

Table IV. Year Effect on pH, Total Acidity, Chlorophyll, and Carotene Content of Broccoli

(Moist basis)

Component Analyzed	1963 ^a	1964 ^b	t ^c
Dry matter, %	11.85	11.45	1.99 *
Total acidity, meq./100 grams	2.37	1.86	7.04 ***
pH	6.61	6.71	4.35 ***
Chlorophylls, mg./100 grams			
a	14.23	11.72	5.91 ***
b	5.21	4.00	8.27 ***
Total	19.43	15.70	6.84 ***
Chlorophylls, % retention			
a	96.2	93.3	2.35 *
b	95.4	92.3	0.78
Total	94.7	92.0	2.17 *
Chlorophylls a to b	2.72	2.89	1.46
Carotene, mg./100 grams	0.88	0.68	5.95 ***

^a Means of 72 samples. ^b Means of 36 samples. ^c One and three asterisks indicate significance at 5 and 0.1% levels, respectively.

coefficients of pigments and plant acids with available weather data were inconclusive for this field study. Variable factors such as lag in effects of climatic conditions, plant age, and metabolism were probably involved in the failure to establish a relationship between climatic conditions and pigments or plant acids.

Total chlorophyll and carotene contents of broccoli had highly significant *r*

values for both 1963 and 1964: 0.75 and 0.84, respectively. This relationship was reported earlier by Porter and coworkers (70), who found a ratio of chlorophyll to carotene in Swiss chard and beet greens of about 24 to 1. In the present study, the ratio for broccoli was 22 to 1 in 1963 and 23 to 1 in 1964.

Total chlorophyll and ascorbic acid contents of broccoli also were highly correlated with an *r* value of 0.51 for 1964. Therefore, the higher the chlorophyll content of the broccoli grown in this experiment, the higher were the ascorbic acid and carotene contents of the broccoli.

A highly significant *r* value (−0.74) for total acids and pH of broccoli was found in 1963. However, the 1964 value (0.15) was not significant. The relationship between total acids and pH of plants is not clear. Highly significant negative correlations between total acids and pH of lima beans have been found by Graham (4) in the author's laboratory. Sideris and Young (71) stated that although pH and acidity in pineapple leaves were in relative agreement, the presence of buffers made perfect agreement impossible. Bonner (2) has stated that a relationship between these two factors is not likely to occur, since pH is determined by pK_a plus amounts of free acids and their salts. Total acidity is a measure of only the free acids present.

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USE OF FORMAMIDE

Formamide as a Component of Liquid Fertilizers

A MAJOR PROBLEM in production of liquid fertilizers is the limitation on nutrient content imposed by the water required to hold the salts in solution. A low nutrient content adversely affects costs of storing, handling, and shipping the product.

One major type of liquid fertilizer, nonpressure nitrogen solution, usually is prepared from aqueous solutions of urea and ammonium nitrate. The solubility of the urea and ammonium nitrate limits the nitrogen content of the solution to 32% at 32° F., 30.8% at 20° F., and

28.7% at 5° F. (7). Somewhat higher concentrations can be obtained by adding ammonia, but the resulting pressure introduces problems in handling, storage, and application to the soil.

A consideration of the properties of formamide led to a study of its suitability as an agent for raising the nutrient content of liquid fertilizers. Formamide, the acid amide of formic acid, contains 31% nitrogen. It compares favorably with urea in greenhouse tests (2). A liquid (f.p. 36° F.) with a low vapor pressure at ordinary temperatures, it is

miscible with ammonia and water. It is a solvent for many fertilizer salts (3).

Salting-out temperatures of various fertilizer salts in formamide, or solutions containing formamide, were measured by cooling a solution of a salt to incipient crystallization, then warming it gently until the salt disappeared. The temperature of disappearance was taken as a conservative value for the salting-out temperature; this value is a little higher than the actual equilibrium temperature at crystallization point. Formamide was the practical-grade product, 30.6% N.

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Formamide, a liquid at ordinary temperatures and containing 31% nitrogen, was used in preparation of nitrogen solutions and liquid mixed fertilizers. Nonpressure solutions containing 34.1 to 35.5% nitrogen and salting out at 5° and 32° F., respectively, were prepared from urea, ammonium nitrate, and formamide. Formamide-urea-water solutions containing 31.5 and 33.6% nitrogen salted out at 0° and 32° F. Salting-out temperature of urea-ammonium nitrate solution was lowered from 32° to 20° F. by addition of formamide; lowering of nitrogen content was only from 32 to 31.8%. Formamide and solutions containing formamide were effective in greenhouse tests. In liquid formulations containing 11-37-0 base solution, potassium chloride, and water, additions of supplemental nitrogen as formamide generally gave lower salting-out temperatures than comparable additions as urea and ammonium nitrate.

Nonpressure Nitrogen Solutions

Nonpressure nitrogen solutions were prepared by dissolving various proportions of urea and ammonium nitrate in either formamide or formamide-water solutions. With formamide alone as the solvent, solubilities of urea and ammonium nitrate were measured over the range 5° to 50° F. The solubility isotherms and isograms of nitrogen concentration for the three-component system, ammonium nitrate-urea-formamide, are shown in Figure 1. The amount of solid (urea + ammonium nitrate) added to formamide ranged from 0 to about 52% of the total weight of the three components.

The maximum nitrogen concentration for ammonium nitrate-urea-formamide solutions that salted out at 50° F. was 36%; at 32° F., 35.5%; at 5° F., 34.5%. The solution containing 35.5% nitrogen and salting out at 32° F. contained about 57% formamide, 26% urea, and 17% ammonium nitrate; about half of the nitrogen was supplied as formamide. The nitrogen content of this product, 35.5%, exceeds the 32% in a comparable commercial urea-ammonium nitrate-water solution. For a 5° F. salting-out temperature, the advantage is even greater—34.5 vs. 28.7% nitrogen.

Since solutions of formamide and

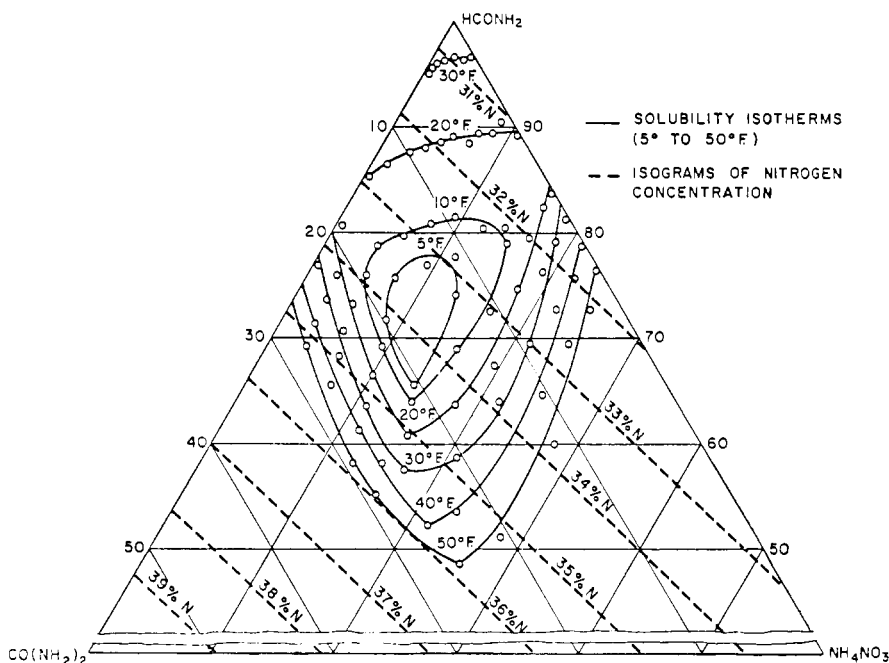


Figure 1. System $\text{NH}_4\text{NO}_3\text{-CO}(\text{NH}_2)_2\text{-HCONH}_2$

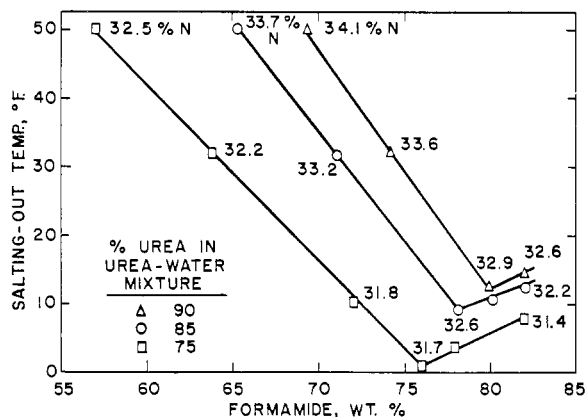


Figure 2. Salting-out temperatures of formamide-urea-water solutions

Table I. Addition of Formamide to Commercial Urea-Ammonium Nitrate-Water Solution.^a Effect on Salting-Out Temperature and Nitrogen Content

Formamide, Wt. %	Total Nitrogen, %	Salting-Out Temp., ° F.
0	32.0	32
0	30.8 ^b	20
2.0	32.0	30
4.8	31.9	26
7.4	31.9	24
9.1	31.9	21
10.7	31.8	20
13.0	31.8	22
16.7	31.8	23

^a Composition: 45% ammonium nitrate, 35% urea, 20% water.

^b Water added to lower nitrogen content from 32 to 30.8%.

water have lower freezing points than either component, tests were made of the effects of formamide additions on nitrogen content and salting-out temperature of a urea-ammonium nitrate-water solution corresponding to the commercial nonpressure solution containing 32% nitrogen [designation 320 (0-45-35)]. The results in Table I show that the

formamide lowered the salting-out temperature at the eutectic (about 11% formamide) from 32° to 20° F. with only a slight decrease in nitrogen content (from 32 to 31.8%). Had water been added to obtain a salting-out temperature of 20° F., as is customary, the solution would have contained about 30.8% nitrogen. In other tests, water was

Table II. Addition of Ammonium Nitrate to Formamide-Urea-Water Mixtures—Effect on Salting-Out Temperature

Ammonium nitrate	Components, Wt. % ^a			Total Nitrogen, %	Salting-Out Temp., ° F.
	Urea ^b	Formamide	H ₂ O ^c		
0	31.5 (42.5)	65.0 (57.5)	3.5	34.6	67
2.9 (2.9)	30.6 (41.3)	63.1 (55.8)	3.4	34.6	63
8.3 (8.4)	28.9 (38.9)	59.6 (52.7)	3.2	34.6	53
9.9 (10.0)	28.4 (38.3)	58.5 (51.7)	3.2	34.6	48
13.8 (13.9)	27.2 (36.6)	56.0 (49.5)	3.0	34.6	41
18.0 (18.2)	25.8 (34.7)	53.3 (47.1)	2.9	34.6	32
20.0 (20.2)	25.2 (33.9)	52.0 (45.9)	2.8	34.7	35
23.1 (23.3)	24.2 (32.5)	50.0 (44.2)	2.7	34.7	42
0	35.1 (46.7)	61.0 (53.3)	3.9	35.0	84
13.0 (13.0)	30.6 (40.7)	53.0 (46.3)	3.4	35.0	57
18.0 (18.0)	28.8 (38.3)	50.0 (43.7)	3.2	35.0	46
20.0 (20.0)	28.1 (37.4)	48.8 (42.6)	3.1	35.0	41
20.6 (20.6)	27.9 (37.1)	48.4 (42.3)	3.1	35.0	40
21.9 (21.9)	27.4 (36.4)	47.7 (41.7)	3.0	35.0	42
23.1 (23.1)	27.0 (35.9)	46.9 (41.0)	3.0	35.0	44

^a Parenthetical figures show per cent of total nitrogen supplied by component.

^b Urea-water mixture (90% urea).

^c From urea solution.

Table III. Solutions for Corrosion Tests

Composition, Wt. %					
Formamide	Urea	Ammonium nitrate	Water	Total N, %	pH
100	0	0	0	30.6	10.5
60.8	23.5	15.7	0	35.0	7.7
68.0	24.0	0	8.0	32.0	8.9
59.0	22.8	15.3	2.9	34.0	7.6

Table IV. Effect of Formamide on Salting-Out Temperature of Liquid Mixed Fertilizers

Grade	Formulation, Wt. %						Fraction of Supplementary N from Formamide, %	Salting-Out Temp., ° F.	
	Formamide	Water	11-37-0 ^a	Potassium chloride	Ammonium nitrate	Urea		Observed	Same grade no formamide ^b
1:1:1 Ratio									
7-7-7	16.1	53.9	18.9	11.1	100	-3	30
8-8-8	18.4	47.3	21.6	12.7	100	2	44
9-9-9	16.1	41.9	24.3	14.2	2.0	1.5	78	28	58
9-9-9	20.7	40.8	24.3	14.2	100	34	58
10-10-10	16.9	34.9	27.1	15.8	5.3	...	74	66	71
10-10-10	16.9	36.2	27.1	15.8	...	4.0	74	72	71
10-10-10	18.4	35.2	27.1	15.8	2.0	1.5	80	68	71
10-10-10	23.0	34.1	27.1	15.8	100	70	71
2:1:1 Ratio									
10-5-5	27.8	50.7	13.5	8.0	100	-10	32
12-6-6	33.4	40.9	16.2	9.5	100	-27	50
14-7-7	34.3	32.1	19.0	11.1	2.0	1.5	88	12	69
14-7-7	39.0	30.9	19.0	11.1	100	29	69
3:1:1 Ratio									
15-5-5	44.1	34.5	13.5	7.9	100	<-30	53
1:3:1 Ratio									
7-21-7	2.5	29.6	56.8	11.1	100	20	8
2:2:1 Ratio									
12-12-6	27.6	30.4	32.5	9.5	100	-10	57
10-10-5	23.0	42.0	27.1	7.9	100	-14	34
3:2:1 Ratio									
12-8-4	31.4	40.5	21.7	6.4	100	-18	30
6:5:4 Ratio									
12-10-8	29.5	30.8	27.0	12.7	100	40	69
12-10-8	24.9	31.9	27.0	12.7	2.0	1.5	84	34	69
14:9:7 Ratio									
14-9-7	30.7	29.5	23.8	11.2	1.9	2.9	82	19	70

^a TVA ammoniated superphosphoric acid.

^b All supplementary nitrogen from urea-ammonium nitrate solution (5).

added to a 36% N solution (20 parts ammonium nitrate, 28 parts urea, and 52 parts formamide) to lower the nitrogen content to 34%. The salting-out temperature was lowered from 50° to 30° F.

Other nonpressure nitrogen solutions were prepared by dissolving in formamide various proportions of urea-water mixtures containing 75, 85, or 90% urea—the range of concentration from commercial urea plants before the evaporation step. The data in Figure 2 indicate that raw solutions from urea plants may be mixed with formamide to yield solutions that contain 31.7 to 34.1% nitrogen and that salt out at 0° to 50° F. Solutions salting out at 32° F. contained 32.2 to 33.6% nitrogen. For the 75, 85, and 90% urea-water solutions, the respective eutectic points were 1°, 9°, and 12° F.; formamide contents of the eutectic solutions were 76, 78, and 80%—total nitrogen contents, 31.7, 32.6, and 32.9%. The eutectic solutions all had higher nitrogen contents and lower salting-out temperatures than comparable commercial solutions prepared either from urea and water or from urea, ammonium nitrate, and water.

The effect of additions of ammonium nitrate on the salting-out temperature of

two urea-water-formamide solutions is shown in Table II. The salting-out temperature of a solution containing 34.6% nitrogen was lowered from 67° to 32° F. at the eutectic (18% ammonium nitrate). The eutectic of a 35.0% nitrogen solution (40° F.) was reached by adding about 21% by weight of ammonium nitrate.

In corrosion tests with solutions containing formamide, specimens of mild steel (A.S.T.M. designation A-285) and aluminum alloy (A.S.A. designation 1100-H14) were moved constantly for 28 days in 750 ml. of liquid held at 120° F. in thermal block equipment. Compositions of the solutions are shown in Table III. Corrosion rate in all the tests was less than 1 mil per year. Some loss of ammonia from the solutions was indicated by a lowering of pH during the tests—about 3 pH units for straight formamide and 1 unit for the other liquids. When the solutions were stored for 4 weeks at 120° F. in vented containers made of the same metals, however, the nitrogen contents, salting-out temperatures, and specific gravities remained essentially constant. Change of pH was significant only with the straight formamide. The liquids can be considered noncorrosive and stable in contact with steel and aluminum.

Low-Pressure Nitrogen Solutions

Large quantities of low-pressure nitrogen solutions are used for ammoniation of superphosphate and for direct surface application to the soil. Introduction of free ammonia into nitrogen solutions containing ammonium nitrate

and urea increases their nitrogen content and lowers the cost per unit of nitrogen.

Formamide was substituted for water in solutions of this type to yield products containing 40 to 45% nitrogen and having vapor pressures below 25 p.s.i.g. at 104° F. Salting-out temperatures of the solutions containing formamide generally were well above those of the corresponding commercial products containing water, however, and this use of formamide was concluded to be impractical.

Liquid Mixed Fertilizers

A factor contributing to low concentration of liquid mixed fertilizers is the low solubility of potassium nitrate. Potassium nitrate, the least soluble salt encountered in liquid fertilizers made from conventional materials, may be formed by reaction of materials in the formulation, commonly urea-ammonium nitrate solution and potassium chloride (6).

In tests of formamide as a means for lowering the salting-out temperature of potassium-containing liquid fertilizers, potassium chloride, formamide, and water were mixed with ammoniated superphosphoric acid (11-37-0 solution) (4). Urea and ammonium nitrate were sources of additional nitrogen in some of the tests. The mixtures, Table IV, covered most of the nutrient ratios found in commercial fertilizers.

Salting-out temperatures of the formamide mixtures generally were considerably below those of commercial solutions of the same grade with urea-ammonium nitrate solution as the source

of supplemental nitrogen. An exception was 10-10-10, for which formamide gave no advantage. The new mixtures containing small amounts of urea and ammonium nitrate along with formamide had even lower salting-out temperatures—a point that was not investigated thoroughly.

Economic Considerations

Although formamide can be used to advantage in liquid fertilizers containing no free ammonia, its cost at its present level of consumption is too high. Production on a much larger scale might bring its cost to a level acceptable for a major component of fertilizers. Also, lower costs may be found in new methods of synthesis. These possibilities are being explored.

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QUATERNARY AMMONIUM COMPOUNDS

Derivatives of (+)-Limonene: Quaternary Ammonium Compounds That Retard Plant Growth

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Ten new quaternary ammonium derivatives synthesized from (+)-limonene have a high order of growth-retarding activity on young bean seedlings. The chemistry and structure-activity relationships of these compounds are discussed. Thirty-four other miscellaneous limonene derivatives had little or no such activity.

WIRWILLIE and Mitchell (9, 14) first reported that certain quaternary ammonium compounds reduced stem elongation of bean plants without gall formation or other formative changes. The most active compound was a quaternary ammonium carbamate, designated

Amo-1618, prepared from the expensive terpene thymol by R. L. Shriner. The most critical part of the molecule was found to be the terpene moiety. This is illustrated by the work of Cathey (3) with carvadan, a position isomer of Amo-1618 made from carvacrol, which was a

growth retardant on poinsettias whereas Amo-1618 was not. Krewson *et al.* (7) studied the synthesis of Amo-1618 and prepared eight additional new, related compounds which were potent growth retardants.

The broad variation in effect of quater-