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by

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PREFACE

There is always the possibility that crops will suffer damage if soluble sources of nitrogen such as urea are used indiscriminantly. This report deals with crop response to biuret, a contaminant that forms during the manufacturing of urea. Hopefully, it will serve as a guide to those faced with selecting a suitable urea production process in relation to content of biuret.

SUMMARY

If improperly used, urea can result in several types of injury to plants. Biuret in the urea can injure crops; damage also can occur from evolved ammonia and from nitrite accumulation. In seedlings, it is difficult to distinguish among these types of injury. However, all types of injury can be avoided by broadcast application. For such use, quite high levels of biuret in urea can be tolerated; in fact, urea manufactured by modern technology would rarely be of concern if applied by the broadcast method.

Therefore, limits on biuret contents in urea are not necessary for broadcast urea. Such limits relate primarily to urea placed near or in contact with seed (a questionable practice) or for foliar application. In some areas of the world, particularly in Western Europe, compound fertilizers containing urea are applied near or in contact with the seed. For this purpose, limits on biuret content in urea—usually between 1 and 2%—are considered necessary.

In the USA, most urea is applied broadcast as either a straight material (solid) or as a component of nitrogen solutions. No problems from biuret contents would be expected with such uses. The same should be true for compound fertilizers containing urea when they come on the market.

Urea is often applied as a foliar spray to sugarcane, pineapples, and citrus crops. The generally accepted maximum level of biuret in urea for foliar application to citrus crops is 0.25%; other crops can tolerate at least 0.5% with little damage.

Urea is widely used in ruminant feeds in the United States and other countries with little attention being paid to biuret content. In many cases urea with biuret contents even slightly higher than those normally used for fertilizing crops appear to cause no problems. This may be due to biuret's slower rate of breakdown to ammonia.

INTRODUCTION

Urea in recent years has become the world's leading nitrogen fertilizer. World production, mostly for fertilizer use, was about 4 million metric tons in 1971. This was nearly twice the 1967 tonnage. Production and use are expected to continue upward in the foreseeable future.

Another important and growing use of urea is as a protein substitute in animal feeds. This use, for example, accounts for about one-fifth of the production in the United States.

Urea is made from carbon dioxide (CO_2) and ammonia (NH_3). Its melting point is 132.7° C. At higher temperatures, urea forms various products. At 140-170° C, the chief product formed is biuret:

$$\underset{\text{urea}}{2(NH_2 \cdot CO \cdot NH_2)} \rightarrow \underset{\text{biuret}}{(NH_2 \cdot CO \cdot NH \cdot CO \cdot NH_2)} + \underset{\text{ammonia}}{NH_3}$$

Some biuret also can be formed at lower temperatures. Redemann *et al* (1958) reported the formation of some

biuret when aqueous solutions of urea were heated above 50° C. Urea stored in solution at elevated temperatures for long periods likely will form small amounts of biuret.

Biuret formation is of concern because it may be toxic to crop plants. Whether toxicity is encountered will depend on the amount of biuret in the urea, the specific crop and its age, rate of application, placement in relation to seed, and other factors.

It should be kept in mind, however, that phytotoxicity caused by something other than biuret can be misinterpreted as biuret damage. As an example, hydrolysis of urea to $(NH_4)_2CO_3$ increases soil pH markedly. At pH 7.0 and above, free ammonia may be evolved and it can injure germinating seeds or young plants. Nitrite accumulation also can occur at high pH levels and this can result in injury to crop plants.

Urea produced during the late 1940's and 1950's usually contained fairly high levels of biuret. Some samples of pelleted urea of foreign origin analyzed by U.S. Department of Agriculture workers contained as much as 5.0% to 5.5% biuret (Starostka and Clark, 1955). Thus, it is not surprising that cases of biuret toxicity were reported by users of these products.

Manufacturing methods are now so improved that the biuret content of urea seldom exceeds 1%. Such products present no toxicity problems when soil-applied, particularly when broadcast. Nevertheless, the question of biuret levels persists, particularly in connection with the design and construction of new urea plants.

Processes are available for making urea containing about 0.3% biuret. They involve supplemental operations of vacuum crystallization, crystal drying, and remelting of crystals prior to prilling. The capital investment for such a process reportedly is 10-15% higher than for the conventional prilling process.

Although this very low biuret level is not necessary for most uses it may be desired if the urea is to be used as foliar sprays, especially on citrus crops.

Otherwise, attention to plant operating techniques is a more practical consideration in controlling biuret level. Melter retention time, for example, is a particularly significant factor.

Biuret content is determined by measuring the green color formed with nickel salts in alkaline solution. Makarevich and Koyander (1970) have described the analytical procedure.

EFFECT OF BIURET ON PLANTS

Plants absorb biuret through their roots and leaves, but metabolize it very slowly, if at all. Thus, biuret toxicity symptoms are apt to persist during the entire growing season in the case of annual crops and even longer in perennial crops. Webster *et al* (1957) suggested that the main effect of biuret probably is inhibition of protein synthesis, but other investigators have been unable to confirm this. For example, Clark and Wallace (1961), using C^{14}-biuret, found no stable combination of biuret with mitochondria or soluble protein in bush beans.

Biuret toxicity symptoms have been described for various crops by a number of workers. Citrus and pineapple exhibit typical "yellow tip" of leaves and leaf tip dieback, whereas symptoms on other crops range from leaf chlorosis to necrosis. The chlorosis can be interveinal or be confined to leaf edges. Corn plants may be stunted and exhibit compressed, rolled, and chlorotic leaves with notched edges (Wilkinson and Ohlrogge, 1961).

Biuret, if banded near the seed in excessive amounts, inhibits seed germination and injures or kills seedlings.

BEHAVIOR OF BIURET IN SOILS

Biuret accumulation in the soil is not a problem for two main reasons: (1) it is relatively mobile and (2) it is readily mineralized during a single cropping season, as illustrated by the data of Starostka and Clark (1955) in table 1. Following mineralization, biuret is a satisfactory source of nitrogen for crops.

RESULTS WITH SOIL APPLICATION

Most crops tolerate relatively large amounts of biuret applied with urea provided that care is taken to avoid placement with seed. Thus, the principle for safe use of biuret-containing urea is the same as for urea free of biuret.

This is indicated in results with maize reported by Wilkinson and Ohlrogge (1960) in table 2. Placement of urea in close proximity to seeds greatly reduced stand and final yield. But adverse effects were more pronounced when the urea contained biuret, with the greatest crop damage occurring when high-biuret urea was applied with the seed.

Low and Piper stated that 1 5 kg biuret/ha in contact with germinating seeds can have phytotoxic effects. They found, on the other hand, that 2 kg biuret/ha topdressed with urea on grass caused no yield losses. They concluded that the main factor in urea toxicity to seeds and seedlings is ammonia formed during ammonification.

Court *et al* (1964) concluded after reviewing the literature that biuret does not seem to cause phototoxicity if content is less than 1% of urea They reported the main causes of toxicity of urea of low biuret content is from free NH_3 and NO_2 accumulation.

Results by Brage *et al* (1960) point to the same conclusion. They conducted extensive field experiments in South Dakota on crops that included winter wheat, barley, and maize. Stands of winter wheat were reduced only slightly when ammonium nitrate containing about 2% biuret was placed with seed (table 3). However, urea with about the same and higher levels of biuret drastically reduced stands. On the other hand, with broadcast treatment, application of 179 kg/ha of N as urea containing 10% biuret did not significantly reduce germination of barley and maize.

Tomlinson (1970) concluded that a content of 2% biuret was acceptable for urea mixed with the soil.

Table 1. Degree of nitrification of ammonium sulfate, urea, biuret, and certain urea-biuret mixtures added at 450 kg nitrogen per hectare

Nitrogen source	Incubation period in weeks			
	3[a]	7[a]	11[b]	15[b]
	% of added N converted to nitrate			
Ammonium sulfate	89.2	90.3	97.7	86.6
Urea	88.7	92.1	96.3	88.2
Urea, 99.5%) Biuret, 0.5%)	89.7	90.5	96.2	88.7
Urea, 99.0%) Biuret, 1.0%)	87.4	89.8	94.4	91.4
Urea, 96.0%) Biuret, 4.0%)	87.4	92.2	94.3	92.5
Urea, 90%) Biuret, 10%)	87.2	89.0	90.7	89.1
Biuret	69.2	76.9	84.3	85.8
L.S.D., 5%	6.4	5.4	4.1	3.0
1%	9.7	8.2	6.2	4.0

[a]Average of two replications.
[b]Average of five replications.

(Starostka & Clark, 1955)

Table 2. Effect of rate and placement of biuret on stand and yield of corn.

Placement	Biuret applied kg/ha	Stand % of planting level	Yield of shelled corn mt/ha
4 cm to side[a] and below seed	0.0	89	8.1
	.2	97	7.4
	.5	100	8.4
	1.0	94	6.0
	2.0	89	5.8
With seed	0.0	57	5.4
	.2	66	3.8
	.5	37	3.9
	1.0	40	2.8
	2.0	20	1.3

[a]11.2 kg N/ha; 24.9 kg urea/ha.

(Wilkinson and Ohlrogge, 1960)

Table 3. Effect of carriers, biuret level, and application method on stand of some field crops.

Crop	Application method	carrier	N applied kg/ha	Biuret applied kg/ha	Stand % of control
Wheat	With seed	TSP[a]	45	0	97
		AN[b]	45	0	88
		AN	45	3.0	84
		Urea	45	2.2	27
		Urea	45	4.4	20
		Urea	45	8.9	9
Barley	Broadcast	AN	179	0	93
		Urea	179	10	98
		Urea	179	20	99
		Urea	179	40	108
Maize	Broadcast	AN	179	0	104
		Urea	179	10	105
		Urea	179	20	102
		Urea	179	40	91

[a]Triple superphosphate.
[b]Ammonium nitrate.

(Brage *et al*, 1960)

Hunter and Rosenau (1966) reported that biuret in urea had little effect on germination, but seriously injured maize seedlings In field trials, when more than 1.7 kg biuret/ha was band-applied about 4 cm from the seed-row, seedlings were stunted and many died. Plants were damaged at lower levels of biuret, but generally survived and outgrew the injury.

Starostka and Clark (1955) applied as much as 122 kg N/ha of a 9:1 urea-biuret mixture to soil in a greenhouse study and observed no injury to corn, cotton, tomatoes or oats. Pot experiments carried out by Mayr and Barbier (1963) showed that tobacco and sunflower yields were reduced only when the biuret content of soil-applied urea exceeded 3%. Neither yield nor quality of sweet corn, peppers, tomatoes, snapbeans, and celery was affected by soil applications of urea containing up to 5% biuret (Drinkwater and Pickering, 1958). Urea containing up to 2.5% biuret appears to have no effect on the yields of sugarcane (Innes, 1960), oranges and lemons (Jones *et al*, 1955), but Robinson (1958) concluded that the biuret content of urea applied to soil for coffee culture should not exceed 2%. Gadet *et al* (1959) reported critical levels of biuret to be 3-4 kg/ha for potatoes, 6 kg for wheat and >15 kg for maize.

Considerable work has been carried out relating to the effects of biuret in urea applied to grass. Jackson and Burton (1959a) reported no toxicity to Coastal bermudagrass when up to 40% of biuret in ammonium nitrate was applied at a rate of 224 kg N/ha. They concluded that poor performance of urea for Coastal bermudagrass could not be due to biuret toxicity. Further research (1959b) indicated that this inferiority of urea on Bermuda sods is largely due to N loss by volatilization during hydrolysis to ammonium carbonate by enzymatic action of urease associated with organic matter.

In a greenhouse experiment, biuret in urea injured ryegrass for a short period after application and laboratory tests showed the rate of nitrification of biuret was substantially slower than for either $(NH_4)_2SO_4$ or urea (Starostka and Clark, 1955).

Devine and Homes (1963) conducted 10 experiments in England and Scotland to compare ammonium nitrate, ammonium sulfate, and urea with less than 1% biuret and urea with about 4% biuret as sources of N for grass. Fertilizers were applied in spring and after each cutting. The urea treatments were lower in effectiveness than either ammonium nitrate or ammonium sulfate. Volatilization of NH_3 was the apparent reason for this poorer performance of urea, rather than the biuret content.

RESULTS WITH FOLIAR APPLICATION

Urea is commonly used as the nitrogen source in foliar sprays. The amounts of nitrogen that can safely be applied in this manner are limited by the tolerance of the plant foliage to urea concentrations. Wittwer, Bukovac, and Tukey (1963) have compiled data on foliage tolerance to urea sprays as shown in table 4. The biuret content of the foliar spray is not given. It is evident from this data that there are wide variations in tolerance of plant foliage to

Table 4. Tolerances of plant foliage to urea sprays in grams of urea per liter of water.

Vegetable crops		Plantation or tropical crops		Deciduous tree and small fruit crops		Agronomic crops	
Crop	Tolerance	Crop	Tolerance	Crop	Tolerance	Crop	Tolerance
Cucumber	3.6-6.0	Pineapple	24.0-60.0	Grape	4.8-7.2	Potatoes	
Bean	4.8-7.2	Cacao	6.0-12.0	Raspberry	4.8 7.2	Sugar beets	24.0
Tomato	4.8-7.2	Sugarcane	12.0-24.0	Apple	4.8-7.2	Alfalfa	24.0
Pepper	4.8-7.2	Banana	6.0-12.0	Strawberry	4.8-7.2	Corn	6.0-24.0
Sweet corn	4.8-7.2	Cotton	24.0-60.0	Plum	6.0-18.0	Wheat	24.0-960.0
Lettuce	4.8-7.2	Tobacco	3.6-12.0	Peach	6.0-24.0	Bromegrass	24.0-960.0
Cabbage	7.2-14.4	Citrus	6.0-12.0	Cherry	6.0-24 0		
Carrots	24.0	Hops	48.0-60.0				
Celery	24.0						
Onions	24.0						

(Adapted from Wittwer, Bukovac, and Tukey, 1963)

urea sprays even within a single species. However, the data are a valuable guide for using foliar sprays containing urea.

In general, crop plants are much less tolerant of biuret in foliar-applied than in soil-applied urea. A biuret content of 1% in foliar-applied urea was sufficient to cause damage to sunflower, soybeans, and cotton plants (Mayr and Barbier, 1963). However, damage caused by the urea itself was often more severe than that caused by the biuret. Urea damage occurred within 24 hours after application, while biuret toxicity symptoms did not appear for more than 21 days. Citrus foliage appears to be particularly sensitive to biuret and some investigators recommend that urea containing more than 0.25% biuret should not be used in foliar sprays for citrus (Jones and Embleton, 1957).

Others have reported applying somewhat higher levels of biuret-urea mixtures to citrus foliage before toxic symptoms appeared. Gadet *et al* (1959) state that orange tree foliage was damaged if the biuret content of urea exceeded 0.5%, while Impey and Jones (1960) reported that foliar sprays containing urea having a biuret content of 2.5% caused damage to Navel and Valencia orange leaves. The spray consisted of 1 kg of urea/100 liters of water applied at the rate of 23 liters per tree.

Pineapple seems to be highly tolerant of biuret. Sanford *et al* (1954) indicated that urea solutions containing up to 3% biuret can be safely used as foliar sprays while Pan and Lee (1963) reported 2% biuret as the critical level for pineapple. Foliar sprays containing up to 150 ppm biuret in solution have been used without damage on grapevines and pear trees and up to 400 ppm on peach trees, wheat was not damaged by 5 000 ppm biuret (Gadet *et al*, 1959).

Drinkwater and Pickering (1958) reported that foliar application of urea containing up to 5% biuret caused toxic symptoms in five species. Snap and lima beans were most sensitive, parsley and tomatoes only moderately so and peppers only slightly so.

UREA IN ANIMAL NUTRITION

Research on the use of urea in animal nutrition has been carried out since the late 19th century. An estimated 20% of U.S.-produced urea is used for this purpose. Urea containing biuret at levels equal to or slightly higher than that used for fertilizing plants can be readily used as a protein substitute. In some cases, urea containing biuret is preferred since biuret converts to ammonia at a slower rate than does urea. For a comprehensive bibliography on the subject, the reader is referred to Stangel *et al* (1963).

REFERENCES

1. Brage, B. L., W. R. Zich, and L. O. Fine. 1960. The germination of small grain and corn as influenced by urea and other nitrogenous fertilizers. *Soil Sci. Soc. Amer. Proc.* 24:294-96.
2. Clark, R. B., and A. Wallace. 1961. C^{14}-biuret accumulation and translocation by bush beans. *Proc. Amer. Soc. Hort. Sci.* 77:393-400.
3. Court, M. N., R. C. Stephen, and J. S. Waid. 1964. Toxicity as a cause of the inefficiency of urea as a fertilizer. I. Review. *J. Soil Sci.* 15:42-8.
4. Devine, J. R., and M.R.J. Holmes. 1963. Field experiments comparing ammonium nitrate, ammonium sulfate and urea applied repetitively to grassland. *J. Agr. Sci.* 60:297-304.
5. Drinkwater, W. O., and E. Pickering. 1958. The efficiency of soil and foliar applications of urea as measured by yield and quality of vegetable crops and the effect of varying percentages of biuret. New Jersey Agricultural Experiment Station Bulletin, Science and the Land.
6. Gadet, R. L. Soubies, and F. Fourcasse. 1959. Recherches sur les effets toxiques du biuret et sur l'evolution de ce compose dans les sols. *Annal. Agron.* 6:609-60.
7. Gasser, J. K. 1964. Urea as a fertilizer. *Soils Fert.* 27:175-80.
8. Hunter, A. S., and W. A. Rosenau. 1966. The effects of urea, biuret, and ammonia on germination and early growth of corn. *Soil Sci. Soc. Amer. Proc.* 30:77-81.
9. Impey, R. L., and W. W. Jones. 1960. Effects of biuret

on nitrogen status of Washington Navel and Valencia orange leaves. *Proc. Amer. Soc. Hort. Sci.* 76:186.

10. Innes, R. F. 1960. The nitrogen, phosphorus and potassium requirements of sugarcane. *J. Sci. Food Agr.* 11:299-309.
11. Jackson, J. E., and G. W. Burton. 1959a. Does biuret in prilled urea inhibit Coastal bermudagrass growth? *Agron. J.* 51:752-53.
12. Jackson, J. E., and G. W. Burton. 1959b. Placement, sod treatment and biuret content as factors affecting the use of urea nitrogen by Coastal Bermuda. *Assoc. Southern Agr. Proc.* 56:82-3.
13. Jones, W. W., T. W. Embleton, and G. E. Goodall. 1955. Urea: source of citrus nitrogen. Calif. Citrograph. 4:4.
14. Jones, W. W., and T. W. Embleton. 1957. Two nitrogen application methods compared in study. Calif. Citrograph. 42 (11):402.
15. Low, A. J., and F. J. Piper. 1961. Urea as a fertilizer. Laboratory and pot culture studies. *J. Agr. Sci.* 57:249-55.
16. Makarevich, V. M., and A. E. Koyander. 1970. Determination of biuret in complex fertilizers. *Agrokhimiya* 1:139-43.
17. Mayr, H. H., and S. Barbier. 1963. Plant tolerance for biuret in urea. *Z. Pflanzenernaehr. Dueng. Bodenk.* 103 (2):107-12.
18. Pan, K. Y., and C. Lee. 1963. Biuret toxicity to pineapple. Taiwan Fertilizer Co., Ltd., Res. Bulletin No. 15.
19. Redemann, C. E., F. C. Riesenfeld, and F. S. LaViola. 1958. Formation of biuret in urea. *Ind. Eng. Chem.* 50:633-36.
20. Robinson, J.B.D. 1958. Monthly bulletin of the Coffee Board of Kenya. 23 (271):181-82, 188.
21. Sanford, W. G., D. P. Gowing, H. Y. Young, and R. W. Leeper. 1954. Toxicity to pineapple plants of biuret found in urea fertilizers from different sources. *Science* 120:349-50.
22. Stangel, Harvey, J., Ronald R. Johnson, and Astrid Spellman, ed. 1963. Urea and non-protein nitrogen in ruminant nutrition. Allied Chem. Corp. 489 pp.
23. Starostka, R. W., and K. G. Clark. 1955. Greenhouse evaluation and nitrification characteristics of biuret and urea-biuret mixtures. *Agr. Chem.* 10 (10):49-50, 103, 105.
24. Tomlinson, T. E. 1970. Urea-agronomic applications. Proceedings No. 113, The Fertiliser Society.
25. Webster, G. C., R. A. Berner, and A. N. Gansa. 1957. The effect of biuret on protein synthesis in plants. *Plant Physiol.* 32 (1):60-1.
26. Wilkinson, S. R., and A. J. Ohlrogge. 1960. Influence of biuret and urea fertilizers containing biuret on corn plant growth and development. *Agron. J.* 52:560-62.
27. Wilkinson, S. R., and A. J. Ohlrogge. 1961. Phytotoxicity of biuret. *Agron. J.* 53:206.
28. Wittwer, Sylvan H., Martin J. Buckovac, and Harold B. Tukey. 1963. Advances in foliar feeding of plant nutrients. IN McVickar, M. H., G. L. Bridges, and L. B. Nelson, eds. Fertilizer Technology and Use. *Soil Sci. Soc. Amer.*, Madison, Wis., 464 pp.

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