

# Hydrolysis, Nitrification, and Nitrogen Availability of Oxamide, as Influenced by Granule Size

J. D. DeMENT, C. M. HUNT, and  
GEORGE STANFORD<sup>1</sup>

Tennessee Valley Authority, Wilson  
Dam, Ala.

In water, oxamide was sparingly soluble and released ammonia slowly at 25° C. In an uncropped soil, conversion of the nitrogen in oxamide to ammonia and nitrate was essentially complete in 1 week with -60-mesh oxamide, but much slower with -4 + 6-mesh oxamide. Nitrogen uptake by one crop of corn forage in greenhouse pots from -4 + 6- and -28 + 35-mesh oxamide was approximately 22 and 89%, respectively, of uptake from ammonium nitrate or 60-mesh oxamide. Nitrogen recoveries by three successive corn crops from 800 mg. of nitrogen applied as oxamide ranged from 44 to 64% on unlimed Hartsells fine sandy loam (pH 5.2) and from 61 to 82% on this soil limed to pH 7.5. These recoveries were similar to those from ammonium nitrate and considerably higher than those from an equal application of nitrogen as urea-formaldehyde.

Most of the nitrogen fertilizers used by farmers are applied as ammonium or nitrate salts. Anhydrous ammonia and urea are quickly converted to ammonium salts in the soil. In the ammonium form, nitrogen is held on the exchange complex and is not lost by leaching or volatilization. In most soils, however, ammonium nitrogen is quickly converted to nitrate nitrogen by the soil microbiological population. The nitrate nitrogen is soluble in water and is subject to loss by leaching. Recent evidence (5) shows that applied ammonium nitrogen fertilizers in the soil are also subject to severe losses by chemical reactions which result in formation of volatile nitrogen compounds which are lost to the atmosphere.

The fertilizer industry and agronomists have long been interested in obtaining a nitrogen fertilizer of low water solubility which would gradually release available nitrogen to the soil over a considerable period of time. Urea-formaldehyde materials have been produced and are now on the market. They are rather expensive and may not release nitrogen rapidly enough to meet the needs of a fast-growing crop (7). Their use has been largely restricted to specialty, high-value crops which require limited amounts of nitrogen over a long period of time.

The value of oxamide as a nitrogen fertilizer for paddy rice was studied by Ogata in Japan (6). He showed that it was a satisfactory source of nitrogen and that its availability decreased with increase in granule size.

The effect of granule size on the availability of phosphorus fertilizers of low water solubility has been intensively

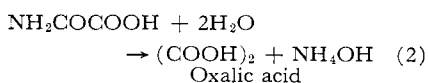
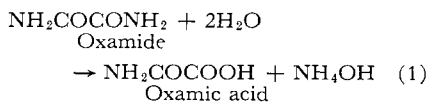
studied and closely related to the geometric surface area of the granules (2). Lowered availability of less soluble potassium fertilizers has also been reported (3), but the variation in rates of solution and chemical changes occurring in nitrogen fertilizers as granule size is changed has not been generally considered.

The purpose of the present experiments was to determine the effect of granule size on the hydrolysis and nitrification of oxamide in soil.

## Experimental Procedure

**Characteristics of Fertilizers.** The oxamide, ureaform, ammonium nitrate, and ammonium sulfate used in the experiments passed a 100-mesh screen (Tyler). Oxamide ( $\text{NH}_2\text{COCOONH}_2$ ) was reagent-grade white crystals containing 31.8% nitrogen and a handbook solubility of 0.04 gram per 100 ml. of water. For granulation, the fine powders were compressed into tablets 0.5 inch in diameter, using 4000-p.s.i. pressure in a Carver press. The tablets were gently crushed and screened to the desired granule size. This resulted in stable, reasonably uniform granules. For experiment 1, oxamide was also granulated at pressures of 1000 and 6000 p.s.i.

**Solution and Hydrolysis in Water.** Oxamide hydrolyzes according to the following reactions:



Fifty- and 100-mg. samples of finely ground oxamide containing 15.9 and 31.8

mg. of nitrogen were suspended in 100 ml. of water and shaken for 1, 2, 8, and 30 days. At the end of each period the suspensions were filtered and three aliquots were taken and analyzed as follows:

A. For ammonium nitrogen, related to the amount of oxamide hydrolyzed to oxamic and oxalic acids

B. For ammonium nitrogen after boiling for 1 hour in 1N hydrochloric acid (this procedure hydrolyzed all of the oxamide in solution and the ammonium was related to the total hydrolyzed and unhydrolyzed oxamide in solution)

C. For oxalic acid, by adding a known excess of calcium chloride to precipitate calcium oxalate, followed by EDTA titration of the excess calcium (oxamic acid was not precipitated by this procedure). Thus, the oxamic acid in solution was calculated by subtracting the amount of oxamic plus oxalic acids calculated in aliquot A from the amount of oxalic acid calculated in aliquot C.

## Hydrolysis and Nitrification in Soil.

Hydrolysis and nitrification rates of oxamide in a soil system were determined as follows: Five milligrams of nitrogen both as -60 + 100-mesh oxamide and as ammonium sulfate in duplicate were mixed with 50 grams of unlimed and limed Hartsells soil and placed in a glass cylinder 1 inch in diameter. In a second series, single granules of oxamide containing 5 mg. of nitrogen were selected from the -6 + 9-mesh granules and placed in the center of 50 grams of soil. Sufficient water was added to supply 20% of moisture (the moisture equivalent). The cylinders were stoppered with glass wool plugs and incubated for 3, 7, 14, 28, 56, and 112 days. Unfertilized soils from each series were included. Additional water was added as required to maintain the soil moisture near 20%.

At the end of the designated incubation period the entire soil culture was ex-

<sup>1</sup> Present address, Hawaiian Sugar Planters' Association, Honolulu 14, Hawaii.

**Table I. Amounts of Oxamide Nitrogen Added, Dissolved, and Hydrolyzed in Water at 23° to 27° C.**

Forms of Nitrogen in Solution, Mg./100 Ml.						
Time, Days	Total N		Total <sup>c</sup>	Ammonium Released by Hydrolysis of Oxamide to:		Unhydrolyzed oxanide
	Added <sup>a</sup>	Solution <sup>b</sup>		Oxalic <sup>d</sup> acid	Oxamic <sup>e</sup> acid	
1	15.9	6.8	0.39	0.22	0.17	6.4
	31.8	6.8	0.61	0.17	0.44	6.2
2	15.9	6.8	0.38	0.11	0.27	6.4
	31.8	6.8	0.39	0.17	0.22	6.4
8	15.9	6.9	0.62	0.06	0.56	6.3
	31.8	7.2	0.80	0.06	0.74	6.4
30	15.9	7.5	3.41	0.00	3.41	4.1
	31.8	8.0	3.80	0.03	3.77	4.2

<sup>a</sup> Equivalent to 50 and 100 mg. of oxamide per 100 ml. of water.<sup>b</sup> Determined as NH<sub>4</sub> after complete hydrolysis of oxamide filtrate in 1N HCl.<sup>c</sup> Total ammonia present in filtrate before hydrolysis in 1N HCl.<sup>d</sup> Calculated from oxalic acid determination.<sup>e</sup> Calculated as difference between <sup>c</sup> and <sup>d</sup>.**Table II. Ammonium and Nitrate Recovery from 5 Mg. of Nitrogen Added as Oxamide and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>**

Time, Days	Increase over No Applied N, Mg. per Sample <sup>a</sup>								
	Oxamide						(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>		
	-6 + 9 Mesh			-60 + 100 Mesh			-60 + 100 Mesh		
	NH <sub>4</sub> -N	NO <sub>3</sub> -N	Total	NH <sub>4</sub> -N	NO <sub>3</sub> -N	Total	NH <sub>4</sub> -N	NO <sub>3</sub> -N	Total
Unlimed Soil (Hartsells), pH 5.2									
3	0.0	0.0	0.0	3.2	0.0	3.2	3.9	0.0	3.9
7	1.9	0.0	1.9	3.5	0.0	3.5	3.7	0.0	3.7
14	1.8	0.7	2.5	3.3	0.6	3.9	3.5	0.3	3.8
28	1.9	2.2	4.1	1.8	2.7	4.5	2.8	1.7	4.5
56	1.1	2.9	4.0	1.2	2.8	4.0	2.4	1.5	3.9
112	0.3	4.3	4.6	0.3	3.0	3.3	0.8	2.1	2.9
Limed Soil (Hartsells), pH 7.5									
3	0.6	0.0	0.6	2.6	0.0	2.6	2.7	0.1	2.8
7	1.7	0.4	2.1	0.0	0.8	0.8	1.8	0.9	2.7
14	0.0	2.3	2.3	0.0	4.1	4.1	0.0	3.3	3.3
28	0.4	2.6	3.0	0.3	3.5	4.0	0.2	2.4	4.6
56	0.0	3.4	3.4	0.0	5.0	5.0	0.0	4.8	4.8
112	0.0	4.4	4.4	0.2	3.4	3.6	0.0	2.8	2.8

<sup>a</sup> Calculated by subtracting ammonium and nitrate N values for unfertilized soils from those obtained with experimental fertilizers.

tracted in duplicate and ammonium and nitrate nitrogen were determined on each extract. Nitrogen recovery from added nitrogen was calculated by subtracting the ammonium and nitrate nitrogen of the unfertilized soils from the values obtained with the fertilized soils. Ammonium nitrogen was extracted with 2N sodium chloride and determined by nesslerization. Nitrate nitrogen was extracted with water and determined by the phenoldisulfonic acid procedure.

**Plant Availability Studies.** Three greenhouse experiments were conducted, in all of which Hartsells fine sandy loam was used as the growth medium. In experiment 1, the short-term method described by DeMent, Stanford, and Hunt (4) was used to compare -60 + 100-, -14 + 20-, and -4 + 6-mesh oxamide, ureaform, and ammonium nitrate. Different pressures for granulating oxamide were also compared. Each fertilizer was mixed with 200 grams of soil to supply 30 mg. of nitrogen.

Uptake of nitrogen by nitrogen-deficient oat plants was measured during a 14-day period.

Experiments 2 and 3 were conventional greenhouse pot tests, in which single-cross hybrid corn forage was grown in plastic-lined gallon food cans containing 3 kg. of soil. Solid concentrated superphosphate was mixed with the soil of experiment 2 prior to planting, to supply 360 mg. of phosphorus per can. Corn forage was harvested, weighed, and analyzed for total nitrogen content. For experiment 2, -60 + 100- and -6 + 9-mesh granules of oxamide, ureaform, and ammonium nitrate were mixed with the unlimed soil, and the -60 + 100-mesh materials were also placed in a band 1.5 inches below the soil surface. All nitrogen fertilizers were added at rates to supply 100 and 400 mg. of nitrogen per can. Following planting, 200 mg. of potassium from the sulfate and chloride salts was added in solution. A single crop of five corn plants was

grown from October 22 to December 3, 1958 (6 weeks).

In experiment 3, -60 + 100-, -28 + 35-, -14 + 20-, -6 + 9-, and -4 + 6-mesh granules of oxamide; -60 + 100-, -14 + 20-, and -4 + 6-mesh granules of ureaform; and -60 + 100- and -4 + 6-mesh granules of ammonium nitrate were compared. Each nitrogen fertilizer was mixed with the unlimed soil (pH 5.2) and the soil limed to pH 7.5 in amounts to supply 200, 400, and 800 mg. of nitrogen per can. A first crop of five corn plants was grown at all rates of applied nitrogen from January 2 to March 19, 1959 (11 weeks). After 3 weeks in a moist condition, the cans receiving the 800-mg. rate were replanted and a second crop of corn was grown for 8 weeks. A third crop was planted immediately after harvest of the second crop and was grown for 7 weeks. Replantings were done by pushing the grains 0.75 inch into the soil without otherwise disturbing the soil in the cans. Supplemental uniform fertilizer applications in solution per can included: 280 mg. of potassium from sulfate and chloride salts and 360 mg. of phosphorus as monocalcium phosphate for the first crop, and 270 mg. of phosphorus and 340 mg. of potassium and trace elements for the second crop.

## Results

### Solution and Hydrolysis in Water.

A laboratory study gave the solubility of oxamide (Table I) as considerably lower than published data for this material. It appeared, however, that a saturated solution was obtained, as the amount of oxamide in solution after 1 day remained about constant for 30 days and was not affected by solid-to-solution ratio. There was essentially no hydrolysis in water for the first 8 days. Traces of impurities which were detected in the oxamide may have been responsible for the small amount of ammonia nitrogen detected in the filtrate during the first week of shaking.

In the period from 8 to 30 days, considerable hydrolysis of the oxamide in solution occurred. This later, more rapid hydrolysis was probably due to microbial contamination, as no efforts were made to maintain sterile conditions.

### Hydrolysis to Ammonia in Soil.

There was no measurable hydrolysis of the larger granules (-6 + 9 mesh) of oxamide during the first 3 days of incubation in the unlimed acid soil and only a small amount of hydrolysis in the limed soil (Table II). This was in sharp contrast to the hydrolysis rate of the finer granules, from which 64% of the added nitrogen was recovered as ammonia at the end of 3 days. At the end of 7 days, ammonia recoveries from fine oxamide and ammonium sulfate were similar and it may

**Table III. Nitrogen Uptake by Oats in 14 Days from 30 Mg. of Applied Nitrogen, as Affected by Source and Granule Size of Nitrogen Fertilizer**

(Experiment 1)

Granule Size	N Uptake, Mg. per Culture					
	Unlimed Soil (pH 5.2)			Limed Soil (pH 7.5)		
	Oxamide	Ureaform	NH <sub>4</sub> NO <sub>3</sub>	Oxamide	Ureaform	NH <sub>4</sub> NO <sub>3</sub>
-4 + 6	21.5	21.3	27.3	25.0	20.9	30.3
-14 + 20	23.8	22.1	28.0	29.5	18.9	31.0
-60 + 100	30.5	24.0	30.5	31.8	20.1	31.0
No N	15.3			14.1		
L.S.D., 5% level	2.6			2.6		

**Table V. Nitrogen Uptake by Corn Forage, as Affected by Rate, Placement, and Granule Size of Various Nitrogen Fertilizers**

(Experiment 2)

N Source	N Applied, Mg. per Pot	N Uptake, Mg. per Pot		
		Fertilizer Mixed		Fertilizer banded,
		-6 + 9 mesh	-60 + 100 mesh	-60 + 100 mesh
Oxamide	100	50.7	70.2	72.3
	400	71.9	239.7	214.3
Ureaform	100	45.7	61.3	50.4
	400	85.7	103.7	91.6
NH <sub>4</sub> NO <sub>3</sub>	100	...	78.8	87.3
	400	...	224.7	245.4
No nitrogen		42.9		

**Table VII. Percentage Recovery of Fertilizer Nitrogen from 800 Mg. of Applied Nitrogen by Successive Crops of Corn Forage, as Influenced by Nitrogen Source, Granule Size, and Soil pH**

Particle Size, Tyler	Crop 1		Crops 1 and 2		Crops 1, 2, and 3	
	pH 5.2	pH 7.5	pH 5.2	pH 7.5	pH 5.2	pH 7.5
OXAMIDE						
-4 + 6	16	13	39	54	46	61
-6 + 9	19	29	41	66	44	70
-14 + 20	36	48	46	63	47	65
-28 + 35	53	72	55	74	56	74
-60 + 100	62	79	63	81	64	82
UREAFORM						
-4 + 6	20	19	21	23	35	29
-60 + 100	45	30	49	40	51	42
NH <sub>4</sub> NO <sub>3</sub>						
-4 + 6	56	72	58	73	58	73
-60 + 100	65	66	67	67	67	72

be assumed that essentially all of the fine oxamide was hydrolyzed. Nitrogen recoveries as ammonia at the end of this reaction time were much greater for fine than for coarse granules. It is not possible to make an accurate comparison of recovery from fine granules of oxamide and ammonium sulfate, since some immobilization of nitrogen by the soil was evident from both sources.

Similar results were found on the limed soil. The principal difference was the length of time during which there was a differential hydrolysis of coarse and fine granules. In the limed soil, this difference had disappeared after 14 days, whereas in the acid soil it persisted for 28 days. This suggests that the coarse oxamide was hydrolyzed somewhat more slowly in unlimed than in limed soil.

**Nitrate Production in Soil.** Only a limited amount of ammonia was converted during the first 2 weeks of contact with the acid soil (Table II). After 28 and 56 days, nitrate content was generally related to the ammonia content of the soil. Ammonium sulfate was nitrified somewhat more slowly than oxamide, because of the greater acidity in the soil which received this fertilizer. There was no evidence that the granule size of oxamide affected the rate of nitrate production, except as it controlled the hydrolysis rate and thus the amount of ammonia in the soil.

**Total Nitrogen Recovery and Losses.** In this study, no provisions were made to measure nitrogen loss from the soil system. Sharp reductions in nitrogen recoveries from the soil appear to have occurred in the periods between 28 and

**Table IV. Nitrogen Uptake by Oats in 14 Days from 30 Mg. of Nitrogen Applied as Oxamide, as Affected by Granule Size and Density**

(Experiment 1)

Pressure for Granulation, P.S.I.	Mesh Size	N Uptake, Mg. per Culture <sup>a</sup>
0	-4 + 6 <sup>b</sup>	11.4
0	-4 + 6 <sup>c</sup>	9.8
1000	-4 + 6	9.5
4000	-4 + 6	10.9
6000	-4 + 6	10.3
4000	-60 + 100	17.7
L.S.D., 5% level		3.4

<sup>a</sup> Uptake with no added nitrogen, 14.1 mg.

<sup>b</sup> -60 + 100-mesh material spot-placed to simulate -4 + 6-mesh granule.

<sup>c</sup> -60 + 100-mesh material granulated with water, dried, and screened to -4 + 6 mesh.

**Table VI. Nitrogen Availability Coefficient Ratios<sup>a</sup> for Various Nitrogen Fertilizers, as Influenced by Granule Size**

(Experiment 3)

Granule Size	Oxamide	Ureaform	NH <sub>4</sub> NO <sub>3</sub>
-4 + 6	0.22	0.29	0.92
-6 + 9	0.38	0.38	...
-14 + 20	0.65	0.38	...
-28 + 35	0.89	...	...
-60 + 100	1.00	0.56	0.97

<sup>a</sup> Averages for unlimed and limed soil.

56 days in acid soil and between 56 and 112 days in limed soil where nitrogen was applied as ammonium sulfate or fine oxamide. These reductions occurred following accumulation of nitrate nitrogen in the soil and were greater on the limed than on the unlimed soil. Reduction did not occur where nitrogen was applied as coarse oxamide. It appears that either there was no loss of nitrogen from the soils treated with this material, or such losses were overbalanced by the production of ammonium nitrogen as a result of continued hydrolysis of these large granules.

**Short-Term Nitrogen Uptake by Oats.** There was no difference (experiment 1) in the uptake of nitrogen by oats from fine oxamide and ammonium nitrate during a 14-day period (Table III), while fine ureaform supplied much less nitrogen than either of the other materials, particularly on the heavily limed soil. Increasing the granule size had essentially no effect on the availability of nitrogen in ureaform or ammonium nitrate, but sharply decreased that of oxamide. Nitrogen uptake from -4 + 6-mesh granules of oxamide was 70 to 79% of that obtained from the -60 + 100-mesh material.

The fairly hard, dense granules used in this experiment were probably much harder than would be found in a com-

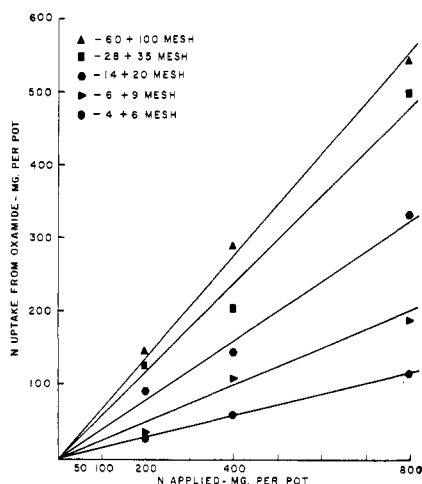


Figure 1. Effect of granule size and rate of application on uptake of nitrogen from oxamide

Hartsells fine sandy loam  
Average for unlimed, pH 5.2; limed, pH 7.5

mercial product. However, the hardness, or density, of the granules was not responsible for lowered availability of the nitrogen, as shown in Table IV. There was no appreciable decrease in availability as the pressure to form the granules was increased from 0 to 6000 p.s.i. Spot-placing of fine material to simulate a granule also led to a sharp decrease in availability. This indicates that the external surface area of the granule was the important factor.

**Uptake in Conventional Pot Tests.** With all sources mixed throughout the soil (experiment 2), nitrogen uptake by corn was the same from fine oxamide and ammonium nitrate, but much less from fine ureaform (Table V). Banding the fine fertilizers 1.5 inches deep in the soil slightly increased nitrogen uptake from ammonium nitrate, but decreased uptake from both oxamide and ureaform.

Availability of ureaform was decreased slightly as granule size was increased. Dissolution of the fine ureaform was so slow, however, that granule-size effects were less pronounced than with oxamide. When the latter was applied as  $-6 + 9$ -mesh granules, nitrogen uptake ranged from 30 to 70% of that obtained with the fines, and dry weight of corn was also much less.

Experiment 3 was designed to measure nitrogen availability of oxamide over a wide range of granule sizes which might

be included in a commercial fertilizer product. Sufficiently high rates of application were included to yield some knowledge of comparative salt injury and to allow a study of residual value of large granules.

A plot of yields of dry matter from experiment 3 against nitrogen uptake indicated that the effectiveness of unit quantity of nitrogen taken up by the plants in increasing dry weight did not differ among fertilizers, granule sizes, or soil pH values. Thus, it appears that the several sources follow a pattern similar to that which would prevail if each material were a dilution of some common source—e.g., ammonium nitrate—and that the principles of biological assay may be applied to the nitrogen uptake data (7). Thus, similar conclusions on relative availabilities of nitrogen sources would have been reached using yields of either dry matter or of nitrogen. Consequently, nitrogen uptake was used as the criterion of availability.

As shown in Figure 1, nitrogen uptake was essentially linear with increasing rates of application for all granule sizes of oxamide. While not shown in the figure, nitrogen uptakes from ammonium nitrate and ureaform were also linear with rates of application. It was possible to express the relative effectiveness of the various materials in terms of the ratios of slopes derived according to the method of concurrent linear analysis described by White *et al.* (8).

Data in Table VI show that  $-4 + 6$ -,  $-6 + 9$ -,  $-12 + 20$ -, and  $-28 + 35$ -mesh granules of oxamide were, respectively, 22, 38, 65, and 89% as effective as  $-60 + 100$ -mesh oxamide per unit of applied nitrogen. The fine granules of oxamide were equally as effective as ammonium nitrate, the availability of which was not appreciably influenced by granule size.

Nitrogen uptake from ureaform was approximately doubled as the granule size was decreased from  $-4 + 6$  to  $-60 + 100$  mesh. The nitrogen uptake from the large granules was slightly higher than from a comparable size of oxamide, but uptake from the fines was much lower than from fine oxamide.

**Nitrogen Recoveries from Repeated Cropping.** Recoveries of nitrogen by the first corn crop from  $-4 + 6$ - and  $-6 + 9$ -mesh oxamide in the limed soil were 13 and 29%, while over 79% of the nitrogen was recovered from  $-60 + 100$ -

mesh oxamide and 66% from ammonium nitrate (Table VII). Total recoveries from the large granules by three crops grown on unlimed and limed soil ranged from 46 to 61% of the nitrogen applied, while recovery from fine oxamide or ammonium nitrate ranged from 64 to 82%.

## Discussion

Granule size has little or no effect on availability of soluble nitrogen materials, but can profoundly affect the characteristics of less soluble compounds. Fine oxamide may be as available to the plant as soluble sources. On the other hand, rates of solution much less than those of some common, soluble nitrogen fertilizers may be obtained by increasing granule size. The rate of solution is undoubtedly largely controlled by the surface area which is in contact with the soil. Any practice which lessens the amount of soil in contact with oxamide would lower its availability. It is conceivable that a mixture of granule sizes to supply both immediate and long-term needs is possible. Oxamide is not now produced as a commercial material, and it is possible that the cost of production will remain too high for its use as a general-purpose fertilizer. The concept of controlling nitrogen availability by varying granule size is nevertheless interesting and could be of practical value in the development of future nitrogen sources.

## Literature Cited

- (1) Black, C. A., Scott, C. O., *Soil Sci. Soc. Am. Proc.* **20**, 176-9 (1956).
- (2) Bouldin, D. R., Sample, E. C., *Ibid.*, **23**, 276-85 (1959).
- (3) DeMent, J. D., Stanford, G., *Agron. J.* **51**, 282-5 (1959).
- (4) DeMent, J. D., Stanford, G., Hunt, C. M., *Soil Sci. Soc. Am. Proc.* **23**, 371-4 (1959).
- (5) Gerretson, F. C., DeHoop, H., *Can. J. Microbiol.* **3**, 359-80 (1957).
- (6) Ogata, Tamotsu, Yoshinouchi, Kenji, *J. Japan. Soil Fertilizer* **29**, 51-6 (1958).
- (7) Scarsbrook, C. E., *Soil Sci. Soc. Am. Proc.* **22**, 442-5 (1958).
- (8) White, R. F., Kempthorne, O., Black, C. A., Webb, J. R., *Ibid.*, **20**, 179-86 (1956).

Received for review October 31, 1960. Accepted March 30, 1961. Division of Fertilizer and Soil Chemistry, 138th Meeting, ACS, New York, N.Y., September 1960.