

Sulfur Coating on Nitrogen Fertilizer to Reduce Dissolution Rate

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Coating of urea granules with sulfur may provide an effective controlled-release nitrogen fertilizer at relatively low cost. Potential benefits are higher yield per unit of applied nitrogen and lower application cost. In small-scale tests, the coating was applied by spraying atomized molten sulfur onto a rolling bed of fertilizer granules. The coating was sealed with a film of microcrystalline wax con-

taining a microbicide and the granules were dusted with a conditioner to assure good flowability. A product with about 20% of its weight as coating (16% sulfur, 3% sealant, 0.5% microbicide, and 1% conditioner) had a dissolution rate in water at 100° F. of about 0.2% per day as compared with 100% for the uncoated urea. The coated urea also gave better nitrogen utilization in greenhouse and field tests.

The agronomic efficiency of water-soluble fertilizer materials, such as urea, ammonium phosphate nitrate, and ammonium nitrate, may be low because of leaching, decomposition, luxury consumption, and toxicity due to heavy application. Losses may vary from 10% under the best field conditions to 75% under the poorest conditions (Allison, 1955). Thus there is a tremendous potential for conserving nitrogen by minimizing these losses.

The potential savings involved in this field have attracted a great deal of study in two broad areas: the synthesis of chemical compounds that are inherently slowly soluble in soil solutions, and the application of coatings, or moisture barriers, to the surfaces of water-soluble fertilizer particles to yield controlled-release fertilizer. Although the production of slowly soluble compounds is technically feasible, the complexity of the processes or the high cost of raw materials has resulted in prices to the consumer that limit their use to specialty crops such as turf grasses and ornamentals. The production of controlled-release fertilizer by coating soluble fertilizer substrates with shells of semipermeable materials has also been widely investigated. A wide variety of natural or synthetic polymers, waxes, resins, and oils have been studied. As in the case of the slowly soluble compounds, the costs of these coated materials have limited commercial production and relegated the materials to specialty uses.

At TVA, several studies of controlled-release fertilizers have been made. The most extensive study has been on use of sulfur to coat water-soluble fertilizers, particularly urea. Sulfur is considered a promising coating agent for several reasons. It is inexpensive as compared with polymeric materials such as polyethylene, polyurethane, or natural resins. It is easily handled in the molten state used in coating granules or prills. Also, it may have residual

value on sulfur-deficient soils, although, for in-year effectiveness, finely divided material generally is recommended.

The work at TVA has resulted in the development of an economical, technically feasible coating process covered in two U.S. patents (Blouin and Rindt, 1967). This work, which was carried out in batch equipment, is described in this paper. Development of a continuous process is under way.

EXPERIMENTAL

Equipment and Procedure. The equipment consisted of a rotary pan in which the granules were sprayed with sulfur, an electrically heated sulfur melt pot and air-atomizing nozzle for spraying sulfur, and a second pan in which wax sealant and conditioner were applied to the sulfur-coated granules. The pan used for application of sulfur (a modified pan granulator) was 22 inches in diameter, 6 inches deep, and contained ten 4-inch flights and a 4-inch retaining ring (Figure 1). It was operated at an

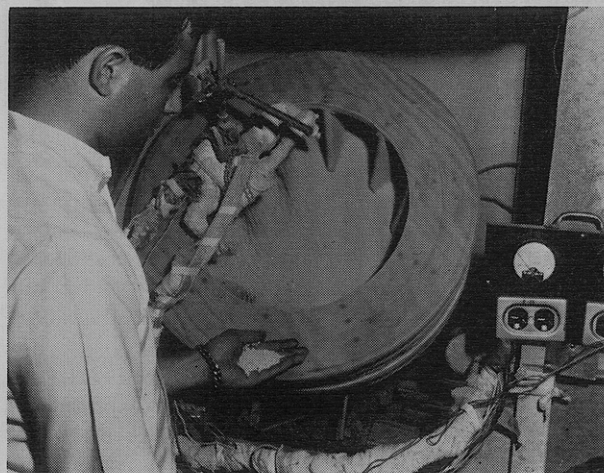


Figure 1. Modified 22-inch batch pan-coating unit

angle of 65° from horizontal and at 22 r.p.m. The hot-air sulfur-atomizing spray nozzle (0.08-inch orifice) was used to deliver a fan-shaped spray pattern of molten sulfur from a distance of about 5 inches above the rolling bed of fertilizer particles. Atomizing air pressure was 20 p.s.i.g. The spray nozzle originally contained a needle valve for flow rate control. This valve was removed to prevent plugging by impurities in dark sulfur, and rate control was accomplished by varying the gas pressure (1 to 2 p.s.i.g.) on the sulfur melt tank. Cylinder nitrogen was used for this purpose. The pan in which the sealant and conditioner were applied was 20 inches in diameter by 18 inches deep and was operated at 30 r.p.m. This pan was lined with a resilient plastic material; such a lining minimized abrasion of the sulfur coating, which was softened temporarily when the hot wax was added.

The procedure generally used was to charge 12 to 15 lb. of granules to the rotating pan and heat to the desired temperature (160° F.) with a hot-air gun. Molten sulfur (290° F.) then was sprayed on the granules, after which they were transferred to the second pan where molten wax (200° F.) was applied by pouring. Waxing was carried out in a separate pan to prevent contamination of subsequent batches of urea with wax before coating with sulfur. After the wax-coated granules were permitted to cool to about 100° F., they were recharged to the pan and coated with conditioner.

Laboratory Evaluation of Product. The basic test for evaluating the relative effectiveness of coatings was degree of dissolution in quiescent water at 100° F. (2-gram sample in 10 ml. of water) in 1 and 5 days. The 1-day dissolution test was taken to indicate the proportion of particles with imperfect coatings. The average of the dissolution rates (per day) for the next 4 days, called differential dissolution rate, was taken to be an indication of moisture permeation of coating on the well-coated particles. Limited data indicate that the differential rate remains fairly constant for 2 to 3 months with well-coated samples. Dissolution was determined by drying and weighing the reclaimed granules. It was visualized that dissolution rates of up to 15 or 20% in the first day might be acceptable because some quick-release nitrogen is desirable for most growing plants. It was assumed that a differential rate of about 1% per day would be satisfactory, since it should result in steady release of substrate over 14 to 16 weeks, the growth period of many crops. Later agronomic tests confirmed that release rates of this order showed controlled-release characteristics by depressing early yields and increasing late yields.

A second test used at times for evaluating coatings involved burial of a 1-gram sample in 250 grams of damp soil at 85° F. and determining substrate losses with respect to time by weighing reclaimed granules. A cutaway photograph of the test vessel with granules in place is shown in Figure 2. Normally, a fine sandy loam soil (pH 5.2) was used. The soil moisture content was maintained at about 20% by weight.

Fertilizer Substrate Tested. Most of the work was done with pan-granulated urea from TVA experimental studies. However, other fertilizer substrates also were tested. Among those that were successfully coated were urea prills, diammonium phosphate crystals and granules,

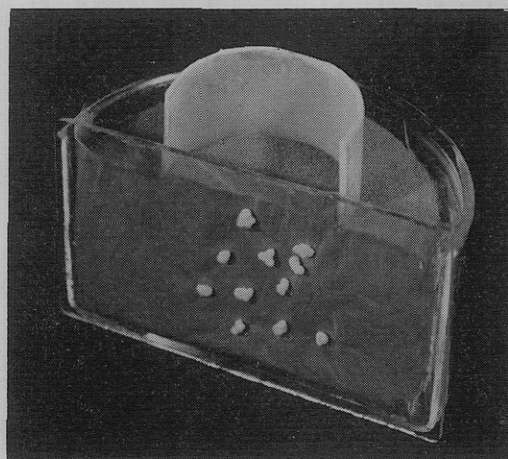


Figure 2. Soil burial test vessel
Cutaway

ammonium phosphate nitrate granules, and potassium chloride granules. The size of the materials was -6+12-mesh (Tyler screens). Ammonium nitrate was not used because of the possible explosion or fire hazard involved.

Sulfur Types and Modifiers. Both "bright" and "dark" grades of commercially available sulfur were used. Although the bright sulfur had a lower impurity content, both types could be handled without difficulty after the valve was removed from the spray nozzle.

Early in the initial phases of the work, it became obvious that sulfur coatings alone did not provide a satisfactory moisture barrier. The fertilizer dissolved almost completely in 24 hours (in water at room temperature) even from samples with a 40% coating, leaving solution-filled sulfur shells. It was evident from this that the sulfur shells had microscopic pores and cracks which allowed moisture penetration. Glasslike coatings, which resulted from proper application conditions, were significantly more effective than the rough coarse coatings resulting from improper conditions; however, none were sufficiently effective to have slow-release properties.

One approach to this problem was use of sulfur additives to minimize the cracks and pores in the sulfur shells. Tests were made with three types of additives—plasticizers, introfiers, and powdered solids. Nine organic polysulfide plasticizers were tested with sulfur in proportions up to 50% of the mix. The effect of plasticizers was to reduce the viscosity of the molten sulfur. As a result, sulfur was atomized more readily over a greater temperature range. The plasticizers also tended to alter the crystalline structure of solidified sulfur by increasing the equilibrium content of the amorphous phase; this theoretically should decrease its permeability to moisture. In practice, only a modest improvement of this nature was noted. Moreover, the plasticizers prolonged the time necessary for solidification of sulfur and aggravated the problem of tackiness. Relatively low spray rates were necessary to avoid tackiness. Also, products with plasticizers tended to cake during storage. Since the disadvantages of the plasticizers outweighed the advantages, their use was discontinued.

An introfier is defined as a sulfur additive that improves the penetration characteristics of molten sulfur. Naph-

thalene, which is an introfier, was added to sulfur in amounts up to 9% by weight. The sulfur adhered more tenaciously to the granules but the moisture resistance of the coatings was considerably less. There was no net advantage.

Powdered solids (-200-mesh) were added to the sulfur as an aggregate to strengthen the coating and prevent the hair-line cracks in the sulfur shells. The amount of solids that could be used was limited because of increased viscosity. Mixes containing more than 10% by weight were handled with difficulty. Micronutrients, including oxides of zinc, copper, iron, or manganese or mixtures thereof, were added by this method, as well as talc and vermiculite. In general, the solids accelerated solidification of sulfur on the granule surface and increased the coating strength and brittleness. Although the coatings were satisfactory, they offered no significant advantage. However, the method might be used as a means of getting uniform distribution when incorporating micronutrients in sulfur-coated fertilizer.

Coating Sealant. Another approach to eliminating the problem of cracks and pores in the sulfur coating was sealing with water-repellent oils and waxes. In initial tests, a nondetergent motor oil (SAE 30) was poured onto the sulfur-coated granules. The oil was an excellent sealant against moisture, as determined in water-immersion tests, but in soil the oil top coat apparently was removed by soil capillary action and became ineffective. Good results were obtained with a hard wax (melting point, 165° F.; oil content, 10%).

Addition of Microbicides. In the course of coating evaluation, some products were subjected to the soil burial test. In general, the dissolution rates in soil were much higher than in water and in some cases products with low water-dissolution rates failed in a few days. This suggested that soil microorganisms might be destroying the coating when soil temperature and moisture conditions were favorable. Soil tests with steam-sterilized soil under otherwise identical conditions did not show the same coating deterioration, thus confirming the theory of microbial attack.

Soil chemists pointed out that the wax sealant is more subject to microbial attack than the sulfur coating. To combat this, a number of known disinfectants or microbicides were added to the wax sealant. The microbicide content of the product was in the range of 0.5 to 2% by weight. Table I shows the relative effectiveness of these materials. The beneficial effects of 0.5% of pentachlorophenol and coal tar are shown in Figure 3. The addition of microbicides was easily accomplished. Additives soluble in wax were dissolved in the wax prior to sealing, and insoluble ones were dusted onto the tumbling granules.

Product Conditioning. Although hard wax proved to be an excellent sealant, an inherent disadvantage of the wax was its tackiness. This was countered by dusting a conditioner over the waxed granules after they had cooled sufficiently (105° F.) to prevent embedding of the conditioner in the wax. About 1% by weight of kaolin clay, diatomaceous earth, or vermiculite was satisfactory.

Operating Temperatures. The coating effectiveness was affected by the temperatures of the molten sulfur, atomizing air, and substrate during the coating operation. Exploratory tests indicated that the best temperature for spraying

Table I. Effectiveness of Microbicides^a in Sulfur Coatings as Determined by Substrate Dissolution Rate in Soil

Effective	Neutral	Increased Dissolution
Coal tar Pentachlorophenol	Naphthalene Potassium azide	Streptomycin Calcium cyanamide, neutral soil
Sodium penta- chlorophenol Camphor Sodium azide Calcium cyanamide, acid soil Cupric chloride Borax	Boric acid	

^a Added in amounts of 0.5 to 2% by weight of finished product.

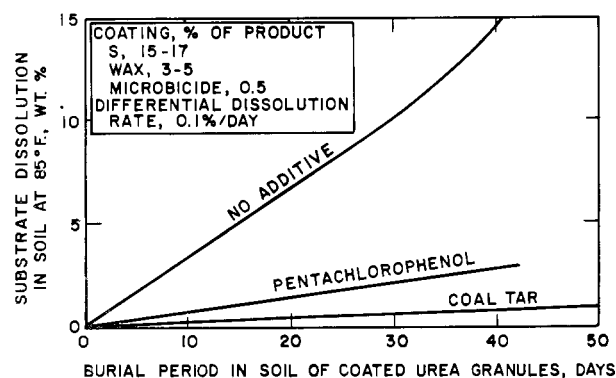


Figure 3. Effect of microbicides on substrate dissolution in soil at 85° F.

the molten sulfur was in the range 275° to 295° F., at which point the viscosity was near its minimum and a good spray pattern was obtained. Air temperatures in this same range were satisfactory. Substantially lower air temperatures tended to freeze the atomized sulfur prematurely. The hard wax could be poured easily at 200° F.

In a series of tests to determine the effect of substrate temperature during sulfur coating and waxing, minus 6-plus 12-mesh (Tyler screens) granular urea was coated and waxed at substrate temperatures in the range of 130° to 175° F. The products contained about 15% sulfur, 5% wax, and 1% conditioner. The molten sulfur and atomizing-air temperatures were in the range 275° to 285° F. The data in Table II show that best results were obtained in tests 3, 4, and 5, in which the substrate temperature was 150° to 170° F. during coating and 150° to 160° F. during waxing. The differential dissolution rate for products from these three tests was about 0.6% per day. The sulfur coating was smooth and glasslike in appearance. When the substrate temperature was lower (130° F., tests 1 and 2) or higher (175° F., test 6), the differential dissolution rates were 2 to 4% per day. At the lower temperature, the sulfur coating was rough because of premature freezing of the sulfur and was difficult to seal. At the higher temperature, the sulfur did not solidify rapidly enough and ran off the substrate.

Table II. Effect of Substrate Temperature on Quality of Product^a

Test No.	Substrate Temperature, ° F.		Substrate Dissolution in Water at 100° F., %		Differential Dissolution Rate, %/Day
	While coating with sulfur ^b	While sealing with wax ^c	24 hr.	5 days	
1	130	130	12.9	23.8	2.7
2	130	130	9.3	24.6	3.8
3	170	150	4.4	6.5	0.5
4	150	150	0.7	1.1	0.1
5	160	160	3.5	6.8	0.8
6	175	175	10.7	19.9	2.3

^a Coating materials, % wt. of product: sulfur 15, hard wax 5, conditioner 1.

^b Sulfur temperature, 275°–285° F.

^c Hard wax temperature, 200° F.

Weight of Sulfur and Sealant. The effect of proportion of sulfur was investigated in a series of tests with urea granules (–6- +10-mesh) in which the sulfur weight was varied from about 7 to 16% of the total weight of the product (Table III). In addition, each product contained 3.0% hard wax, 0.5% coal tar (microbicide), and 1.0% conditioner (parting agent). Both the 24-hour and the differential dissolution rates were inversely proportional to the proportion of sulfur used. With 7% sulfur, both the 24-hour and the differential dissolution rates were relatively high—27% in 24 hours and 2.8% per day during the next 4 days (differential rate). In the range of 9 to 16% sulfur, the 24-hour rates were 4.0 to 0.4% and the differential rates were 1.0 to 0.1% per day.

As shown in the following tabulation, increasing the proportion of hard wax from 2 to 5% improved coating effectiveness. The improvement beyond 3%, however, was not significant at the higher proportions of sulfur.

Hard Wax, %	Sulfur, %		
	7	9	13
	Differential Dissolution Rate, % per Day		
2	2.0	1.1	0.6
3	1.7	0.8	0.3
4	1.3	0.7	0.2
5	1.1	0.6	0.2

Table III. Effect of Sulfur Coating Weight on Water-Dissolution Rates

Sulfur Coating, Wt. % of Product ^a	Substrate ^b Dissolution in Water at 100° F., %		Differential Dissolution Rate, %/Day
	24 hr.	5 days	
7	27.0	38.0	2.8
9	4.0	8.0	1.0
12	2.6	5.6	0.8
13	2.0	5.4	0.8
14	1.1	2.4	0.3
15	0.8	1.7	0.2
16	0.4	0.9	0.1

^a Additional coating, wt. % of product. Hard wax 3%, microbicide 0.5, conditioner 1.

^b Size of substrate, –6 +10 mesh.

Effect of Substrate Particle Size. Tests were made to determine the effect of urea substrate size on coating effectiveness (Table IV). Commercial prills “as received” (1% –6- +8-, 97% –8- +16-, 2% –16-mesh) or screened to –6- +10- and –10-mesh (5% –16-mesh) fractions were coated with about 14 to 16% by weight of sulfur, 3% of wax, and 1% conditioner, and subjected to 24-hour and 5-day dissolution tests in 100° F. water. One product also contained 1.0% by weight of coal tar (microbicide), but this would not affect the rate of dissolution in water significantly.

The 24-hour dissolution rates ranged from 3.5 to 42% and indicated that the proportion of defective coatings increased with decrease in particle size. The differential dissolution rates were low (0.8 to 1.1%) in all cases.

The unscreened prills with 16% by weight of sulfur (20% total coating weight) are considered to have satisfactory slow-release properties, since the differential dissolution rate was about 1% per day or less. As stated earlier, the 24-hour dissolution rate of about 15% is not considered to be a serious disadvantage. The 24-hour dissolution rate obtained with –6- +12-mesh TVA experimental pan-granulated urea (Table IV) coated with 15% sulfur was lower (0.8%) than that obtained with the –6- +10-mesh fraction of commercial prills. The reason for the lower rate was that 70% of the pan-granulated material was –6- +8-mesh whereas the prills were 98% –8- +10-mesh.

AGRONOMIC EVALUATION

Figure 4 relates the dissolution rates of sulfur-coated urea granules as measured in the laboratory to cumulative yield curves of a 17-week greenhouse test with Bermuda grass. Two levels of sulfur were used: 9 and 15%. The differential dissolution rates of these products in water at 100° F. were 1.0 and 0.3% per day, respectively. Both contained 3% wax sealant, 0.5% microbicide (coal tar), and 1% conditioner. A test also was made with a 40:60 mix-

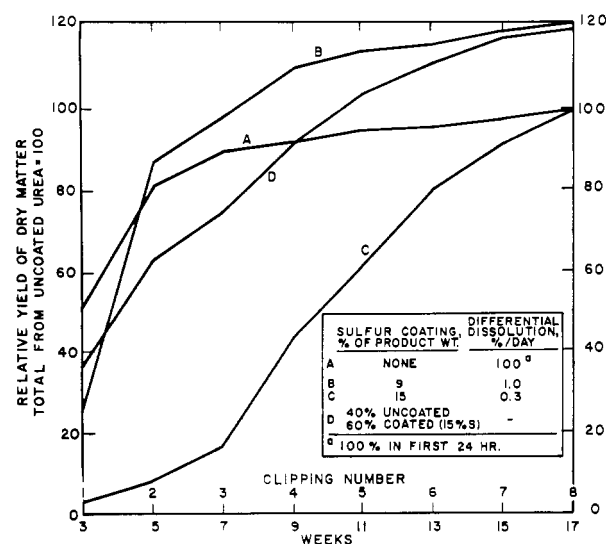


Figure 4. Cumulative yields of Bermuda grass from coated and uncoated urea

Table IV. Effect of Urea Prill Particle Size on Coating Effectiveness

Prill screen size, mesh	Dissolution Rate					Substrate Dissolution in Water at 100° F., %		Differential dissolution rate, %/day
	Sulfur	Coating, by Wt. % of Product				24 hr.	5 days	
		Wax	Coal tar	Conditioner	Total			
Commercial prills								
-6 + 10	14	3.0	0	1.0	18.3	4.1	7.1	0.8
-6 + 10	16	3.0	1.0	1.0	20.6	3.1	7.5	1.1
As received	16	3.0	0	1.0	19.7	15.8	19.2	0.9
-10	14	4.0	0	1.0	19.1	41.7	45.4	0.9
Experimental TVA pan-granulated urea								
-6 + 12	15	3.0	0.5	1.0	19.6	0.8	1.7	0.2
	Screen Analysis							
	Screen Size Distribution, % Tyler Mesh							
Size	+6	-6 +8	-8 +10	-10 +12	-12 +14	-14 +16	-16 +20	-20
Commercial prills								
-6 + 10	0	2	98
As received	0	1	57	19	18	3	1	1
-10	0	0	0	45	44	6	2	3
Experimental TVA pan-granulated urea								
-6 + 12	0	70	29	1	0	0	0	0

ture of uncoated urea and urea with a 15% sulfur coating. The fertilizers were applied by mixing with the soil, and clippings were made every 2 weeks after the first 3-week period.

The data show that, with uncoated urea, 50% of the total 17-week yield was obtained in the first clipping (3 weeks) and 80% in the first two clippings (5 weeks).

The initial yield with the product having a differential dissolution rate of 1.0% per day was 50% of that with uncoated urea but the rate of increase was considerably greater. The cumulative yield was equal to that with uncoated urea at the second clipping and exceeded it by 20% at the end of the test (17 weeks).

Total yield from tests with coated urea that had a dissolution rate of 0.3% per day (15% S) was equal to that with uncoated urea in 17 weeks and indications were that the yield would have exceeded that from uncoated urea if the test period had been extended. In addition, the rate of growth was much more uniform. Uniform growth of forage crops may be an advantage in farm management.

The data also indicate the feasibility of controlling response curves by mixing uncoated and coated fertilizers. With the mixture of uncoated and coated (15% S) urea, the initial yield was only slightly lower than that with uncoated urea, but the slope of the curve was more uniform and paralleled that of the coated urea used in the mixture. With this mixture also, the 17-week yield was about 20% more than with uncoated urea.

Other greenhouse tests showed that coating urea with sulfur also reduced the apparent loss of ammonia to the atmosphere in surface application (Terman and Hunt, 1964) and minimized damage to seedlings when the fertilizer was placed close to the seed (TVA, 1965).

In limited field tests with forage crops, such as fescue and hybrid summer grasses, yields with sulfur-coated urea were

Table V. Estimated Cost of Coating Urea

[70,000 tons of product (37% N)/yr.]

Raw Materials	Lb./Ton	\$/Ton of Product	\$/Unit N
Sulfur (\$39/ton)	320	6.24	0.17
Wax sealant (\$100/ton)	60	3.00	0.08
Microbicide (\$80/ton)	10	0.40	0.01
Conditioner	20	... ^a	... ^a
Subtotal		9.64	0.26
Operating cost		2.00	0.05
Return on investment and working capital ^b (20% pretax)		0.74	0.02
Total		12.38	0.33

^a No added cost, since uncoated urea would be conditioned.

^b Plant investment \$100,000; working capital, \$160,000.

at least equal to, and in some tests were, as much as 10% more than those obtained with uncoated urea. Rate of growth generally was more uniform with the sulfur-coated product. Products tested had differential dissolution rates ranging from 0.3 to 3% per day.

TVA plans more extensive agronomic testing to evaluate further the potential of sulfur-coated fertilizers. One possibility is that this type of product may reduce losses sufficiently to make heavy single applications feasible as a substitute for multiple applications.

Promising results also have been observed in fertilization of seedling trees (TVA, 1968) and horticultural plants (Furuta *et al.*, 1967).

ECONOMICS

An estimate of the cost of coating urea is shown in Table V. Hot urea prills from a prilling tower are fed to the coating operation. It is assumed that 70,000 tons per year (200 tons per day) of product containing 37% nitrogen is produced for the farm market. The product contains 20% by weight of coating (including 1% conditioner). Cost of sulfur is based on present list price; costs of the sealant and microbicide were quoted by manufacturers of these materials. Cost of conditioner is not included, since the difference in cost of conditioning this product and fertilizer-grade urea would be small.

The cost of coating, including a 20% return on investment and working capital, is estimated to be about \$0.33 per unit of nitrogen. This is about 20% of the estimated

market price of uncoated urea—\$1.69 per unit (\$76 per ton bulk, f.o.b. plant).

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