

Nitrogen Fertilizer Additives

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Nitrogen fertilizer is by far the most extensively applied fertilizer for agronomic crop production in Arkansas. Urea [$\text{CO}(\text{NH}_2)_2$] is the most commonly used nitrogen fertilizer because of its low price and high nitrogen analysis relative to other granular nitrogen fertilizers. However, the urea-nitrogen is subject to volatilization as ammonia (NH_3) gas if not properly incorporated shortly after application. Once incorporated into the soil, urea and other ammonium-forming (NH_4^+) nitrogen fertilizers will eventually be converted to nitrate (NO_3^-), which is prone to leaching and/or denitrification. (For more information on the nitrogen cycle, refer to Extension fact sheet *FSA2148, Nitrogen and Phosphorus Cycle in Soils*.) The purpose of this fact sheet is to present current research on the potential benefits associated with the use of urease and nitrification inhibitors under Arkansas conditions.

Nitrogen fertilizer additives are substances added to a water-soluble or readily-available fertilizer that extend the time a particular form of nitrogen remains in the soil. Nitrogen fertilizer additives are added to nitrogen fertilizer by the manufacturer when the nitrogen fertilizer is made or by local fertilizer dealers shortly before the fertilizer is applied to the field. In most cases, these products temporarily inhibit or delay but do not permanently prevent the specific process of the nitrogen cycle.

The emphasis on responsible and efficient nutrient management is now greater than ever. The development of conservation programs that offer partial payment for farmers

to implement efficient nutrient management practices and the rising cost of fertilizers make products that stabilize fertilizer nutrients a lucrative market. Reducing soil and fertilizer nitrogen movement from agricultural fields into the surrounding landscape has both environmental and agronomic benefits and has led to the marketing of a number of products that claim to “stabilize” nitrogen. Many of these products are unproven in laboratory and field research conducted by unbiased and knowledgeable researchers. Oftentimes, these products are highly marketed with well-designed advertisements, informational brochures and web sites, but lack specific information regarding their mechanisms or modes of action that explain how they “stabilize” nitrogen (or other nutrients). Although some products provide a mode of action with wording that includes scientific terms, the wording is usually vague and lacks scientific support.

The use of legitimate nitrogen fertilizer additives does not guarantee that maximum crop yield can be produced with lower nitrogen rates. While use of lower nitrogen rates to produce maximum yield is a possible outcome, the expected benefits of additives occur when conditions exist for significant loss of conventional nitrogen fertilizers via ammonia volatilization and/or leaching, runoff and denitrification of nitrate. Unfortunately, the frequency and magnitude of nitrogen losses cannot always be predicted since they are often the result of weather-related events.

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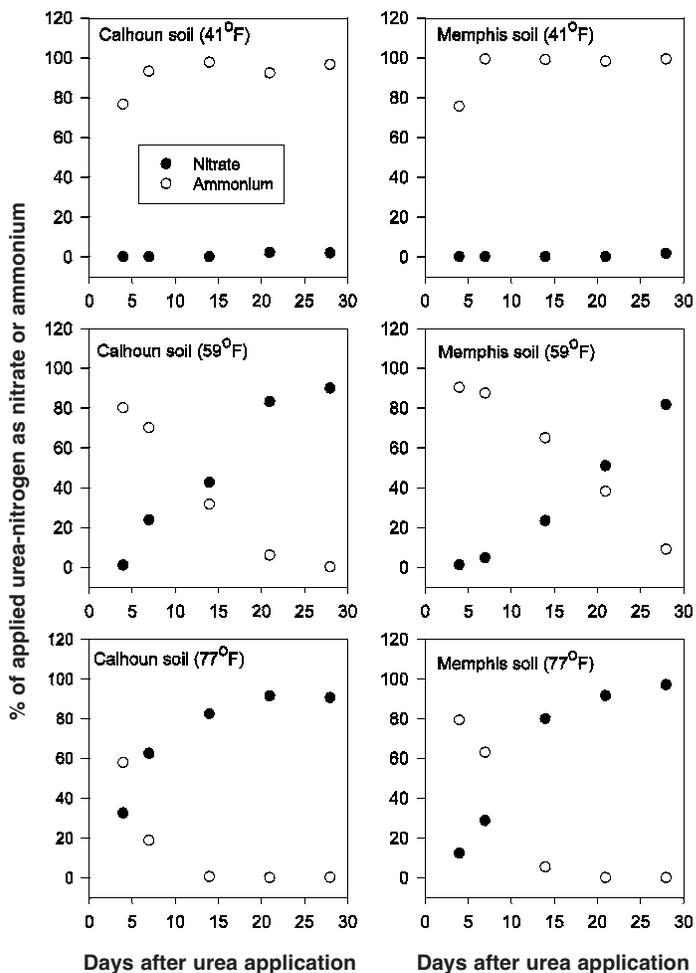
Nitrification Inhibition

Nitrification is the two-step microbial process that converts ammonium (NH_4^+) into nitrite (NO_2^-) and eventually into nitrate (NO_3^-). The first step of the process is performed by specific ammonia-oxidizing bacteria (*Nitrosomonas* spp. being the most common one) and the second step by nitrite-oxidizing bacteria (*Nitrobacter* spp.). Ammonium and nitrate are both plant-available nitrogen forms, but ammonium is the more stable nitrogen form in the soil. Ammonium is a cation and can be retained by the soil's cation exchange properties, making it far less mobile than nitrate. Nitrate is susceptible to loss by runoff, leaching in permeable soils (sands and sandy loams) and denitrification [reduction to nitrous oxide (N_2O) and dinitrogen (N_2) gasses] in poorly drained soils. Applying ammonium or an ammonium-forming nitrogen fertilizer is desirable since ammonium is less susceptible to denitrification and leaching losses. Eventually, however, the nitrification process converts ammonium supplied from fertilizer or mineralized from organic matter, manures or biosolids into nitrate.

The requirements for nitrification are ammonium, a population of nitrifying organisms, oxygen and a suitable environment (e.g., pH, temperature and moisture). The nitrification process is affected by soil chemical and physical properties associated with different soil types. In general, nitrification increases as soil temperature, moisture and pH increase. Near optimal soil conditions for nitrification include a temperature range of 77°-95°F, soil moisture near field capacity and pH near 8.0. The nitrification process is very slow or negligible at soil temperatures <40°F, and soil bacteria become inactive when the soil becomes very dry. The nitrification process ceases under anaerobic conditions (saturated), such as when the permanent flood is established on a rice field.

Laboratory incubation experiments using Memphis (6.4 pH) and Calhoun (7.5 pH) silt loams show the effect that three constant temperatures had on the nitrification rate of urea fertilizer when soil moisture was near optimal (20% moisture, -85kPa; Fig. 1). In both soils, soil microbial activity was negligible at the lowest temperature, and all of the nitrogen added as urea remained as ammonium for 28 days. For the Memphis soil, nearly all of the added urea-nitrogen had been converted from ammonium to nitrate by 14 days at 77°F and 28 days at 59°F. Nitrification was slightly more rapid in the Calhoun soil with most of the added urea N converted from ammonium to nitrate by 14 days at 77°F and 21 days at 59°F. Average soil temperatures in Arkansas are warm enough for nitrification from March through November of most years (Table 1).

FIGURE 1. The effect of three temperatures (laboratory incubation) and time on the proportions of soil nitrate and ammonium (nitrification) for 28 days following urea fertilizer application on Calhoun (pH 7.5) and Memphis (pH 6.4) silt loam soils.



Nitrification inhibitors are chemicals that temporarily delay or slow down nitrification by affecting the activity of the *Nitrosomonas* spp. bacteria. Nitrification inhibitors have been used mostly in the Midwest for fall application of anhydrous ammonia. Generally, nitrification inhibitors have not been used extensively in the Mid-South and southern USA because they have not been highly effective. By “highly effective” we simply mean that the length of time these products delay nitrification has not offered a significant nitrogen management advantage across a wide array of soils. Preliminary results from recent laboratory experiments have shown that dicyandiamide (DCD) and nitrapyrin (Dow AgroSciences, LLC, Indianapolis, IN) have effectively delayed nitrification on some soils but had little or no effect on the nitrification rate of other soils (Table 2). For example, the DCD in Super U (Koch Fertilizer, LLC, Wichita, KS) had little or no effect on the amount of ammonium remaining after 10 days for the Calhoun soil

TABLE 1. Average monthly soil temperatures (4-inch depth of bare soil) during 2009 and 2010 for three sites in eastern Arkansas.

Site	Year	Month											
		Jan	Feb	Mar	April	May	June	July	Aug	Sept	Oct	Nov	Dec
Rohwer (Gallion sl)	2009	40.8	43.2	49.5	56.1	64.7	73.8	75.8	75.8	71.8	56.6	49.4	42.0
	2010	37.8	37.5	42.5	61.7	72.2	83.6	82.3	md†	md†	md†	52.1	42.0
Marianna (Calloway sl)	2009	42.0	46.6	53.1	51.7	72.0	83.5	83.6	84.9	79.5	63.3	57.1	43.9
	2010	40.8	40.1	51.5	66.2	76.1	87.7	88.8	90.8	82.2	70.4	56.1	42.9
Keiser (Sharkey cl)	2009	38.3	44.1	50.1	58.4	69.7	78.3	81.6	81.0	75.9	60.6	53.8	41.3
	2010	38.3	36.2	49.1	63.2	72.5	85.5	87.7	90.7	80.1	67.5	52.5	40.1

†Missing data.

TABLE 2. The net percentage of urea or Super U fertilizer remaining as ammonium after 10 and 20 days in three silt loam soils incubated at 77°F and 25% gravimetric soil moisture (Golden et al., 2009).

N Fertilizer	Time days	Soil†		
		Calhoun series	DeWitt series	Henry series
		% of added fertilizer present as ammonium		
Urea	10	<1	36	11
	20	0	4	<1
Super U	10	8	77	54
	20	0	65	49

†Soil properties: 1.0% total C, 0.10% total N and soil pH values of 6.2 (DeWitt), 7.3 (Henry) and 7.6 Calhoun.

but delayed nitrification in the DeWitt and Henry soils. Additional research is needed to identify the soil characteristics that would allow us to accurately predict whether a nitrification inhibitor would be of significant benefit in reducing nitrate nitrogen losses.

Nitrogen management strategies for corn, cotton, rice and wheat in the Mid-South usually involve split applications with the majority of the nitrogen fertilizer side-dressed near the onset of rapid crop growth. These nitrogen management strategies minimize the benefits of a legitimate nitrification inhibitor. However, there is still interest and a place for nitrification inhibitors in our nitrogen management systems, especially on sandy-textured soils and for nitrogen that is applied preplant. The ability to apply a greater proportion of nitrogen fertilizer preplant or weeks in advance of planting would be advantageous for many growers. University researchers will continue to evaluate potential nitrification inhibitors in laboratory and field experiments and incorporate legitimate nitrification inhibitors into nitrogen management recommendations when appropriate. The legitimacy of a product's claim as a nitrification inhibitor can be quickly and efficiently examined in the laboratory before it is field tested.

Several products (active ingredients) are currently recognized as legitimate and documented nitrification inhibitors; however, our discussion here will concern the two nitrification inhibitors being marketed in Arkansas and surrounding states. The active ingredients in these products have proven to be effective at inhibiting nitrification in industry and university research, which has been peer reviewed and published in refereed journals. The process (e.g., mode of action) by which a chemical inhibits nitrification can differ. For example, the inhibitor nitrapyrin is a bactericide and has been registered with the EPA as a pesticide since 1974. Dicyandiamide (DCD), on the other hand, is not a bactericide and is not required to be registered with the EPA. The mode of action of DCD is by inhibition of *ammonium monooxygenase*, an enzyme required by ammonia-oxidizing bacteria to metabolize ammonium into nitrite.

Nitrapyrin is the active ingredient in N-Serve and Instinct. Instinct is the newest formulation of nitrapyrin and, compared to N-Serve, has the advantage of being encapsulated. Encapsulation allows Instinct to be impregnated onto the surface of granular (ammonium) fertilizers or be spray-applied to the field without immediate volatile loss of the active ingredient. Dicyandiamide is the active ingredient in Agrotain Plus (Koch Fertilizer, LLC, Wichita, KS), Super U and the product sold as Guardian (Conklin Company, Inc., Shakopee, MN) and is applied directly onto or incorporated into the fertilizer granule. A number of other products that have shown to be effective nitrification inhibitors have been registered previously or are available in other countries. The publication entitled "Nitrification Inhibitors for Corn Production" (<http://www.extension.iastate.edu/publications/NCH55.pdf>) provides a list of product trade and chemical names and gives an excellent review on the use of nitrification inhibitors.

FIGURE 2. Ammonia volatilization losses of urea, NBPT-treated urea, ammonium sulfate and a urea/ammonium sulfate blend on a Calloway silt loam. Flood was applied on day 10. (Norman et al., 2009)

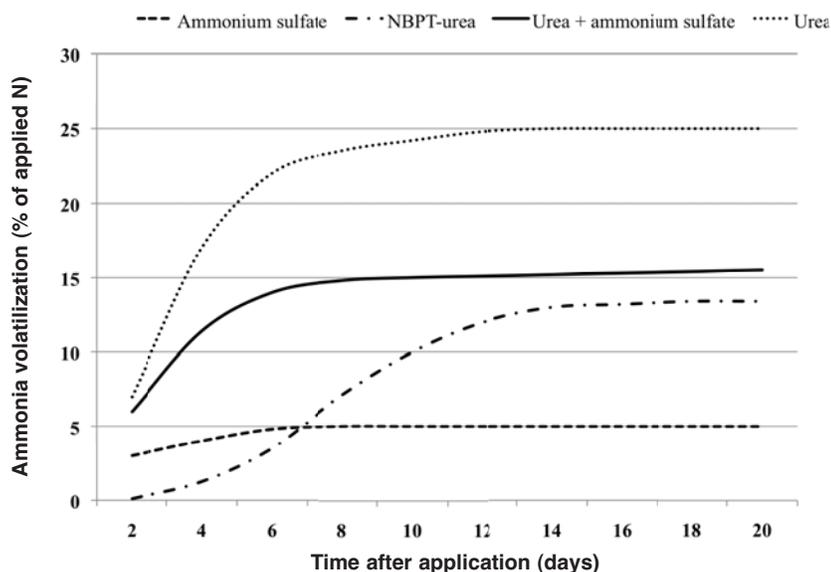


FIGURE 3. Ammonia volatilization losses when urea and NBPT-treated urea were applied to a dry or muddy soil 5 days prior to flooding. (Norman et al., 2006)

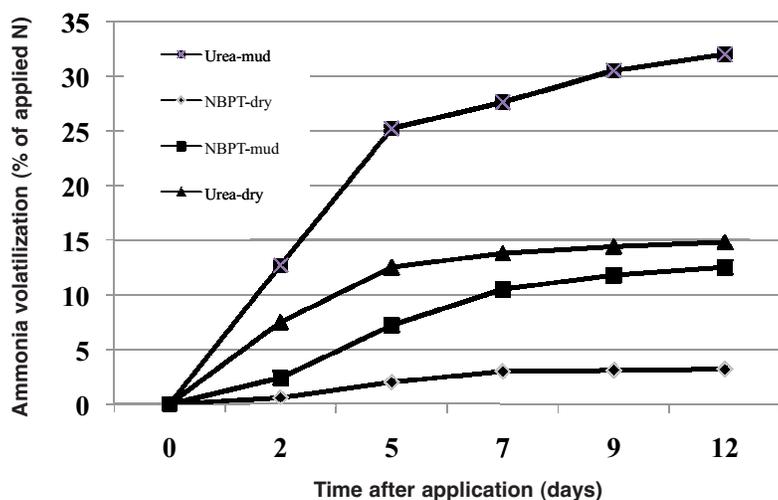
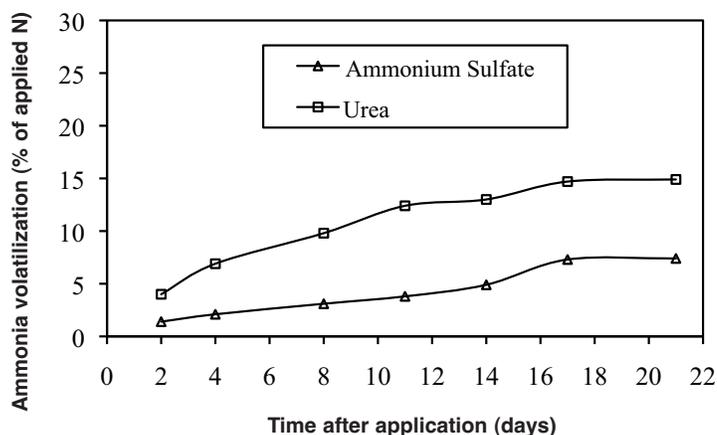


FIGURE 4. Ammonia volatilization loss of urea and ammonium sulfate when applied to a Perry clay. (Griggs et al., 2007).



Ammonia Volatilization Inhibition

Ammonia (NH_3) volatilization is a surface loss mechanism that occurs when an ammonium or ammonium-forming fertilizer is surface applied and not incorporated immediately. All ammonium fertilizers can to some degree be lost via ammonia volatilization, but since the first reaction in the hydrolysis of urea is alkaline forming, urea is more prone to loss by this mechanism than ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$, which is an acid-forming nitrogen fertilizer. Urea nitrogen when applied to a soil is hydrolyzed by the urease enzyme (urea amidohydrolase) and converted first to ammonium carbonate $[(\text{NH}_4)_2\text{CO}_3]$ and then to ammonia gas. Urease is ubiquitous in the environment and can be found in soils, manures, on plants and plant residues. The urease enzyme is believed to be released to the environment from living and disintegrating microbial cells.

Losses of urea as ammonia gas increase as wind speed, soil moisture, humidity, soil pH and temperature increase. Under warm (spring and summer) conditions, urea needs to be incorporated with tillage, rainfall or irrigation immediately and at least within 2 days following application to significantly reduce gaseous ammonia loss. Ammonia volatilization loss of surface-applied urea to a dry silt loam soil can typically reach 20% to 30% in 5 days when the temperature exceeds 75°-80°F (Fig. 2). The speed of the urea-urease reaction decreases as temperature declines, and thus there should be less ammonia volatilization loss of urea when applied in the winter to wheat compared to in the spring or summer to corn, cotton or rice. Ammonia volatilization loss of urea is much more rapid and extensive when urea is applied to a muddy silt loam soil compared to a dry silt loam soil (Fig. 3). Also, the ammonia loss potential tends to be lower

in clayey soils because of their higher cation exchange capacity compared to silt or sandy loam soils (Fig. 4).

One approach to decreasing ammonia volatilization loss of urea when immediate incorporation is not possible is to amend urea with a chemical compound that inhibits or slows urease activity, or conversion of urea to ammonia gas. A urease inhibitor allows the urea prill time to dissolve and move into the soil before hydrolysis to ammonia occurs or allows time to be incorporated either mechanically or by water (e.g., irrigation or rain). Enabling the urea to hydrolyze to ammonia (NH₃) after it has been dissolved or moved into the soil allows the ammonia produced from the urea to acquire a hydrogen (H⁺) atom from the soil and become ammonium (NH₄⁺), which is a salt that is retained by the soil's cation exchange properties. Only a few chemical compounds have been shown to effectively inhibit urease activity. While all the compounds listed in Table 3 can minimize ammonia volatilization of urea, the compound N-(n-butyl) thiophosphoric triamide (NBPT) is considered the most effective and the only one that has seen widespread implementation on a commercial scale. The urease inhibitor NBPT is the active ingredient in Agrotain (Koch Agronomic Services, LLC). The patent on NBPT has expired (circa 2002) allowing other companies to develop and market their own formulations that include NBPT such as Arborite (Weyerhaeuser and Gavilon Fertilizer, LLC)

A good number of trials have been conducted in Arkansas over the last 10 years that have consistently shown the effectiveness of NBPT in reducing ammonia volatilization losses from surface-applied urea. Table 4 shows rice yield as affected by flooding 1, 5 and 10 days after urea and NBPT-treated urea were applied to the dry soil surface of a Calloway silt loam. Results from this study underscore the importance of timely soil incorporation of the urea fertilizer and utility of NBPT when timely incorporation is not possible. When flooding was conducted the day after, N fertilizer application urea produced a grain yield similar to NBPT-treated urea. However, rice grain yield significantly decreased when the flood was delayed until 5 days after application when urea was the N source, but not when NBPT-treated urea was the N source. Rice grain yield for all of the N fertilizer sources significantly decreased when the flood was further delayed until 10 days compared to 1 day, but more so for urea compared to NBPT-treated urea. Research in Arkansas shows that under warm/summer conditions, ammonia loss from surface-applied urea occurs most rapidly the first 5 days after application to a silt loam (Fig. 2) and the first 10 days when applied to a clay soil (Fig. 4). The use of NBPT can help minimize urea loss via ammonia volatilization when applied to a muddy soil;

TABLE 3. Documented Urease Inhibitors†

Abbreviation	Active Ingredient
NBPT	N-(n-butyl) thiophosphoric triamide
PPD	phenylphosphorodiamidate
TPT	thiophosphoryl triamide
ATS	ammonium thiosulfate
TU	thiourea
MU	methyl urea

†Research has shown NBPT to be the most effective urease inhibitor.

TABLE 4. Rice grain yield when urea, NBPT-treated urea, ammonium sulfate (AS) and a urea/AS blend were applied 1, 5 and 10 days prior to flooding. (Norman et al., 2009)

N Source	N rate (lb N/A)	Application Time (days)		
		1	5	10
		Bu/acre		
Urea	120	187	160	154
Urea + NBPT		188	182	175
AS		181	178	171
Urea/AS blend		179	166	161
LSD (0.05)		8.6		

however, every effort should be made to apply urea to a dry soil even when NBPT is used. A typical rate of NBPT treatment on urea prills is 4 qt ~20% a.i. NBPT per ton of urea or 3 qt ~25% a.i. NBPT per ton of urea.

Farmers have adopted the use of NBPT as a management tool for surface-applied urea, particularly in rice fields where establishing a flood in 2 days or less is difficult or in upland crops where surface-applied urea may remain on top of the beds. The high adoption rate of products containing NBPT has stimulated the marketing of numerous products with claims of similar benefits (i.e., reducing ammonia volatilization). Before the University of Arkansas Division of Agriculture recommends a product that claims to have inhibitory effects on the enzyme urease or simply “ammonia volatilization loss of urea,” the products must be subjected to a laboratory test, which measures ammonia volatilization from urea amended with the commercial product of question compared to that of urea and NBPT-treated urea. At the time of the writing of this fact sheet only, the NBPT-containing products Agrotain and Arborite have been tested and shown to effectively inhibit ammonia volatilization of urea.

An alternative to NBPT-treated urea for minimizing ammonia volatilization losses is the use of ammonium sulfate. Ammonium sulfate is much less prone to ammonia volatilization loss compared to urea due

to its slightly acidic properties (Figs. 2 and 3). Ammonium sulfate can result in grain yields similar to NBPT-treated urea when ammonia volatilization loss is a concern (Table 4). Also, when sulfur is required in addition to nitrogen, ammonium sulfate is the logical fertilizer choice. Shortcomings of ammonium sulfate are that it typically costs considerably more than urea, on a N weight basis, and the lower N analysis of ammonium sulfate compared to urea could increase application expenses. Ammonium sulfate is typically not used solely as the pre-flood N source but is blended with urea to offset some of the costs and still possibly gain some of the beneficial effects of the ammonium sulfate. Although blending ammonium sulfate with urea can lower ammonia volatilization loss (Fig. 2), the decrease in loss from the blend may not be enough to result in significantly higher grain yields compared to urea nor grain yields similar to ammonium sulfate or NBPT-treated urea (Table 4).

Summary

- Nitrification inhibitors delay the conversion of ammonium to nitrate by temporarily inhibiting the activity of *Nitrosomonas* bacteria and have the potential to reduce nitrate, leaching and denitrification losses. However, the longevity and effectiveness of nitrification inhibitors in the Mid-South are limited due to the warmer climate (compared with the Midwest).
- Research of nitrification inhibitors will continue in the hope of understanding the soils, crops and situations where and when they can be of benefit in the Mid-South. Split applications of nitrogen fertilizer are recommended until we understand when a nitrification inhibitor is a viable option.
- Urease inhibitors work on the enzyme urease, which is responsible for the conversion of urea to ammonium. During this process, nitrogen can be lost by volatilization of ammonia if the urea is not properly incorporated soon after application. Ammonium sulfate is less prone to ammonia volatilization loss compared to urea and is an alternative to NBPT-treated urea.
- The only documented urease inhibitors currently being marketed contain NBPT, the active ingredient in Agrotain and Arborite. NBPT-treated urea should be used if >2 days are required for incorporation on a silt loam soil and when >7 days on a clay soil.
- Any other purported N stabilization products that claim inhibition of ammonia volatilization of urea cannot be recommended for use because we have tested them and they do not inhibit this process, we have not tested them or we are currently testing them.

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