

## Controlled Release Fertilizers by Chemical Modification of Urea: Triuret

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Triuret,  $\text{NH}_2\text{CONHCONHCONH}_2$ , has been shown in soil incubation experiments to release its nitrogen completely and gradually over a 6–12-week period. This corresponds to the release pattern required by certain agricultural crops. An increase in particle size was shown to reduce the rate of nitrification significantly and thus to offer additional control of availability of triuret nitro-

gen. The initial slow nitrification of biuret,  $\text{NH}_2\text{CONHCONH}_2$ , has been confirmed; this effect was greatly reduced in a 2:1 biuret-triuret mixture. Triuret can be prepared in 72% yield from urea hydrochloride, but higher yield, recycle of reagents, and recovery of ammonia evolved would probably be necessary to produce triuret at a low enough cost for agricultural use.

Controlled release nitrogen fertilizers generally are less soluble than the common quickly available types. They thus do not leach readily and do not burn or damage plants. Accordingly, they can be applied in relatively large amounts which will last over an extended period due to their gradual release of nitrogen. Ideally, however, a controlled release fertilizer should release its nitrogen at the rate required by the plant throughout the entire growing season. This would result in improved efficiency by avoiding losses and by avoiding deficiencies at critical growth periods.

Chemical modification of urea gives products with reduced solubilities which approach the ideal fertilizer properties to various degrees. The most important commercial products are the ureaforms, which are produced by reaction of urea and formaldehyde. They release their nitrogen over somewhat more than a single growing season, however (Hays, 1963; Hays *et al.*, 1965). Although such a release pattern works out well for turfgrass, complete release over a much shorter period would be better for certain agricultural crops. For example, in vegetable crops most of the nitrogen absorbed by the plant is taken up in 12–15 weeks, with the most rapid uptake occurring over a shorter period of 6–12 weeks (Lorenz and Bartz, 1968). Preparation of a fertilizer with this type of release pattern has been the objective of recent work on chemical modification of urea.

Products of reaction of aldehydes with urea were recently reviewed (Hays and Haden, 1969), along with substituted ureas and methylenediureas. Preparation of controlled release fertilizers by pyrolysis of urea has also given interesting results (Clark *et al.*, 1957; Hauck and Stephenson, 1964; Terman *et al.*, 1964). Biuret,  $\text{NH}_2\text{CONHCONH}_2$ , the simplest condensation product of urea, was found to nitrify slowly at first and to reach its maximum rate of nitrification in 3–6 weeks (Clark *et al.*, 1957). A negative factor for biuret in fertilizers is its reported detrimental effects on seed germination and in foliar sprays (Kilmer and Webb, 1968).

Triuret,  $\text{NH}_2\text{CONHCONHCONH}_2$ , also obtained by self-condensation of urea on pyrolysis, appears attractive as a controlled release fertilizer on the basis of its low solubility and its structure. It has been suggested for this use in the patent literature and its effectiveness has been qualitatively demonstrated (Schmitt *et al.*, 1970; Scholven-Chemie, 1966). Triuret has also been reported to accelerate the delayed decomposition of biuret in soils (Ogata and Yoshinouchi, 1958). In this paper we show that triuret has a nitrogen release pattern approximating the needs of one-season crops.

### MATERIALS

**Triuret.** Methods used were treatment of urea with thionyl chloride (Haworth and Mann, 1943) and reaction of urea with phosgene (Hoechst, 1943). Yields were low but authentic samples were obtained by both methods: % N, 38.1; calcd, 38.3. Solubilities by activity index (AI) procedure (AOAC, 1965): WIN (% water-insoluble N), 35.7; HWIN (% hot water-insoluble N), 0; AI 100; mp,  $>280^\circ$ .

Melting points are of little value in characterizing triuret, since decomposition to a very high melting product occurs during heating. The identity of our synthetic triuret samples was confirmed by infrared curves identical with published curves (Griffin, 1961).

Triuret was made into  $\frac{3}{8}$ -in. pellets using a hand pellet press (estimated pressure  $>2000$  psi). The pellets were gently crushed and screened; two fractions,  $-12$  on 16 mesh and  $-40$  mesh, were used in nitrification experiments.

### PROCEDURES

**Nitrification.** The procedure was that previously described (Clark *et al.*, 1959; Hays *et al.*, 1965), as modified in a recent publication (Smith *et al.*, 1971). The term nitrification, as previously, is used to cover the combined processes of ammonification and oxidation, rather than just the latter reaction.

### RESULTS AND DISCUSSION

**Solubility.** Triuret would be an excellent source of water-insoluble nitrogen (WIN) in fertilizers, as indicated by its WIN of 93.7% in the activity index procedure (AOAC, 1965). It is completely soluble in hot water, which gives it an activity index (AI) of 100 and of course suggests ready availability.

**Nitrification.** Rate of conversion to nitrate (Hays *et al.*, 1965) was used to assess the availability of triuret nitrogen. Curves 1 and 2 in Figure 1 show the slower rate in comparison with urea. (Curves 1 and 2 are duplicates run at different times.) These results indicate that triuret nitrogen would be completely available under practical conditions in 6–12 weeks, and that it would be released at a gradual rate over this period.

In view of the reported inhibition of nitrification for biuret (Clark *et al.*, 1957), there was concern that triuret might show a similar effect (Schmitt *et al.*, 1970). Examination of the early stages of nitrification in Figure 1 shows that there is no effect. The behavior of triuret during the first week of incubation is closely similar to that of urea. In the initial stage the rate is slow while nitrifying bacteria build up. After this stage, urea nitrogen nitrifies rapidly while the rate of nitrate formation from triuret is much slower, presumably determined by the rate of ammonification (Hays and Haden, 1966).

**Particle Size.** As pointed out for oxamide (DeMent *et*

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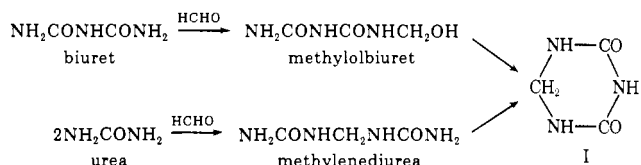
Table I. Nitrification of Biuret-Triuret

Material	Conversion to NO <sub>3</sub> <sup>-</sup> (weeks)	
	3	8
Biuret	3.9%	98%
2 Biuret + 1 triuret	35.3	100
Triuret	58	100

al., 1961) and magnesium ammonium phosphate (Bridger *et al.*, 1961), particle size can profoundly affect the availability of nitrogen from difficultly soluble compounds. To test this factor for triuret, a sample of relatively large particle size (-12 + 16 mesh) (Curve 4, Figure 1) was compared with a small particle size (-40 mesh, Curve 3). Curve 3 is only slightly different from Curves 1 and 2, but the rate indicated by Curve 4 is strikingly lower than for the smaller particle size. In fact, the result of this single run shows a greater effect of particle size than the work cited on oxamide and magnesium ammonium phosphate. However, the fact that the fines from the same preparation (Curve 3, Figure 1) behaved more or less normally convinces us that we have at least a qualitative demonstration that the rate of release of triuret nitrogen can be varied over a considerable range by variation in the particle size.

**Biuret-Triuret Mixtures.** Urea yields mixtures of biuret and triuret when heated with acidic reagents. Typically a 2:1 ratio of biuret to triuret is obtained (Werner and Gray, 1946). It was therefore of interest to check the nitrification of biuret and biuret-triuret mixtures (Table I). The expected slow initial rate of nitrification was shown by biuret. This delay period was greatly reduced in the 2:1 biuret-triuret mixture, although nitrification in the first 3 weeks was notably less than for triuret alone. The biuret-triuret result confirms the report by Ogata and Yoshinouchi (1958).

The results in Table I indicate that a 2:1 biuret-triuret mixture would release its nitrogen at a rate suitable for agricultural use. Biuret, in addition to possible harmful effects would, however, be too soluble for such use. Wiesboeck (1969) has reported conversion of methylolbiuret to the cyclic ureidomethylenehydrotriazinedione (I), which is insoluble in cold water but soluble in hot and is reported to have desirable slow release properties. This is the same material, characterized originally as 2,4-dioxohexahydro-1,3,5-triazine, obtained from methylenediurea (Diels and Lichte, 1926; Wiesboeck, 1969).



**Triuret in Fertilizers.** Although its solubility and rate of release make triuret appear of direct interest in fertilizers, the methods of preparation from urea (Haworth and Mann, 1943; Werner and Gray, 1946) or from phosgene and urea (Hoechst, 1943) appear expensive either because of low yields or high cost of reactants. Preparation from urea hydrochloride in 72% yield is the most attractive direct reaction reported (Scholven-Chemie, 1969). While some increase in price over urea could be tolerated, it would probably be necessary to achieve high yields, to recycle reagents, and to recover the ammonia evolved to produce triuret from urea at a low enough cost for agricultural use.

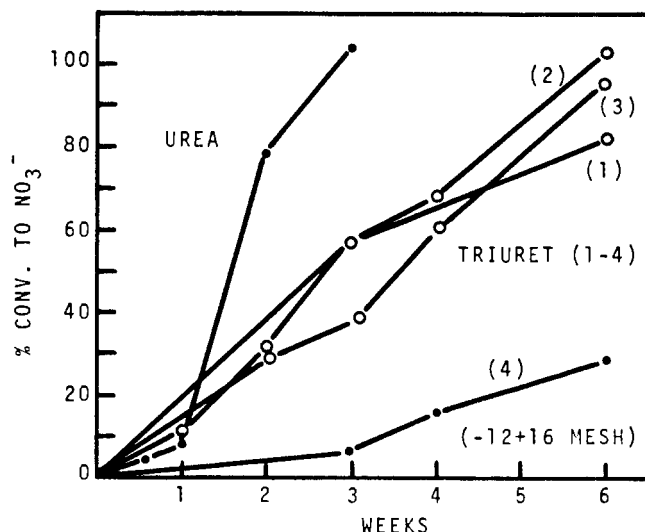


Figure 1. Nitrification of triuret.

## ACKNOWLEDGMENT

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## LITERATURE CITED

- Association of Official Agricultural Chemists (AOAC), "Official Methods of Analysis," 10th ed., (2.062), 1965, p 19.
- Bridger, G. L., Salutsky, M. L., Starostka, R. W., "Metal Ammonium Phosphates as Fertilizers," 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961.
- Clark, K. G., Yee, J. Y., Lamont, T. G., "Nitrification Characteristics of Urea Pyrolyzates, Cyanurates, Melamine and Related Compounds," Abstracts, 132nd National Meeting of the American Chemical Society, September, 1957, p 10J.
- Clark, K. G., Yee, J. Y., Lundstrom, F. O., Lamont, T. G., *J. Ass. Offic. Agr. Chem.* **42**, 596 (1959).
- DeMent, J. D., Hunt, C. M., Stanford, G., *J. Agr. Food Chem.* **9**, 453 (1961).
- Diels, O., Lichte, R., *Ber.* **59**, 2778 (1926).
- Griffin, J. L., *Biochim. Biophys. Acta* **47**, 437 (1961).
- Hauack, R. D., Stephenson, H. F., *J. Agr. Food Chem.* **12**, 147 (1964).
- Haworth, R. C., Mann, F. G., *J. Chem. Soc.* 603 (1943).
- Hays, J. T., "Fertilizers for Controlled Release of Nitrogen," 11th Annual California Fertilizer Conference, Riverside, Calif., January 28, 1963.
- Hays, J. T., Haden, W. W., *J. Agr. Food Chem.* **14**, 339 (1966).
- Hays, J. T., Haden, W. W., *J. Agr. Food Chem.* **17**, 1077 (1969).
- Hays, J. T., Haden, W. W., Anderson, L. E., *J. Agr. Food Chem.* **13**, 176 (1965).
- Hoechst, "Plant Directions," PB Report 70254, available from National Technical Information Service, Springfield, Va., 1943.
- Kilmer, V. J., Webb, J., "Changing Patterns of Fertilizer Use," Soil Science Society of America, Madison, Wis., 1968, pp 44-45.
- Lorenz, O. A., Bartz, J. F., "Changing Patterns of Fertilizer Use," Soil Science Society of America, Madison, Wis., 1968, pp 330-335.
- Ogata, T., Yoshinouchi, K., *Nippon Hiryogaku Zasshi* **29**, 21 (1958); *Chem. Abstr.* **53**, 19246 (1959).
- Schmitt, K., Heumann, H., Pollack, W., to Veba-Chemie Akt. formerly Scholven-Chemie Akt., British Patent 1,183,863 (March 11, 1970).
- Scholven-Chemie Akt., French Patent 1,441,915 (May 2, 1966).
- Scholven-Chemie Akt., British Patent 1,156,028 (June 25, 1969).
- Smith, W. H., Underwood, H. G., Hays, J. T., *J. Agr. Food Chem.* **19**, 816 (1971).
- Terman, G. L., DeMent, J. D., Hunt, C. M., Cope, J. T., Ensminger, L. E., *J. Agr. Food Chem.* **12**, 151 (1964).
- Werner, A. E. A., Gray, J., *Sci. Proc. Roy. Dublin Soc.* **24**, 111 (1946); *Chem. Abstr.* **41**, 710 (1947).
- Wiesboeck, R. A., to U.S.S. Agri-Chemicals, U. S. Patent 3,470,175 (September 30, 1969).

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