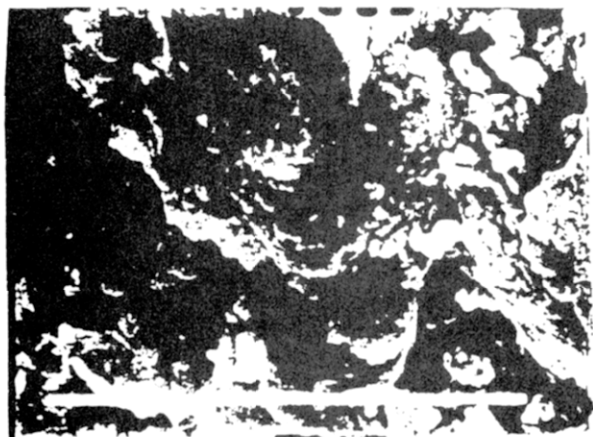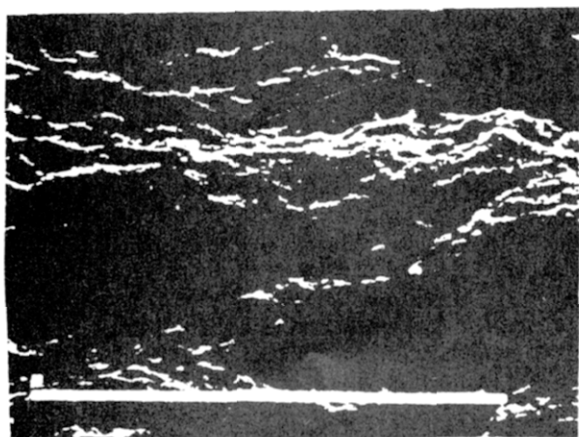

Figure 8. Effect of LDPE solution viscosity on 7-day dissolution at 22 °C.

coating film is expected to be more uniform and the dissolution rates lower. In a commercial process, lower flow rates have the disadvantage of increasing operating time and consequently energy costs. Therefore, a compromise is necessary between good quality coating and energy savings.

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(a) Low viscosity

(b) High viscosity

Figure 9. Scanning electron microscope observations of the exterior surfaces of LDPE-coated urea: (a) low-viscosity LDPE-coating solution (20.3 cp); (b) high-viscosity LDPE-coating solution (4.4 cp).

Table I. Effect of LDPE-Coating on Moisture Content and Crushing Strength of Urea

coating, %	moisture content, %	crushing strength, kg/cm^2		
		2 mm	1.7 mm	1.4 mm
0	0.29	32	27	29
4.3	0	44	51	40
4.75	0	77	71	49
5.8	0	127	126	141
6.65	0	127	176	140
7.65	0	127	133	107

Two of the most important parameters affecting the quality of coating are the size and physical characteristics of the urea substrate. Urea prills must be spherical, smooth, hard, and closely sized. Granules with sharp corners or dimples are difficult to coat completely and uniformly. Also, soft prills give less support to the coating material, making it more susceptible to cracking and fracturing upon handling.

Improving Storage and Handling Characteristics. The encapsulation of urea prills by LDPE film has other advantages besides reducing the rate of nutrient release. The crushing strength is improved, and there is almost no water content (Table I). For example, at a prill size of 1.7 mm, there is a factor of 4.7 increase for the 5.8% LDPE-coated urea over that of uncoated urea, and the moisture content dropped from 0.29% to a nondetectable value.
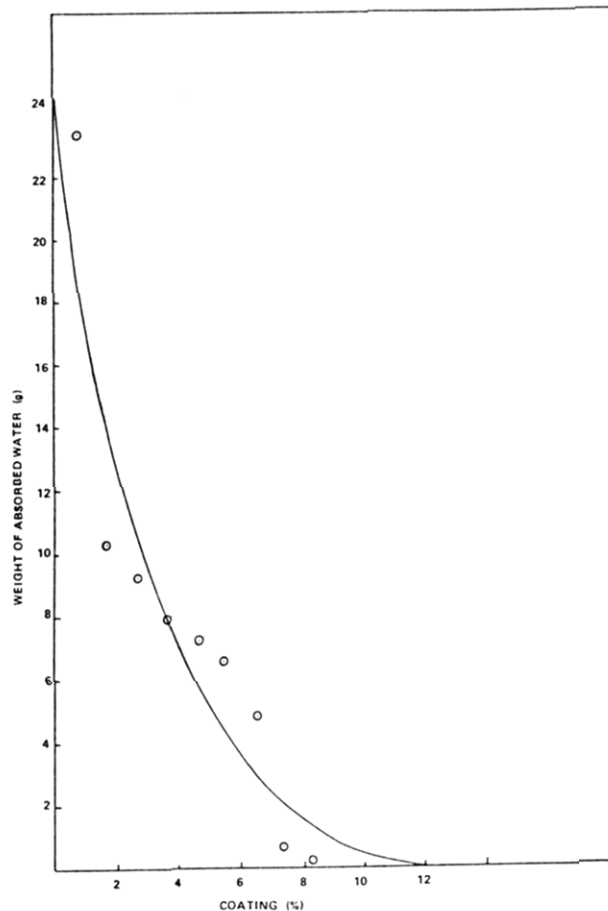

Figure 10. Effect of LDPE coating percentage on water absorption at a relative humidity of 45% and a temperature of 42 °C.

A second test showed the effect of LDPE coating on reducing water absorption by the urea. Twenty grams of uncoated urea and LDPE-coated urea at a coating percentage range of 1–8% were exposed to a relative humidity of 45% and a dry bulb temperature of 40 °C for 24 h in a controlled-humidity chamber. The weight of water absorbed by each sample was then determined. The amount of water absorbed was reduced from 24 to 0.2 g as a result of 8.2% LDPE coating (Figure 10); 5% LDPE-coated urea absorbed moisture at one-fourth the rate of uncoated urea.

The increase in crushing strength and the decrease in moisture absorption for coated urea improve its storage and handling characteristics. First, particle attrition is reduced because of the strong encapsulating film, so the powder content of the product is very much reduced. Second, the coated product resists caking in humid conditions, thus avoiding the use of anticaking agents such as kaolinite. Finally, the need for polyethylene-lined bags is eliminated, and the fertilizer can be shipped in bulk, giving rise to lower costs.

Finally, it is interesting to compare LDPE-coated urea with the commercially available sulfur-coated urea. Figure 11 shows the effect of total coating on the 7-day dissolution for SCU 164D and LDPE-coated urea. SCU-164D refers to a sulfur-coated urea containing 2% of a mixture of polyethylene (30%) and brightstock (70%) as a sealant and 2.4% diatomaceous earth as a conditioner typically produced by TVA's 1 ton/h (NFDC, 1976). It is clear that, for the same dissolution, the total coating is much lower for LDPE-coated urea. Therefore, if we consider a dissolution of 25%, SCU-164D contains 20% coating materials whereas LDPE-coated urea contains only 5.6%. This
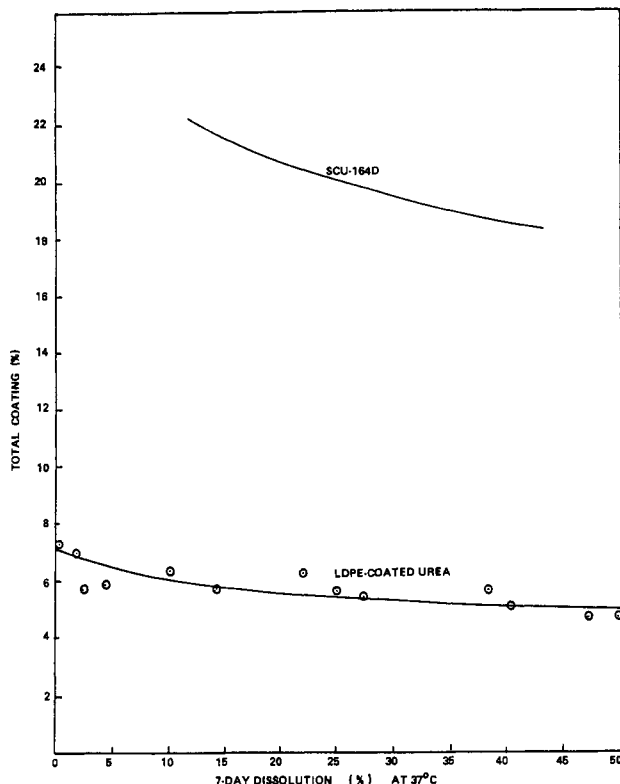
Figure 11. Comparison of the 7-day dissolution of sulfur-coated urea (SCU-164D, TVA) and LDPE-coated urea.

corresponds to a nitrogen content of 36.8% for the former and 43.4% for the latter.

A second advantage of LDPE-coated urea over SCU is its higher crushing strength. The crushing strength for a 1.7-mm prill of LDPE-coated urea is 126 kg/cm² (5.8%

coating). A granule of SCU with a prill diameter of 1.7 mm has a crushing strength of 37 kg/cm². This makes SCU more susceptible to fracture upon handling, increasing the powder content and the dissolution.

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Occurrence and Chemical Determination of Zearalenone and Alternariol Monomethyl Ether in Sorghum-Based Mixed Feeds Associated with an Outbreak of Suspected Hyperestrogenism in Swine

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Swine fed sorghum-based mixed feeds in South Africa developed clinical signs of hyperestrogenism, a disease known to be linked to zearalenone contamination of feed. Thin-layer and high-performance liquid chromatographic analysis of feed samples indicated the cooccurrence of zearalenone and alternariol monomethyl ether (AME). The major contaminant was found to be AME, present in all samples at levels of 1.2–2.25 μg/g, while zearalenone was found at levels of 0.85–1.25 μg/g. With the optimization of fluorescence detector parameters, existing methods dedicated to the determination of zearalenone and its derivatives were found to be suitable for the coextraction of AME. One of these methods extracted AME at an average recovery of 91.8%, and the limit of detection was found to be in the order of 10 ng/g for both AME and zearalenone. It is concluded that zearalenone was probably responsible for the clinical signs of hyperestrogenism and that AME can easily be mistaken for zearalenone in TLC analysis of sorghum-based mixed feeds.

During 1986 four samples of mixed feeds associated with a field outbreak of suspected hyperestrogenism in swine in South Africa were received for analysis. Clinical signs observed during the field outbreak included pseudoestrus

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and swollen vulvas in young gilts and reduced lactation in sows with piglets. Only one field outbreak of hyperestrogenism in swine has previously been reported in South Africa, and this was associated with corn infected by *Fusarium graminearum* Schwabe and contaminated with zearalenone (Aucock et al., 1980). In the present case, the mixed feeds were sorghum based and corn free (Table I). Although zearalenone (Figure 1A) has been reported to occur naturally in sorghum in the United States (Schroeder