

# UREA-FORMALDEHYDE FERTILIZERS

## Condensation Products of Urea and Formaldehyde As Fertilizer with Controlled Nitrogen Availability

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Novel and useful nitrogen fertilizers with controlled availability for plant growth can be made by the acid-catalyzed condensation of urea with formaldehyde. These products, which contain about 38% nitrogen, can be prepared with three quarters of the nitrogen in the slowly available form, generally referred to as water-insoluble nitrogen. By controlling the reaction conditions, a product can be obtained that exhibits 55 to 60% nitrification of the water-insoluble nitrogen in 6 months in an average soil. The rate at which these products nitrify is affected by the type, pH, and other plant nutrient content of the soil. Of these variables, soil type has the greatest effect. These compounds are exceptionally safe nitrogen fertilizers. With them single applications may be made at higher nitrogen levels than are possible with the soluble sources; a full year's nitrogen supply may be applied at one time. They are ideally suited for turf and other long-season crops, greenhouse plants, and crops grown in irrigated or high-rainfall areas. A simple reliable method has been developed for rapid evaluation of the agronomic availability of the water-insoluble nitrogen in urea-formaldehyde products.

NITROGEN FERTILIZER WITH CONTROLLED AVAILABILITY has been a goal of agriculturists for many years. The natural organic materials have been used as sources of slowly available nitrogen, but these have certain disadvantages; most of their available nitrogen is converted to nitrates in a relatively short period, and much of their total nitrogen is unavailable, according to Rubins and Bear (14). In 1946, Yee and Love (15) of the U. S. Department of Agriculture, Beltsville, Md., showed that water-insoluble nitrogen fertilizer with exceptional controlled availability for plant growth could be made by reaction of urea with formaldehyde.

The use of urea-formaldehyde (U-F) reaction products as slowly available nitrogen fertilizers is not entirely a new development. Since 1939, synthetic slowly available or water-insoluble nitrogen has been made in mixed fertilizers by ammoniation with Uramon (Du Pont) ammonia liquor (7). The small amount of formaldehyde in this liquor reacts with some of the urea to form water-insoluble nitrogen during ammoniation and subsequent storage of the fertilizer. The value of this insoluble urea-formaldehyde nitrogen as nitrogen fertilizer was demonstrated by McCool (9). However, only relatively small amounts of insoluble nitrogen can be made with this method in mixed fertilizer—for example, about 1% in a 10-10-10 grade. The work by Yee and Love was important, however, because it demonstrated that water-insoluble urea-

formaldehyde nitrogen fertilizer could be made with any desired rate of nitrogen availability.

In 1948, Clark, Yee, and Love (4) presented additional information on urea-formaldehyde fertilizer compounds and proposed the generic name "urea-form" for these products. Recently patents for the production of urea-formaldehyde fertilizer compounds were granted to Rohner and Wood (13), Patry, Dhers, and Paul (12), and Kralovec and Huffman (8).

### Urea-Formaldehyde Fertilizer Compounds

Urea-formaldehyde fertilizer compounds are made by the acid-catalyzed reaction of urea with formaldehyde. They differ from the highly insoluble urea-formaldehyde resins of the plastics field in that a urea-formaldehyde mole ratio of greater than 1 is employed. Depending upon the reaction conditions, a range of products is formed, varying

from those that nitrify in soil almost as rapidly as urea to those requiring 2 to 3 years. Clark, Yee, and Love (4) showed the important processing variables to be urea-formaldehyde mole ratio, pH, temperature, and time. Decreasing the urea-formaldehyde mole ratio, lowering the pH, raising the temperature, or lengthening the reaction time will give products that nitrify more slowly. These products are believed to be mixtures of straight-chain urea-formaldehyde polymers having two to more than six urea molecules per chain. They also contain small amounts of unreacted urea.

Some chemical and physical properties of a typical product are given in Table I. This is one of the many urea-formaldehyde fertilizer compounds that have been tested within the past few years as sources of slowly available nitrogen. It contains about 38% nitrogen, three quarters of which is in the slowly available form, generally referred to as water-insoluble nitrogen. The product exhibits 55 to 60% nitrification of water-insoluble nitrogen in about 6 months in an average soil. The slow availability of the nitrogen in this compound is shown graphically in Figure 1. The rapid nitrification during the first month is due to the readily soluble fraction, which consists of unreacted urea and urea-formaldehyde polymers of low molecular weight; about 25% of the nitrogen is in this form. The nitrification of the soluble urea-formaldehyde nitrogen is about as rapid as that of urea or ammonium sulfate.

Table I. Typical Urea-Formaldehyde Fertilizer Compound

Total nitrogen (TN), %	38.5
Insoluble nitrogen (IN), % <sup>a</sup>	29.0
IN/TN	75.0
Availability index (AI)	55-60
Free urea, %	6.0
Water, %	3.0

<sup>a</sup> Cold water (25° C.)-insoluble nitrogen by A.O.A.C. method.

## Availability Index Method

Nitrification studies are the generally accepted procedure for measuring the rate at which nitrogen becomes available to plants. However, they are time-consuming, requiring 6 to 12 weeks. There are two chemical methods given by the Association of Official Agricultural Chemists for determining the activity or quality of cold water-insoluble nitrogen (7): the neutral permanganate and alkaline permanganate methods. The values obtained by either method serve only to distinguish between the better and poorer sources of water-insoluble nitrogen. Rubins and Bear (14) have shown that the neutral permanganate method, the more widely used of the two, is not reliable for all types of urea-formaldehyde products. Clark, Yee, Love, and Boyd (5) demonstrated a correlation between water solubility and nitrification and suggested a technique for measuring availability based upon two consecutive water extractions of a 1-gram sample at 30° C. This procedure has the disadvantage of requiring 48 hours for the extractions.

The availability index method for the rapid estimation of the agronomic availability of the insoluble nitrogen in urea-formaldehyde fertilizer compounds was developed by the authors (10). This method is based upon the percentage of the cold water-insoluble nitrogen that dissolves in a hot aqueous phosphate buffer solution. Values obtained are an index of the agronomic availability of the cold water-insoluble nitrogen. The availability index (AI) approximates the amount of insoluble nitrogen that nitrifies in about 6 months in an average soil.

**Apparatus** A water bath with circular openings in the cover through which 400-ml. beakers can be suspended is required. The heat capacity of the bath should be such that the bath temperature of 99° to 100° C. is maintained.

**Reagents** Monopotassium phosphate ( $\text{KH}_2\text{PO}_4$ ), anhydrous, reagent grade.

Dipotassium phosphate ( $\text{K}_2\text{HPO}_4$ ), anhydrous, reagent grade.

Phosphate buffer solution, 0.063M  $\text{PO}_4$ . Dissolve 14.3 grams of monopotassium phosphate and 91.0 grams of dipotassium phosphate in 1 liter of water. Dilute 100 ml. of this solution to 1000 ml. with water. The pH of the diluted solution should be 7.5.

Hydrochloric acid solution, 0.5N.

Sodium hydroxide solution, 0.5N, standardized.

Methyl red indicator, 0.5%. Dissolve 1 gram of methyl red in 200 ml. of alcohol.

**Procedure** Preparation of Sample. Crush the polymer sample to pass 20-mesh Tyler standard sieve, avoiding fine grinding.

**Determination of Cold Water-Insoluble Nitrogen (1).** Weigh rapidly and accurately a 1.0 to 1.4-gram sample, place in a 50-ml. beaker, add 20 ml. of water at  $25^\circ \pm 2^\circ \text{C}$ ., and allow to stand 15 minutes with occasional stirring. Transfer the supernatant liquid to 11-cm. Whatman No. 2 filter paper and wash the residue four or five times by decantation with water at  $25^\circ \text{C}$ . Finally transfer all residue to the filter and complete washing until the filtrate measures 250 ml. Determine per cent nitrogen in wet paper and residue by the usual Kjeldahl procedure (7).

**Determination of Hot Water-Insoluble Nitrogen (Buffer).** Weigh rapidly and accurately a sample containing 0.3 gram of cold water-insoluble nitrogen. The sample weight may vary  $\pm 5 \text{ mg}$ . but must be accurately weighed to  $\pm 0.0005 \text{ gram}$ . Place the sample in a 400-ml. beaker. Add 250 ml. of boiling diluted buffer solution from a borosilicate glass graduate, stir, cover the beaker with a watch glass, and immerse the beaker in a boiling water bath so that the liquid in the beaker is below the water line in the bath. This is done by hanging the beaker through a slightly larger concentric ring in the bath cover. Stir the solution gently for about 5 seconds after 10, 20, and 30 minutes, then remove at once from the bath and filter without delay through a Whatman No. 12 15-cm. folded filter. Wash the insoluble residue onto the filter with near boiling water and wash the filter four times from the top down. Total wash water will be about 75 to 100 ml. Determine per cent nitrogen in the wet

paper and residue by the usual Kjeldahl digestion and distillation, using an 800-ml. flask (7).

**Calculation of Availability Index of Cold Water-Insoluble Nitrogen.**

$$\frac{(\% \text{ IN}_{25} - \% \text{ HWIN}) \times 100}{\% \text{ IN}_{25}} = \text{AI}$$

where  $\text{IN}_{25}$  is cold water-insoluble nitrogen and HWIN is hot buffer-insoluble nitrogen.

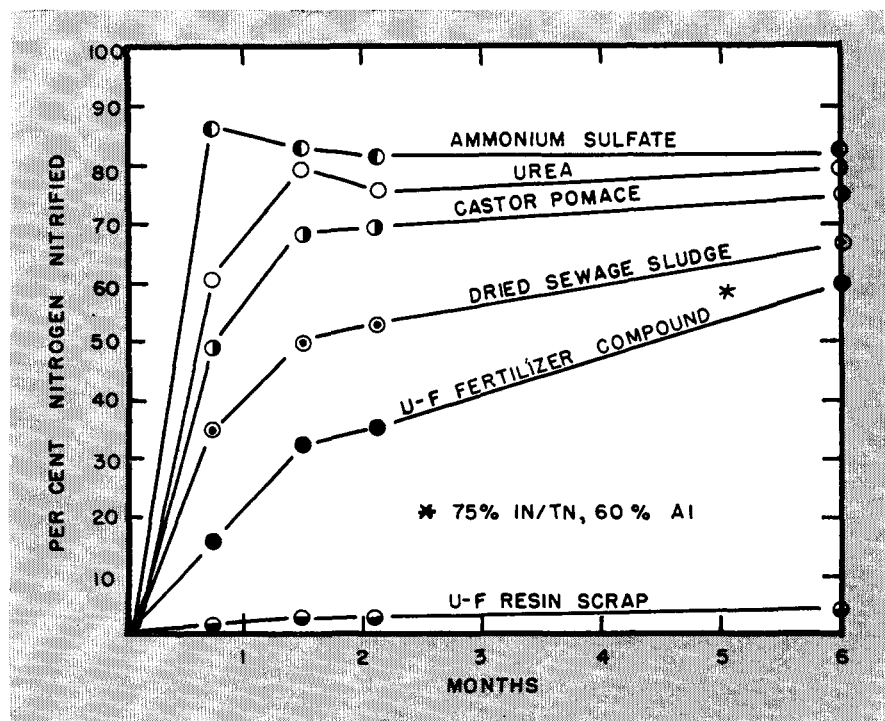
That the availability index can be used for predicting the agronomic availability of the cold water-insoluble nitrogen in urea-formaldehyde polymers is shown in Figure 2. The more rapidly the nitrogen nitrifies, the higher the availability index becomes. The availability index for urea-formaldehyde resin scrap was found to be between 2 and 10%.

## Nitrification of Urea-Formaldehyde Fertilizer Compounds

Usually the nitrogen in a nitrogenous material requires conversion to nitrates by the soil microorganisms in order to be useful for plant growth. During this conversion to nitrates, several transformation products are formed, one of which is ammonia. The agronomic availability rate for urea-formaldehyde nitrogen, therefore, is directly proportional to the rate at which this nitrogen is converted to nitrates by the soil microorganisms.

Fuller and Clark (6) found that soil microorganisms are responsible for the complete conversion of urea-formaldehyde nitrogen to nitrates. In sterilized

Figure 1. Nitrification rates of nitrogenous fertilizers



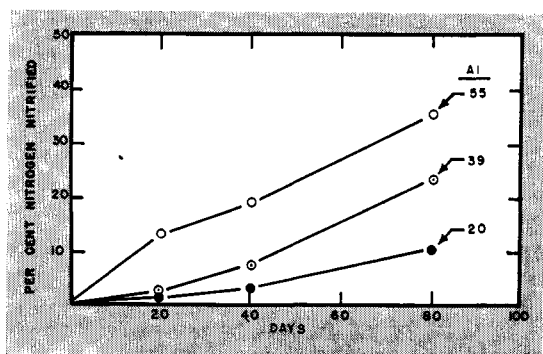


Figure 2. Nitrification rates compared with availability indexes for water-insoluble fractions in urea-formaldehyde polymers

soil very little ammonia and no nitrate is formed. They concluded that strict chemical hydrolysis assists only to a minor extent in the decomposition of urea-formaldehyde fertilizer compounds to ammonia and that the hydrolytic enzymes are necessary for the liberation of the ammonia. At no time did they detect formaldehyde in water extracts of soil treated with urea-formaldehyde fertilizer compounds. Apparently, either the formaldehyde is not liberated as such during the enzymatic hydrolysis of urea-formaldehyde fertilizer compounds or the microorganisms are able to utilize the formaldehyde as fast as it is liberated. On the other hand, if formaldehyde were liberated, then high concentrations of the urea-formaldehyde fertilizer compounds would be inhibitory to the microorganisms; this is not the case, because even at applications of 1%, which is well beyond practical field use, these preparations are stimulating. The carbon of the urea-formaldehyde fertilizer compounds, apparently, is as available as that of soil organic matter for microbial activity.

In using nitrification experiments for comparing the agronomic availability of urea-formaldehyde preparations and checking availability index measurements, an effort was made to hold all possible variables constant. Soil from the U. S. Department of Agriculture Plant Industry Station, Beltsville, Md., was used throughout most of this investigation. Other soils were tested, but this was used for the routine evaluation work. This soil contained relatively little nitrogen and had good nitrification activity. Sufficient calcium carbonate was added to maintain a relatively constant pH throughout the experiment. A water concentration optimum for nitrification was used and maintained. When the microbiological activity was low, as was experienced with air-dried soil stored for some time, the soil was inoculated at the start of the test with a water suspension of a fresh field sample. Other plant nutrients such as phosphate

and potash were added as desired. The tests were conducted at 30° C., the optimum temperature for nitrification.

The following is essentially the procedure used throughout this investigation for testing nitrification.

An amount of urea-formaldehyde preparation equivalent to 20 mg. of nitrogen was added to 100 grams of test soil previously limed with calcium carbonate to give an initial pH of about 7. This was placed in a 500-ml. Erlenmeyer flask. Water equal to 50% of the total moisture-holding capacity of the soil was then added. The flasks containing the treated soil were held at 30° C. Water was added at intervals to compensate for evaporation. After incubation periods of approximately 20, 40, and 80 days, or longer if desired, the soil was extracted and nitrate nitrogen determined colorimetrically by the phenoldisulfonic acid method (7). Duplicate or triplicate flasks were analyzed at these intervals. Urea or ammonium sulfate was included as a standard. A blank was also run without added nitrogen.

### Agronomic Factors Affecting Nitrification

An attempt was made to control the agronomic variables that affect nitrification when nitrification tests were used to compare urea-formaldehyde preparations. In the field, however, standard conditions do not prevail. The soils differ in type, pH, buffer capacity, microbiological activity, plant nutrient content, and climatic conditions such as temperature and rainfall. Furthermore, field plants gradually absorb the nitrates, an accumulation of which retards nitrification.

**Soil Type** The nitrification of urea-formaldehyde fertilizer compounds was tested in 17 soils, most of which were from the nitrogen-free plots at locations where field trials were

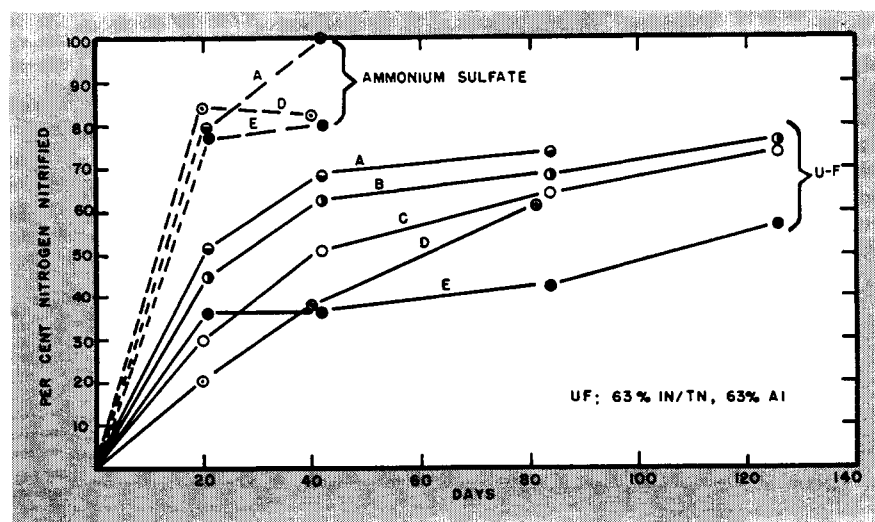
being conducted. The rate and extent of nitrification for a urea-formaldehyde fertilizer compound during the first 40 days varied by as much as 100% in these soils. Beyond this period there was a gradual approach to complete nitrification, which apparently was reached sooner in those soils in which the urea-formaldehyde fertilizer compound nitrified more rapidly at the beginning. The results obtained with some of these soils are shown graphically in Figure 3. These results were obtained early during the course of the investigation with a product having 63% IN/TN and a 63% availability index.

**Soil pH** The average pH for most mid-western and eastern soils on which turf is grown is about 6. Because most nitrification experiments were conducted at about pH 7, the effect of lower pH's upon the nitrification of urea-formaldehyde products was tested. In soil with an initial pH of 6, these products nitrified more rapidly than at pH 7 or 5. This effect is shown graphically in Figure 4. In these tests maintaining the lower pH's at constant level was very difficult. Without the added calcium carbonate to neutralize the nitrate formed, the pH's dropped after 21 days to about 4. Even so, the urea-formaldehyde product continued to nitrify more rapidly where the initial pH was 6. Under field conditions plant growth would lessen nitrate accumulation and acidity build-up; and, accordingly, the urea-formaldehyde product would probably nitrify faster than indicated by the test.

**Other Plant Nutrients** The effect of added phosphate and potash upon the nitrification of urea-formaldehyde nitrogen was determined because this nitrogen will be used with other plant nutrients. The urea-formal-

Figure 3. Nitrification of urea-formaldehyde fertilizer compound in different soils

- A. From State College, Pa.
- B. From Tifton, Ga.
- C. From Lake Alfred, Fla.
- D, E. From Beltsville, Md.



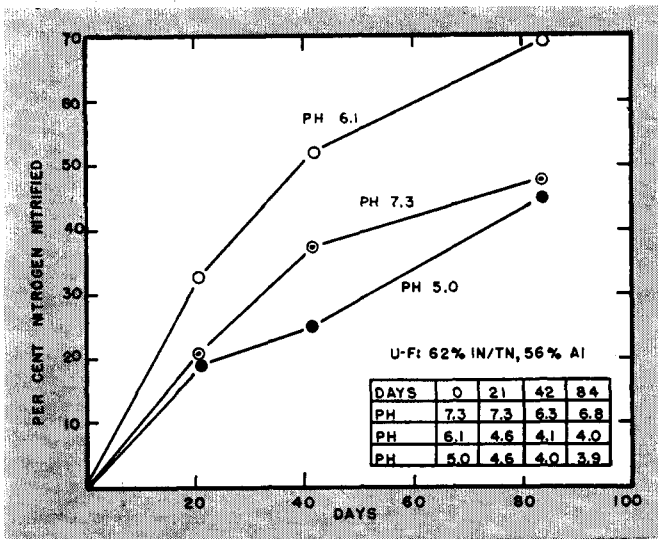


Figure 4. Effect of initial pH of soil nitrification of urea-formaldehyde fertilizer compound

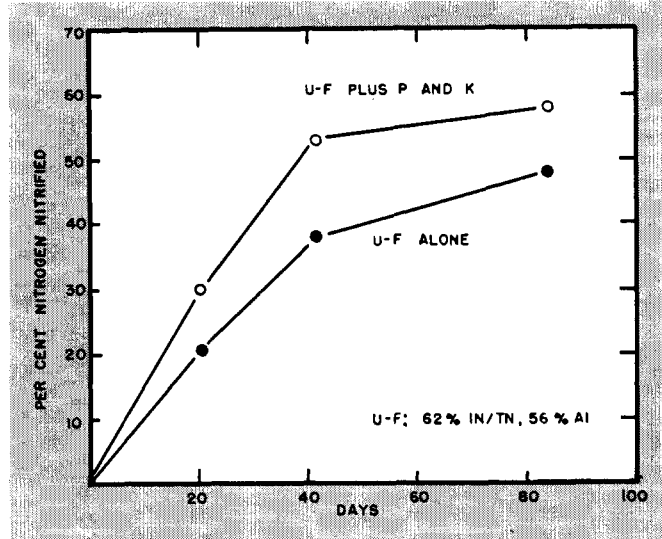


Figure 5. Nitrification of urea-formaldehyde fertilizer compound in presence of added phosphate and potash

dehyde fertilizer compounds were found to nitrify more rapidly in the presence of these major nutrients than when applied alone. This is shown in Figure 5. In the test illustrated, 266 p.p.m. of phosphate and 133 p.p.m. of potash were added to the soil along with 200 p.p.m. of nitrogen.

**Temperature and Moisture** The natural organic materials decompose almost as rapidly as urea when soil temperature and moisture content are relatively high. It has been assumed that urea-formaldehyde fertilizer compounds will nitrify more rapidly when the soil temperature and moisture content are relatively high. Tests to show the effect of these variables are being conducted and the results will be reported later.

#### Greenhouse and Field Trials

The ability of urea-formaldehyde fertilizer compounds to supply nitrogen at a uniform rate for plants throughout a growing season is being tested in greenhouse and field trials. Most of these trials have been and are being conducted with turf because the nitrification characteristics of these compounds make them well suited for this type of long-season crop. Others include greenhouse floral plants, ornamentals, tobacco, hay, and those crops such as corn, cotton, citrus, and pineapple which are grown in irrigated or heavy rainfall areas.

The first greenhouse and field tests with urea-formaldehyde fertilizer compounds on turf were conducted by the U. S. Department of Agriculture (2, 3) at Beltsville, Md., and by H. B. Musser *et al.* (17), Pennsylvania State University, at State College, Pa. Since 1951, extensive field demonstrations have been conducted by K. G. Clark of the U. S.

Department of Agriculture at Beltsville, Md., A. E. Cooper of the Pennsylvania State Extension Service at golf courses throughout Pennsylvania, F. V. Grau of the U. S. Golf Association at golf courses throughout the Baltimore-Washington area, and H. B. Musser at State College, Pa., and golf courses in the Philadelphia area.

These trials demonstrate that the desirable slow, uniform nitrogen response for turf can be obtained with a single application of a suitable urea-formaldehyde product. Four pounds of nitrogen per 1000 square feet applied in this form will supply an average turf with sufficient nitrogen for satisfactory growth for a full year. From five to ten times this amount of nitrogen have been applied in this way at one time without injury to the turf. The efficiency of a single application equals or exceeds that of multiple applications of the soluble nitrogen fertilizers. High quality urea-formaldehyde fertilizer compounds are equal or superior to the other forms of slowly available nitrogen, such as the natural organic materials, sewage sludges, and tankages.

#### Summary

Urea-formaldehyde fertilizer compounds offer nitrogen in slowly available form. Nitrification experiments, greenhouse tests, and field trials have demonstrated that suitable products of this kind have nitrogen availability rates approximating the nitrogen demand of long-season crops such as turf. With them a full year's nitrogen supply may be applied at one time without injury to the plants. The availability index method described here is believed to be suitable and necessary for rapid evaluation of their agronomic usefulness.

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